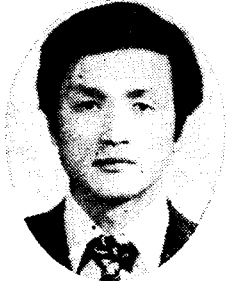

Capacity Analysis of the Silver Oxide Zinc Cell



(Phase 3 High Rate Pulsed Discharge)

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Abstract

Preliminary investigation have been made on what the capacity of high rate pulsed discharge of Ago-Zn button cells were associated with the changes of cathode construction feature, mix formulation, separator and electrolyte concentration.

— 요 약 —

단추형 제 2 신화은전지의 고주파형 방전용량의 변화를 음극의 구조, 합제배합, 음극 소제의 모양, 격리막, 전해액농도와 연결지어 조사하였다.

I. Background

Silver oxide zinc cell using divalent silver oxide cathode recently raised up as attentive compared to other cell systems, provided some limitations were under controlled.

It has been pointed out by LED watch markers that AgO system button cells have not been applicable successfully to their LED or LCD watches because of its inferior current drain, being insufficient to make the back light work, whereas being almost perfect and sufficient to run other watch functions in the low current drain below 100 micro ampere per square centimeter.

To supply enough current density for the back light plus LED module to work needs as for two cells in series about 120mA/cm².

In establishing AgO-Zn button cell, special attentions must be exercised during manufacturing operation to remove high AgO voltage level, consequently adhering problems like impedance up and voltage up must be raised up and they are known associated to the layer thickness of Ag and Ag₂O, and Ag₂O thickness control is important more than that of Ag.

Ag₂O layer formation in the plain AgO-Zn cell is known due to the reaction of AgO+Ag→Ag₂O and its reaction speed would depend on the thickness of the original Ag₂O layer produced upon AgO.

Generally, although AgO button cells in low rate continuous discharge are not showing

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critical problems but it was common to the silver cased AgO-Zn cells failed to meet standard CCV requirement with the beginning of cell assembly and above all they used to fail to illuminate the back light of LED watch along with watch functions, that is so called the DIMMING.

However, such problems were not common to Ag₂O-Zn system. Therefore the high rate capacity of Ag₂O system have been used as a control for minimum requirement in developing high rate AgO button cells.

There are supposedly many possible variables or factors influencing to the lower CCV behaviors or the inferior high rate pulsed discharge characteristics, being deviated slightly from cell assembly process and chemical phenomenon such as CO₂ pick up in the air.

Eventhough they were all assembled under specification control, the local current density change may differs or converts AgO morphorlogy resulting in unacceptable to proceed in high rate pulsed discharge.

In this paper discussion shall go over the relationship of the high rate pulsed discharge capacity against to the electrolyte concentration, AgO properties cathode construction, pellet formulation, separator system and electrolyte concentration variation.

2. Experimental

To draw up more adquate view of the facts, tried to extend experimatal methods in many ways.

2.1 AgO powder and pellet formulation

1) Two AgO powder samples were adopted for evaluation, Relatively large tap density, ~3.0gr/cm³ (gassing rate is around or higher 90μl/gr/hr in 75°C40% KOH+1% ZnO),

Relatively small tap density~2.0gr/cm³(gassing rate around 200μl/gr/hr in 70°C 40% KOH +1% ZnO)

Otherwise unspecified used the AgO powder with tap density of 3.0gr/cm³

2) As pellet formulation abopted following three different compositions with mix density around 4.0gr/cm³

A. 100 part Ag₂O mixed with Ag metal plus lubricant and gas suppressant

B. 50 part AgO-50 part Ag₂O plus lubricant and gas suppressant

C. 100 part AgO plus lubricant and gas suppressant

3) Above three mixes were pressed to pellets by rotary tablet press in sige of HT 0.040'' ×Dia 0.270'' at 5000LB/in².

The completed mix pellets with increased density were subjected to a chemical reduction process which used methanol in a heated caustic solution which producing Ag₂O (thickness 0.2mm) so that a cell may be constructed which discharges primarily at a monovalent silver oxide voltage level.

The pellets were then placed in a cathode can, nickel plated steel can with nickel plated pellet retainer ring, and then fed into another rotary press for recompression of the entire assemble to provide maximum density and acceptable electrical contact between the active materials and the can so called consolidations(Ht 0.03736'').

This consolidation is then treated for 5min in a solution of hydrazine to reduce monovalent layer to metallic Ag in thickness of 0.003149'' to assure discharge rea-ction at movalent

voltage level.

Polystyrene insulating washer is then placed on to separator of the treated consolidation, if necessary. This assembled consolidation is then moved toward cell assembly line and to cell closing press. After the cell closing operation, the cells were washed, dried and kept under 25°C air conditional box for various discharge testings, the final assembled cell is looking like(1).

4) Separator—4 types were adopted

- A. "Cellophane barrier"—composite of two layers of cellophane between which there is a filler of magnesium hydroxide, cadmium sulfide and carbopol mixed with 40% KOH.
- B. "P-2291 40/30"—a weak cation low density polyethylene film 30 milliohms in², supplied from RAT Research Corporation U.S.A.
- C. "P-2192 40/30"—a laminate of one layer of p-2291 40/30 and two layers of cellophane, the permion is sandwiched between two cellophane layers, its overall resistance is about 50 millions in²
- D. "NP-2192" —same one as indicated in above C, but its ion exchangability and resistance around 100 millions in.²

2.2 Processes for experiments

Sample cells were experienced in their assemblings like following.

EX.	Mix formulation	Pellet structure	Electrolyte	Separator	Remarks
1	100-AgO	Ag-Ag ₂ O-AgO	40%KOH+I%ZnO	N P-2192	No washer, AgO 4.0gr/cm ³
2	100-AgO	Ag-Ag ₂ O-AgO	40%KOH+I%ZnO	N P-2192	
3	50-50Ag ₂ O/AgO	Ag-Ag ₂ O-AgO	40%KOH+I%ZnO	P-2192	
4	100-AgO	Ag-Ag ₂ O-AgO	40%KOH+I%ZnO	P-2192	
5	100-Ag ₂ O	Ag ₂ O	40%KOH+I%ZnO	A	Ag ₂ O-5.0gr/cm ³
6	100-AgO	Ag-Ag ₂ O-AgO	40%KOH+I%ZnO	A	
7	100-AgO	Ag-Ag ₂ O-AgO	35%KOH+I%ZnO	P-2192	
8	100-AgO	Ag-Ag ₂ O-AgO	40%KOH+I%ZnO	P-2192	AgO-2.0gr/cm ³
9	100-AgO	Ag-Ag ₂ O-Ago	40%KOH+I%ZnO	P-2192	No washer
10	100-Ag ₂ O	Ag ₂ O	40%KOH+I%ZnO	A	No washer Ag 0-5.0gr/cm ³
11	100-Ag ₂ O	Ag ₂ O	40%KOH+I%ZnO	P-2192	
12	100-AgO	AgO-Ag	40%KOH+I%ZnO	P-2192	siver plated mix sleeve used instead of Ni-Pit

After characterization of LED watch modules button cells for testing are subjected to a continuous background load of book ohms and pulsed every hour for 1.25 seconds on an 86 ohm load. This life test represents a pulse of approximately 32 MAH/cell for 1.25 seconds. Dimming occurs below 2.20 volts for 2 cells in series.

3. Results and Discussion

Electrically, cells troubled by dimming have indicated inferior CCV trends and current density as compared to normal cells, and normally there appeared deep crack in the pellets between discharged and undischarged boundaries, and showing separator laminate-

deteriorated. Capacities to all experiments noted in proceeding section are represented in Fig 1

Ag₂O systems incorporating proper separator are generally showing superior performance to AgO systems.

The cathode pellets in poorly discharged cells seem to be dried, specially for the case of EX8.

On the separator side usually a greenish, gelatinous layer adheres to the pellets which is regarded deteriorated cellophane layer. On the separator side the pellet shows gray-brown color of reduced silver, whereas the back color.

The boundary between the grey silver layer and the black Ag₂O layer appears to be relatively deep.

3. 1 Cathode Construction

Comparison was made in between EX1 Vs. EX2 and EX4 Vs. EX9, namely, between those cases with and without styrene washer. As resulted apparently, cells with styrene ring have remarkable performances for both Ag₂O and AgO systems in the continuous low rate discharge, it doesnt make much difference between them.

The reason is understood in high rate discharge with styrene washer regulates or retards OH transference to some extent, more pronouncedly than the case of low rate.

3.2 Mix Formulation

Comparison was made between EX3 vs, EX4 and EX5 vs, EX6, say, the change of composition ratio of AgO and Ag₂O. Full Ag₂O systems revealed stable than either full AgO or partial AgO systems regardless separator alteration.

This means high rate discharging reactions in the experimental button cells proceed majorly under the polarization of Ag₂O→Ag reaction. To meet this reaction in continuous satisfaction, AgO-Ag₂O reaction should be establishing to the same degree as the reaction Ag₂O-Ag undergoes.

In another words O ions transference forwarding to reactive sites must be supplied in continuous and in sufficient volume. After the results obtained herein we can see cellophane system separators profit in 100-part Ag₂O system while high resistive separator profit in AgO system. So in choosing silver oxide system as power source, its far more important concerning appropriator system, as well as noticed earlier from examination of the bad cells EX4 with low ccv with the beginning of cell assembly.

3.3 Pellet Construction

This test aims to find what the effects are associated with cathode construction feature of which variation is according to pellet treatment.

Comparison was made between EX4 vs, EX12. For EX12 AgO pellet was just cased by silver plated mix sleeve to produce Ag₂O layer through the reduction process of AgO+Ag=AgO

EX4 performed superior to EX12 and the reason can be interpreted in as for high rate

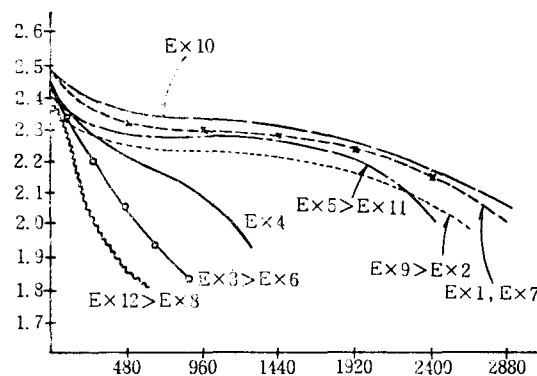


Fig 1. "A" Type cells discharge capacity in high pulsed rate, as averaged

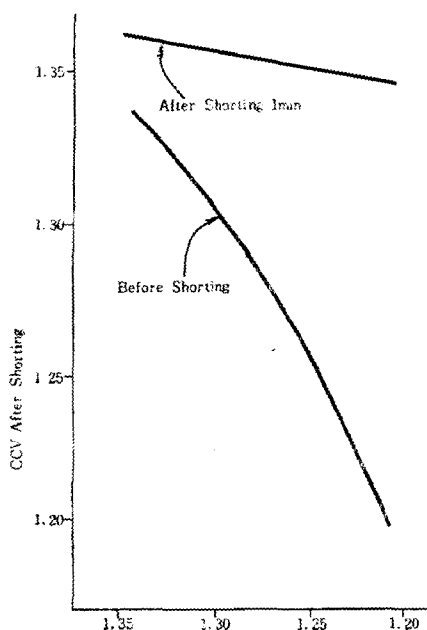


Fig 2. "A" Type cell CCV Before After Shorting, Construction EX2.

pulsed discharging requires bulk of Ag_2O existence to support the continuous reduction.

By shorting the cells, for 10 sec, EX4 showing bad ccv, cell resistance sharply improved as indicated in the Fig 2 while forming coarse gray metallic Ag layer between Ag_2O and separator, which reflects sharp and agglomerate coarse textures.

The discharge reaction, the electrochemical reduction of silver oxide to Ag metal starts and occurs from and near the surface of the separator, and if the surface were strong and rigid, the OH^- transference shall be bolted to some extent.

Therefore, the current path which is capable in maximum condition shall be important for high rate pused capacity, it is because the fact is ragarded as that OH^- ions begins to

migrate from the areas where the current enters the electrode.

3.4 Separator

Comparisons were made between EX4vs, EX6 vs, EX2 and EX5 vs, EX11.

Performance results rated in after EX2>EX4>EX6 for AgO system. However for Ag_2O system separator variation seemed not to influence significantly in high rate discharging.

The reason might be attributed basically to decomposition and dissolution degrees of the AgO and Ag_2O layers fromed in the pellet, and further influenced by the dissolved species.

For dissoloved species of Ag_2O and Ag, or the $Ag(OH)_2^-$ was detected from the system of $Ag-Ag_2O-AgO$.

According to the result of the transference testing of the dissolved species and the resistance of of the used separator, it is thought special care must be exercised to construct the proper separator because there would happen to form direct short ci-rcuit.

Considering the prime and necessary characteritics of a separator in an alkaline cell of AgO system, resistance of the separator onto the diffusion of dissolved silver oxi- de species shall be put in first place, then follows chemical stability and electrolyte absorption. For they shall affect to the life of an electrchemiccal cell in several ways.

Because of the reason that silver oxide being in direct contact with cellofane actactks cellulose layers of the separator, there often appeared small amounts of dissolved state of silver oxide migrated into the zinc electrode, accelerating the corrosion of the zinc, and resulting in self discharge and hydrogen evolution.

It is noted that P-2291 discolored due to some surfactant contained therein, and plays role in the trapping of silver species. It was same to the cellophane-used-separator, which dissolving silver and silver oxide and making metallic silvere deposits within the membran due to incorporation with aldehydes. But this showed more or less lighter permeabili'

rather than the case of P-2291.

3.5 Electrolyte Concentration

For comparison, EX4 and EX7 was provided with changing electrolyte concentrations from 40% KOH to 35% KOH. The reason EX4 performs better than EX7, could be explained due to higher diffusion rate.

Due to greatly reduced diffusion rates at rather higher KOH concentrations above 40% KOH, the concentration gradient at a given current density increases slightly and consequently polarization increases slightly.

With increasing KOH concentration above 40%, at a given current density AgO discharge reaction seems not to be rapid and lasting, but with lowering KOH concentration below to 30%, then the discharging profile level increases to some extent but not significantly as represented in the Fig 1.

But the rate of decomposition or gassing rate depends on with increasing KOH concentration as described in the paper (2).

Because the increased concentration polarization could be also observed around in KOH 40%, it can be seen at high KOH concentration, the high rate pulsed discharge capacity is tend to decrease but not in proportional ratio corresponding to the increased KOH%. Then the KOH concentration change might govern directly the entire cell discharge reaction through the effect on the AgO or Ag₂O crystal morphology. It can be said now that the KOH concentration has some effects, but not appreciable.

The rate of decomposition of Ag₂O was effected by several factors and then the reaction was not very sensitive to KOH concentration in the range of 30%-40% KOH, however, the rate was higher than those concentration elevation in the range of KOH 20%-30%, But the decomposition or gassing rate of AgO drastically increased from above 40% KOH.

Although present experiments has not involved other concentration realm, below 30% and over 40%, it is known the available capacity has decreased slowly below 28% whereas at high concentration over 40% it has decreased drastically both for continuous and high rate pulsed discharge.

It can be said therefore that the KOH concentration should determine the cell life capacity through morphology change in major, and the better results obtained even in AgO cell with using lower KOH concentration 32-35%.

But if the discharge reduction rate is controlled by the charge transfer reaction the KOH concentration would not go to alter reduction processes significantly.

Since AgO reduction in practical cell produces OH⁻ ions and the OH⁻ concentration would increases locally within cathode pores to shift more negatively polarization remarkably during low rate discharge.

Thus OH⁻ concentration changes in the pores would possibly serve to chemical decomposition of AgO in more increased speed than that of AgO reduction due to electrochemical reaction, consequently resulted in rather unacceptable dissolved compounds for further electrochemical reduction.

4. Conclusion

AgO morphology during high rate pulsed discharging shall be attributed to the used AgO grain properties particularly, most to AgO surface area which characterizes rates of gassing along with the decomposition, through that electrochemical properties subjects to the electrolyte concentration variation, but not appreciable, but it is noted significantly vigorous in the range of above 40% KOH, so alike is in the relatively lower tap densities.

In the high rate discharge, among the two steps of reducing reactions, the reaction of $Ag_2O \rightarrow Ag$ seems to proceed faster than $AgO \rightarrow Ag_2O$ therefore, to obtain unique one reaction profile of $Ag_2O \rightarrow Ag$, while giving long lasting capacity it becomes necessary to utilize the KOH concentration around 35%-38%, which might also approves leakage stability.

It does require for a cell therein a minimum thickness of Ag_2O layer must be provided before cathode construction as well as retaining it during the discharge reaction.

Consequently, the Ag_2O system using nonreducible cellophane separator shows to perform long capacity in the lower KOH concentration below 38% KOH.

For AgO system, pellet construction is very important and also the AgO particles size used in the pellet because they will be affected by the KOH concentration, possibly changing them into electrochemical immune-morphology.

Reference

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