and add 5 ml. of 10*N* sulfuric acid, 20 ml of 2.5*M* manganese sulfate, and 2 ml. of 0.02% methylene-blue solution. Cool, dilute to 50 ml. with water, mix thoroughly and allow to stand for about 30 minutes for the small amount of lead sulfate to precipitate. Then deaerate a portion and record a simultaneous or single polarogram over the range 0 to -1.0 V *vs.* S.C.E. As the steps of bismuth, antimony, and the first and second of arsenic occur at about -0.04, -0.15, -0.44 and -0.67 *vs.* S.C.E. respectively, measure the wave heights of bismuth, antimony, and the second or the total of arsenic and calculate the amounts of each element from the calibration curves obtained by the same procedures.

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Sintered-Type Alkaline Storage Batteries. III. Preparation and Cell Performance of the Positive Plate (II). Influence of Lithium Hydroxide on Its Durability

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Subject of Experimentation

It was suggested in the previous report, part 2,¹⁾ that LiOH added to the alkaline electrolyte might have influence on the durability of nickel positive plate. In this report, several positive plates were prepared and one of these test plates was combined with two negative plates of pocket type which have larger capacity than the test plate. Cells thus constructed were repeatedly charged and discharged in cycles by the automatic apparatus and influence of LiOH on the test plate was examined.

The change in the capacity was observed on every 100th cycle. Consequently, it was made clear that LiOH added to the electrolyte affects remarkably the durability of the positive plate. After the conclusion of a life test, the active materials in the test plates were examined by electronmicroscopy and counter-diffractometer. The action of LiOH upon active material was considered.

Experiments

a) Preparation of the Test Plate The grid-nickelplated stainless steel net (0.2 mm dia., distance of the wire, 2.0 mm) was welded to a nickel frame (58×72 mm) by a spot-welder. Powder—reduced nickel powder—was used for the plaque material. The preparation of the powder is as follows. Fine nickel powder reduced from Ni(OH)₂ which was precipitated from the aqueous solution of nickel salt with the addition of caustic alkali is unstable in the air. On the other hand, the powder reduced from Ni(OH)₂ which was precipitated from the same salt with the addition of ammonia is thoroughly stable in the air²⁾. Two kinds of fine nickel powder were prepared from Ni(OH)₂ which was precipitated from 1 kg/l of boiled aqueous solution of Ni(NO₃)₂·6H₂O and NiCl₂·6H₂O with the addition of 150 cc of 28% NH₄OH. Reduction was carried out in hydrogen atmosphere at 500°C.

Apparent density of the powder obtained was 0.9 and 0.5 g/cc, respectively. Sintering of the plaque and impregnation of the active material was carried out by the ordinary method¹⁾ and five test plates (from No. 1 to No. 5) were prepared. Data of sintering and impregnation are given in Table 1.

b) Construction of the Cell Each cell was constructed with one of the test plates and two negative plates of pocket type. Capacity of the single negative plate was five ampere hours. The plates were hung on the wall of a glass jar (500 cc) and the plates were separated with glass rods. Then

400 cc of KOH solution, sp. gr. 1.240 at 20°C, was added. No cover was put upon the jar. The cells were put into an air-thermostat with the temperature maintained at 30°±2°C throughout the life test.

c) Capacity and Life Test Influence of LiOH on the test plate: After the completion of formation, capacity and life tests were carried out. Conditions of the tests:

Capacity test—current, 0.5 A, final voltage 1.0 V for every one hundred cycles; life test—discharge approx. 1.2 A, 1 hour; charge, approx. 1.0 A, 2 hours, using constant rheostat, and automatic apparatus. 10 g/l of LiOH were added to the electrolytes of cells, No. 2 and No. 3 after a lapse of 15 cycles. 5 g/l of LiOH were added to the cells, No. 4 and No. 5 after a lapse of 800 cycles. Number of the cells is equal to that of the test plates (Table 1). Electrolytes were exchanged at every 1000 cycles or so and LiOH was renewed each time. Results of the life test are shown in Fig. 1. Sediments of the cells are given in Table 2.

Table 1 Sintering and Impregnation of Plaques

Design of plates	Powder app. den.	Wt. of powd. (g)	Impreg. cycle No.	Wt. of act. mat. (g)	Thick. of plate (mm)
1	0.9	8.5	8	8.1	1.70
2	0.9	10.5	6	8.0	1.82
3	0.5	10.5	6	9.5	2.03
4	0.9	10.5	6	8.5	1.90
5	0.5	10.5	6	10.0	2.03

Table 2 Total Weight of the Sediments

No. of cell	1	2	3	4	5
Wt. of sediments	0.5	0.6	0.5	0.5	0.6

Fig. 1 Durabilities of sintered positive plates

Examinations and Considerations on the Results

LiOH has a large effect on the life of the positive plate as shown in Fig. 1. Since the sediments are equally very slight, the cause of the reduction of capacity should be sought in something other than shedding. Table 3 shows the difference of the porosity between the plates subjected to long repeated cycles and the ones freshly prepared. The porosity measurement was carried out by Drottschmann's method³⁾. Porosity of the freshly prepared plate (1N) is the largest, followed by plate No. 3 (10 g/l of LiOH, 5000 cycles), and that of plate No. 1 (none of LiOH, 3000 cycles)

X; for counter-diffractometer
E; for electronmicroscopy

Fig. 2 Test pieces for physical examination

Table 3 Comparison of Porosities

Plates	Add. of LiOH	Porosity	Per. cent of reduction of porosity
Freshly prepd. pos. plate	—	63.9 %	— %
After 3000 cycles	none	52.1	18.5
After 5000 cycles	10 g/l	53.8	11.1

is the smallest. After the measurement, three kinds of positive plates (1N No. 1 and No. 3) were completely charged again, thoroughly washed and dried at 120°C for one hour. Then the plates were cut off as shown in Fig. 2 and examined by an electron-microscopy and a counter-diffractometer. Contours of active materials existing on the surface of the plate were observed and photographed under the

Freshly prepared
positive plate (a)

Freshly prepared
positive plate (b)

After 3000
cycles (a)

After 3000
cycles (b)

LiOH, after 5000
cycles (a)

LiOH, after 5000
cycles (b)

Fig. 3 Electron micrographs of the sintered-type positive active materials

electronmicroscope. The photographs are shown in Fig. 3. Contours of the freshly prepared materials are mostly amorphous and large cracks are recognized between the amorphous materials.

Meanwhile, the large cracks disappeared from the material No. 1 but crystallized particles are recognized in some parts. In the material No. 3, fine irregularities are observed in increased LiOH quantities although large cracks likewise are no longer present.

Lastly, active materials on the different plates were examined by a counter-diffractometer. The results are shown in Fig. 4. Lattice-spacings of the nickel oxides recorded and cited from literatures are shown in Tabl 4. Materials of the freshly prepared plates look mostly amorphous. On the other hand, the crystal growth of the materials is notable on plate No. 1. The degree of crystallization in the material of plate No. 3 is intermediate between the two. The materials on the surface of the plates are higher oxides than those in the interior. The results of X-ray diffraction mentioned above agree with the observation under the electronmicroscope.

Conclusion

Sintered nickel positive plates were prepared with reduced nickel powder for plaque material

Fig. 4 Records by the counter diffractometer

Table 4 D-spacings of Positive Plates and Nickel-oxides

Freshly prepared (a)		4.7				2.42				
" (b)	7.1					2.40				
3000 cycles (a)	*7.7(3.1)		*3.85(3.95)	*2.60(2.54)						
3000 cycles (b)		4.67		2.70			2.44	1.75	1.57	1.43
5000 cycles LiOH 10g/l (a)	7.7	4.7	3.85							
" (b)		4.72				2.42				
β NiOOH ⁴⁾		4.84								
Ni ₂ C ₂ (OH) ₄ ⁴⁾				2.63		2.41				
4 Ni(OH) ₂ -NiOOH ⁴⁾	7.7		3.85	2.53	2.55		2.31, 2.03, 1.75			
Ni(OH) ₂ ⁵⁾		4.50		2.70			2.33	1.75	1.53	1.43

Notes: 1 (a) surface of the plate (b) pulverized

2 * show figures corrected from deviation of diffraction angle on Ni° and parenthesized figures are calculated from Fig. 4.

and a life test was carried out. If no LiOH was added to the electrolyte, the capacities increased by 13-21% after 200 cycles, but decreased subsequently, diminishing to 57% of the initial capacity after 3000 cycles. On the other hand, the change in capacity was little when 10 g/l of LiOH was added to the electrolyte in the fifteenth cycle and the capacities retained 97 and 88% of the initial value after 5000 cycles. The change in the capacities of the plates added with 5 g/l of LiOH at 800th cycle was intermediate between the two.

2. Active materials having undergone the life test were studied by physical methods such as measurement of porosity and examination by an electronmicroscope or X-ray diffraction and were compared with the freshly prepared material. On these results, it is contended that the reduction of capacity depends upon the decrease of active surface which is caused by the crystal-growth of the active materials. It is considered that LiOH added to the electrolyte prevents the crystal-growth.

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Study on the Electrochemistry of Fused Electrolyte. VII. On the Thermodynamical Properties of Fused MnCl_2 (l)- [LiCl, KCl (Eutectic)] (l) System

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Introduction

Continued from the preceding report, this report^{1)~6)}, dealt with the system of MnCl_2 (l) (N_1)-[LiCl(43.9 wt%), KCl] (l) (N_2) measuring the electromotive force of the, $\text{Mn(s)}/\text{MnCl}_2$ (l) (N_1), [LiCl(43.9 wt%), KCl] (l) (N_2), 1 atm. Cl_2 (g)/C.

The observed electromotive force E of these cells is represented by the following equation,

$$E = E^\circ - (RT/2F) \ln a_{\text{MnCl}_2} = E^\circ - (RT/2F) \ln f_{\text{MnCl}_2} \cdot N_{\text{MnCl}_2} \quad (1)$$

where a_{MnCl_2} , f_{MnCl_2} , and N_{MnCl_2} , are the activity, activity coefficient and mole fraction of manganous chloride, respectively, and E° is electromotive force in the solution of unit activity of manganous chloride or in the melts of pure manganous chloride.

From the observed values of E , E° and dE/dt , the thermodynamical values of this system may be calculated.

Experimental In this study, the apparatus and the method were all the same as described in the previous paper¹⁾. The manganese electrode used was prepared by the electro-deposition on a pure nickel wire (dia. of 1 mm) in the fused bath.

Results and Discussion

Fig. 1 shows the liquidus curve of this system. The relationship between the electromotive force E at various mole fraction of manganous chloride N_1 and temperature is shown in Fig. 2, and the linear dependency of the electromotive force on temperature is given in Table 1.