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Short communication

Zinc electrode with reduced dendritic propagation

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Abstract

Microporous separators conventionally used in lead-acid accumulators are proposed to substitute rayon-type separator during discharge of zinc anode alkaline accumulators, while the same accumulator is charged mainly through rayon-type separator. Thus the positive qualities of rayon-type and microporous-type separators are amalgamated. This is achieved by new cell design and charging method. Enhanced characteristics are obtained versus the conventional setups.

Keywords: Secondary zinc electrode; Dendritic propagation; Microporous separator

1. Introduction

Among other rechargeable zinc electrode problems (shape change, passivation, zincate electrolyte aging, corrosion, etc.), short-circuiting caused by zinc dendrites' propagation towards the counter electrode is considered as the main culprit of reduced cycle-life of accumulators with zinc electrodes.

Practically everywhere, where alkaline rechargeable zinc electrode is employed, multilayer rayon-type film is used as separator. This separator has many shortcomings and the only purpose of its use is to suppress dendritic propagation taking place during charging. However, rayon-type separator deepens passivation, active mass redistribution and zincate ion aging thus lowering the cell characteristics [1]. On the other hand, microporous separators conventionally used in lead-acid accumulators, considerably stabilize zinc electrode characteristics [2]. However, microporous separators are unable to withstand zinc dendrites' puncturing during cell charging.

The aim of this work is to charge the zinc electrode through rayon-type separator (to suppress dendrites' formation), while discharge it with microporous separator (to suppress passivation, active mass redistribution, zincate ion aging). This is achieved by the cell setup and cell charging technique described below.

Thus, this method combines positive qualities of rayon-type and microporous-type separators.

2. Experimental

For the experiments, paste type zinc electrodes are used based on stable binder which is insoluble in strong alkaline media. Electrodes are of 40 mm × 80 mm × 1.5 mm size. Mean capacity of the electrode is ca. 4 Ah (theoretical value). Porosity of the ready-made electrodes, measured by BET method, was at $62 \pm 10\%$. Commercially produced nickel-oxide sintered electrodes (having the same size) are used as positive electrodes (Lugansk accumulator production Plant, Ukraine).

The cell is first filled and first-charged (formatted) with 7 M KOH solution, which is substituted with zincate saturated electrolyte after the charging. The basic electrolyte has the following composition: $7\,\text{M KOH} + \text{sat. ZnO} + 5\,\text{g l}^{-1}\,\text{LiOH} + 50\,\text{g l}^{-1}\,\text{KF}$. All the used chemicals were pure grade and water distilled.

Amalgamated zinc-coated copper mesh is used as current collector. The cell is made of polymethylmethacrylate.

Referred potentials are given versus 7 M KOH mercury oxide electrode used during overpotential determination. Two salt bridges in fine polyvinylchloride tubing abutting to each side of the same zinc electrode are used to cut the potential values of different faces of the same zinc electrode. They are made of flexible polyvinylchloride tubes and filled with 7 M KOH solution.

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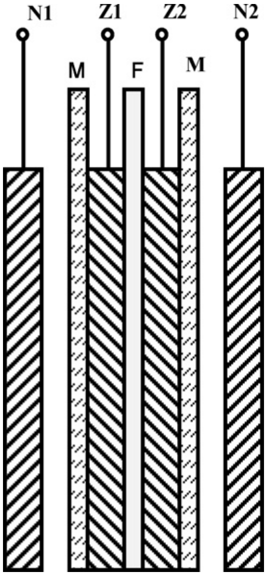

Fig. 1. Setup 1 N1 and N2: nickel oxide electrodes; Z1 and Z2: zinc electrodes; M: microporous separators; F: rayon-type separator.

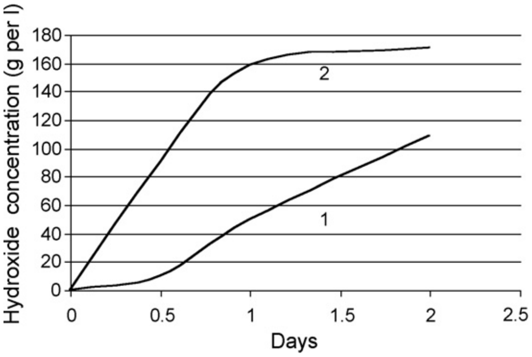

Fig. 2. Diffusion of OH$^-$ ions through separator F and M (1) microporous separator; (2) rayon-type separator.

Rayon (type #100) and microporous separators have been used in experiments.

3. Results and discussion

In all figures, zinc electrodes are denoted by letter Z, nickel oxide electrodes by N, auxiliary electrodes by A, reference electrodes by R, rayon-type separators by F, and microporous separator by M.

The first type of cell setup (setup 1) is presented in Fig. 1. The accumulator has four-leads. Between zinc electrodes and counter electrodes are placed microporous separators (M), while between the twinned zinc electrodes is placed from three-to-five-layer-rayon-type-separator (F). Twinned zinc electrodes with three separators are sealed together on the edges making single zinc electrode pack.

Zinc electrodes (Z1 and Z2) face each other and are charged in different phases. If Z1 is charged with N2, then Z2 and N1 are idling. The process reversed after some period: Z1 and N2 electrodes are disconnected from charging while Z2 and N1 are connected to charger. The zinc electrode pack is closely fitted with cell walls so as only a tiny fraction of total current is possible to leak through the small amount of electrolyte present in between the zinc electrode pack's edge and cell wall abutting to pack's edge. During charging, the front of the dendrites initiating from each zinc electrode is directed towards each other (to separator F) as there is a potential drop inside the zinc electrode which makes the side of the zinc electrode facing other zinc electrode to be more negative than the side which faces the counter electrode, which is proven by potential measurements with the R1 and R2 mercury oxide reference electrodes mounted on two sides of the same zinc electrode.

Many-layered (10 or more layers) rayon-type separator (F) – standing between the zinc electrodes – could be used to withstand dendrites' growth. The inner resistance of this rayon-type separator (F) has no impact on cell characteristics during discharge. This is because during discharge the twinned zinc electrodes as well as the counter electrodes are connected together and the accumulator is discharged similar to conventional ones. The inner resistance and porous characteristics of microporous separators (M) determine other critical aspects of zinc electrode's reversible work conditioned by lesser shape change, low passivation and smaller zincate electrolyte aging compared with rayon-type ones [2]. M separators are of microporous type, the inner resistance of which is much lower than that of five layer of separator F (Table 1), which explains the behavioral differences of separators M and F. Primarily, the lessened resistance of separator M is conditioned by alleviated diffusion of hydroxide ions (Fig. 2). This diffusion picture was

Table 1
Comparative characteristics of the cells

Characteristic	Discharge current density (mA cm^{-2})					
	Setup 2		Setup 1		Conventional (five layer of rayon-type)	
	15.6	100	15.6	100	15.6	100
Active mass usage effectiveness (%)	45	35	45	35	25	15
Specific capacity (Ah kg^{-1})	55	40	50	40	31	16
Specific energy (Wh kg^{-1})	75	55	80	55	51	16
Specific power (W kg^{-1})	27	140	27	140	26	30
Mean discharge voltage (V)	1.62	1.40	1.64	1.48	1.63	1.0
Cycle life	200	150	150	100	50	15
Inner resistance (Ω)	0.015		0.01		0.035	

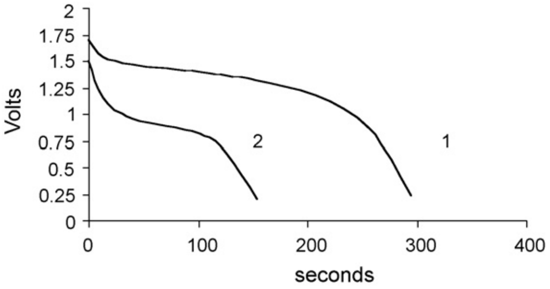

Fig. 3. Discharge characteristics of ZnNi cells (setup 1 and three layers of rayon-type) (1) setup 1; (2) conventional setup with three layers of rayon-type separator.

obtained from hydroxide concentration determinations in measurement cell having two-compartments divided by either M or F separator.

For juxtaposition, in Fig. 3, ZnNi accumulator discharge plots are presented for setup 1 (curve 1) and conventional setup with three layers of rayon-type separator (curve 2) at 100 mA cm^{-2} discharge load. As the active mass redistribution of zinc electrode is minimized, so the cycle life is increased with stabilization of discharge characteristics over time (Table 1).

It is possible to charge this four-lead accumulator with the AC current with the help of blocking diodes.

However, this setup has one drawback: during the period when zinc electrode is idling (i.e. is disconnected from the charger) it works as bipolar electrode. In this case the side of the Z1 electrode facing the N1 counter electrode becomes cathode versus the other side of the same electrode when Z2 is charged with N1. So, dendrites are appearing on this side of the idling (disconnected at this moment from the charger) electrode (facing to counter electrode) which eventually short circuits the accumulator poles, although with lower probability than is with conventional setup case.

Another setup (setup 2) presented in Fig. 4 is suggested to eliminate this bipolar effect. A1 and A2 auxiliary electrodes are made of Ni metal meshes which alternately charge Z1 and Z2 zinc electrodes in one phase and N1 and N2 electrodes in another phase. As was with the case of setup 1, here also it is possible to charge the accumulator with AC with the help of diodes as is shown in Fig. 4.

Similar to setup 1, here A1 auxiliary electrode is wrapped with up to 10 layers of rayon-type separator, while S1 separators are of microporous type.

During high-load discharge of the cells, the voltage drop is mainly determined by separators' resistance, which is minimal in this setup as these separators are of microporous type. Actually, it was possible to cycle setup 1 accumulator some 15 cycles with super-high current loads (the current density is 500 mA cm^{-2}). The performance (efficiency of usage of active mass versus the theoretical value) is ca. 20% which is considerably higher compared to known ones at such heavy loads.

In Fig. 5 the overpotentials of the two faces of the same Zn electrode are given (setup 2) from whence it follows that this technique greatly shifts the dendrites' propagation front towards inner auxiliary electrode, thus reducing the probability of appearing the dendrites between counter electrodes (i.e. zinc electrode and nickel oxide electrode). This setup has a major drawback as double charge goes for accumulator charging.

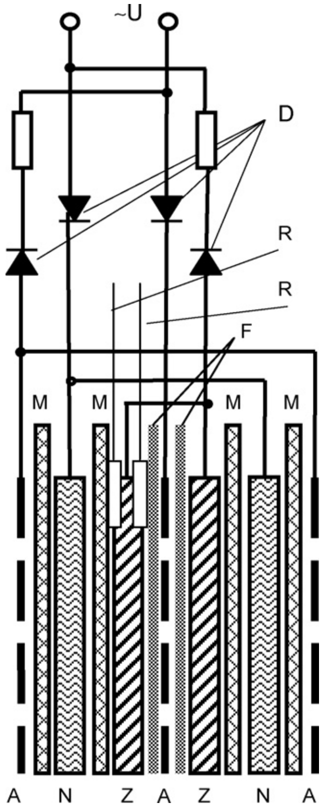

Fig. 4. Setup 2—Z: zinc electrodes; N: nickel oxide electrodes; A: auxiliary electrodes; M: microporous separator; F: microporous separator; R: reference electrodes; D: diodes.

The effectiveness of the setups was directly assessed in following manner. Conventional accumulator, setups 1 and 2 have been charged until stable short circuiting between cell poles appear when charging voltage drops precipitately from ca. 2.2 V down to 1.5–2.0 V. Conventional cell showed stable short circuiting at $0.9 \pm 0.2C$ (C is the theoretical value of zinc electrode capacity), while for setup 1 at $1.3 \pm 0.2C$, and with setup 2 at

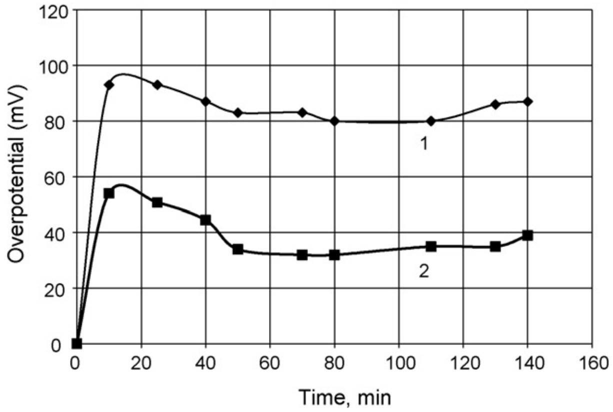

Fig. 5. Charging overpotentials of two sides of the same Zn electrode (current density is 20 mA cm^{-2}) (1) overpotential of the side of the zinc electrode facing other zinc electrode; (2) overpotential of the side of the zinc electrode facing nickel oxide electrode.

1.7 ± 0.3C. Post mortem examination of zinc electrodes of setup 2 showed practically no dendrites.

4. Conclusions

It is possible to reduce shape change and passivation by substituting the rayon-type separator with microporous one, at the same time dendritic propagation was contained as is with rayon-type separator.

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