



The effects of electrolyte composition and water contents in manganese dioxide cell

유닉스電子(株)理事 李 完 求*

— 要 約 —

이산화망간 乾電池에 實使用되고 있는 電解液 $ZnCl_2-NH_4Cl-H_2O$ 의 組成 變化에 따른 乾電池의 特性變化를 比較 檢討하여, 乾電池性能向上의 基本因子 및 그 變化程度를 調査코자 하였다. $ZnCl_2$ 主使用 電池系는 特히 重負荷連續放電이 優秀하였으며 그 理由로는 濃度分極現象이 적음에 基因되며 이는 Zn^{++} 이 本系에서는 쉽게 移動함에 있다고 看做되며 그 Zn^{++} 이온의 빠른 移動은 理論치보다도 多量使用하게 되는 물의 役割에 기인되고 放電에 直接 必要한 水分量과, 其他의 目的 即 反應沈澱物의 再溶解, ion carrier 等으로서 利用되는 水分量은, MnO_2 와의 比率 및 放電 負荷크기에 따라 다르다.

1. Introduction

Today, with the trend of miniaturizing of the handheld electronic products, or for portable, further for appearance of high cost appliances it now demands dry cells with long storage life, highly resistant to leakage along with steady powerful currents without serious loss of designed capacity. For to meet this requirement Zinc Chloride cells is today well used with distinct advantages over conventional Leclanche cells so far concerned leakage resistance and heavy discharge purposes.

Leclanché cell involves mainly NH_4Cl as for its electrolyte which was terribly weak at leakage resistant due to extreme creepage effects of NH_4Cl . Although nowadays many of dry battery manufacturers are in competition in producing this sort of zinc chloride batteries, nevertheless there were still some headache works left to take care for in their production lines that is to keep on precision accuracy in those production machineries, the reason is that cathode mix made of this zinc chloride goes easily to dry up due to higher evaporation pressure, and the separator alike and so whenever air or oxygen is introduced to this electrolyte a passivation generates drastically upon zinc surface owing to oxidation reaction, wherefore proper seal is not provided tightly menaces storage life to a critical state. Thus effective sealing of cells

* (化工技術士·電氣化學)

through by preventing oxygen access to the zinc electrolyte interface becomes an important requirement for making long life cells, further necessary also to prevent loss of moisture which is very important for direct discharge reactions. As improved and reinforced through time consumed trials, today many companies has arrived to adopt a certain cell construction for their commercial purposes as following.

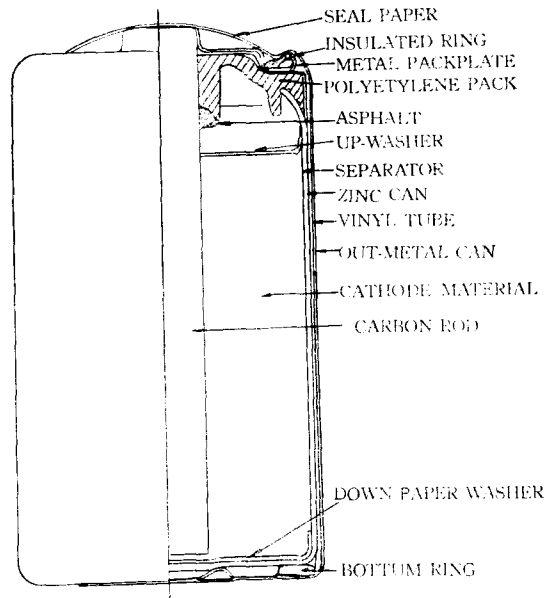
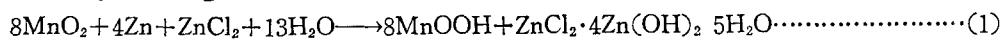
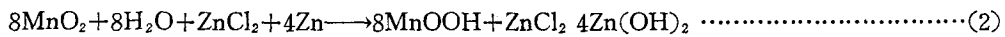


Fig. 1. Uptodate cell construction, DMSIZE feature scaled up

Super performance of the zinc chloride cell over to the Leclanche' system in its leakage resistance was proposed by many electrochemists, one of them Huber ① gave presentation to answer that by showing a cell over all reaction for Zinc chloride system;



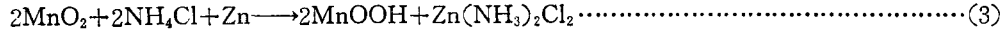
This cell reaction continues to dry out with continued discharge, presumably due to the large amount of water bound up in the reaction product alike $\text{ZnCl}_2 \cdot 5\text{H}_2\text{O}$ $4\text{Zn}(\text{OH})_2$. However, general expression for over all cell reaction is,



All the water contained in a cell anyway is to consume up in the course of proper discharging to the end.

Effective performances of the zinc chloride cell against high current drains are understood by the reason of its less polarization characteristics as compared to the conventional Leclanché system. Obviously the polarization governing the whole cell polarization is considered as the concentration polarization which owes to the accumulation of ZnCl_2 upon the anode surface, as far this product diffuses away from the anode toward cathode mix core, the anodic potential shall be returning back to a original level thus with thanks of this effect or a ready diffusibility of ZnCl_2 helps to establish a polarized condition for a continuous discharge reaction.

NH₄Cl-rich electrolyte normally once employed before ago for Leclanché cell has following cell reaction,



Zinc chloride cell or Leclanché cell available on current commercial market utilizes one electrolyte system chosen from following ZnCl₂-NH₄Cl-H₂O triangular system (Fig. 2)

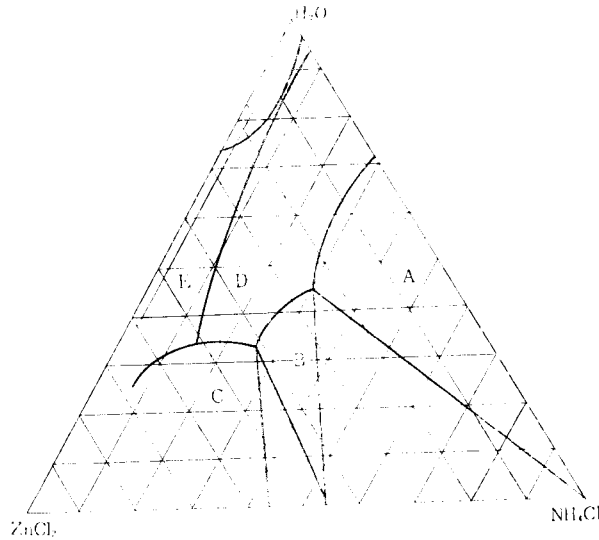
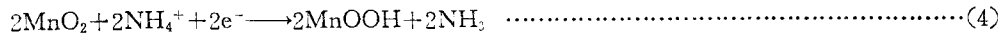


Fig. 2. The electrolyte system ZnCl₂-NH₄Cl-H₂O for manganese dioxide cells

Area	A	Solid Phase	NH ₄ Cl
"	B	"	ZnCl ₂ ·3NH ₄ Cl
"	C	"	ZnCl ₂ ·2NH ₄ Cl
"	D	Ammonia Added	ZnCl ₂ ·2NH ₃
"	E	"	ZnCl ₂ ·4Zn(OH) ₂

A certain NH₄Cl rich electrolyte at the anode surface starts to shift in the direction to some point Zn(NH₃)₂Cl₂ whereas for ZnCl₂ electrolyte toward ZnCl₂·4Zn(OH)₂. The electrolyte reactions in NH₄-rich cell at the cathode are more complex in that ammonia is generated as a cathodic by-product.

The by-product occurrence of ammonia in the cathode during cell discharge is shown in the reaction



2. Experimentals and Discussions

2.1 Electrolyte composition variation and the discharge capacity

Proper electrolyte composition, of course, while harmonized to meet various requirements would be very important for super performances in cell discharge life as shown in Fig. 3.

Herefore, this author selected several different electrolyte compositions to study their behaviors in relation to discharge life, predominant reaction, and its reaction mechanism.

Case	Electrolyte system used in
A	20% ZnCl ₂ only
B	ZnCl ₂ +NH ₄ Cl 5%
C	" 10%
D	" 15%
E	" 20%
F	" 27%
G	" 30%
H	" 35%

With use of electrolyte compositions above, sample cells were packaged into as Fig.1 that is "DM" size.

Sample cells were put in constant discharge tests at 2 ohms, 4 ohms and 20 ohms and intermittent on 4 ohms, and 20 ohms,

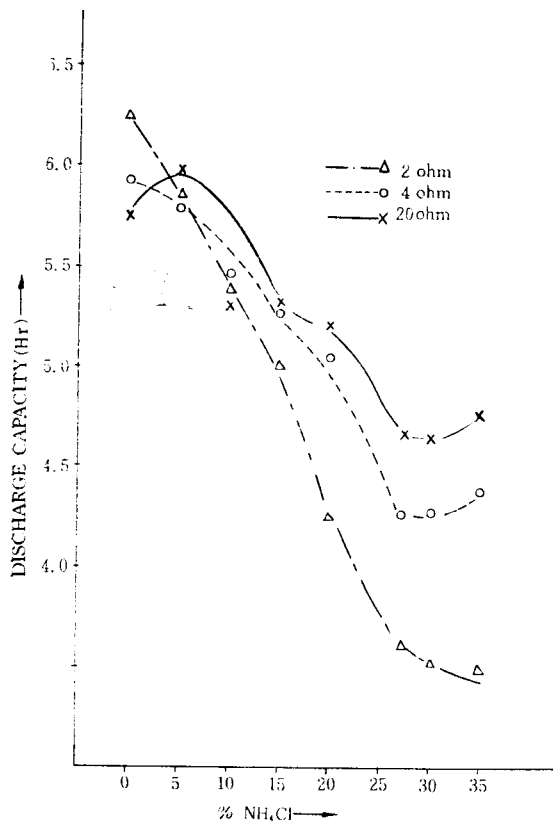


Fig. 3-1. NH₄Cl content and Constant discharge

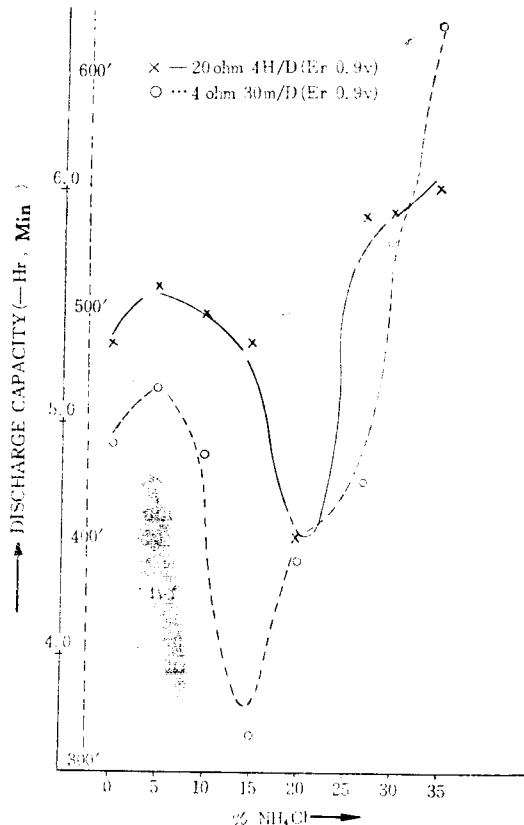
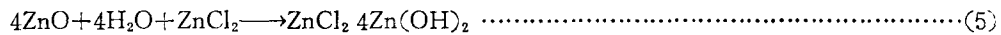


Fig. 3-2. NH₄Cl content and Intermittent discharge

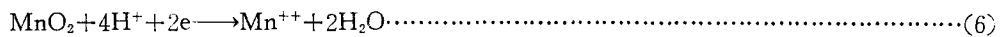
In those low NH₄Cl concentrations, especially for below-5%, showing long discharge capacity at even high drain on constant, but terribly worse in high NH₄Cl-rich solutions "E, F, G, H", getting worse and worse according to the richness of NH₄Cl. It can be said generally, through

the result of Fig. 3, NH_4Cl -rich cells when discharged at intermittent loads performs better capacity rather than ZnCl_2 cells for the ranges of 0-10% NH_4Cl along with the NH_4Cl saturated case, likewise for both loads high and low. But one thing to be attentive on, in a case of high drain intermittent discharge, the presence of NH_4Cl was not so influential toward across whole range except some ranges, much more have degraded as compared to the case of low drain. Today it is well acknowledged to recommend to add small amounts of NH_4Cl into a electrolyte is, as one of means to increase intermittent discharge capacity.

Those cells made of less NH_4Cl contents, below 5%, shows abundant $\text{ZnCl}_2 \cdot 4\text{Zn}(\text{OH})_2$ precipitates on separator section and N.C Cahoon (2) proposed a formula which was formed under following process, under a basic compound identified by Fries as $\text{ZnCl}_2 \cdot 4\text{ZnO}$,



However it has not been yet well explained about the lower performances out of the electrolytes composing of NH_4Cl 15-20% at intermittant discharges, this author would like to express the reason in light of its pH characteristics (see Fig. 4) that $[\text{H}^+]$ activity would give much influences in those contents by modifying the electrochemical reaction which produces later on manganous ions,



then furthermore, hastening a step-following chemical reaction to waste up active materials

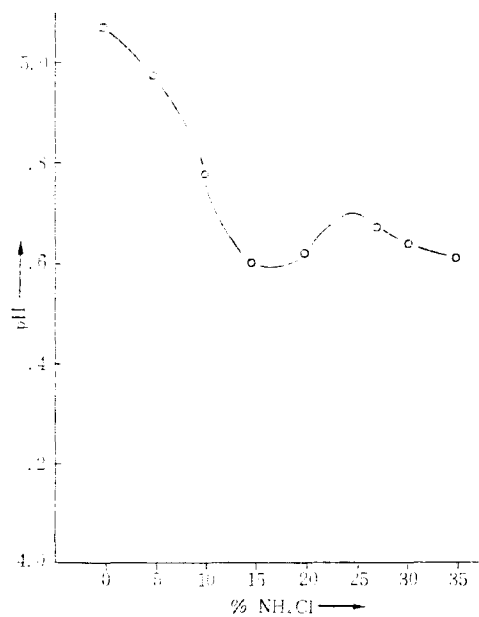
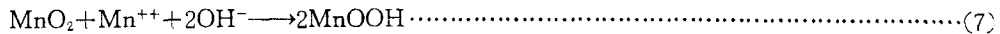


Fig. 4. pH characteristics upon different NH_4Cl contents

For those intermittent-discharge testings under a fairly low load like 20 ohms, the solubility of $\text{ZnCl}_2(\text{NH}_3)_2$ seems to increase more as compared to those constant discharge testings under heavy load, that is possibly linked to above ascertained facts that cells performs improved output

at much higher NH_4Cl -rich contents.

2.2 Chemical analysis and electrochemical reaction

2.2.1 Zn^{++} behaviors

Chemical analysis results (see Fig. 5) from those cells, made of "case A" electrolyte, discharged continuously at 20ohms indicated that Zn^{++} generated from the anode has migrated and diffused deep into mix core in overwhole and there on just being left below 10% around in the separator and/or anode surface. However, for "cases of D and E", it was different story as much as about 50% of Zn^{++} was still shown in the portion of separator and/or anode surface.

In light of this experimental result, $\text{ZnCl}_2 \cdot 4\text{Zn}(\text{OH})_2$ presumed to have higher migration tendency.

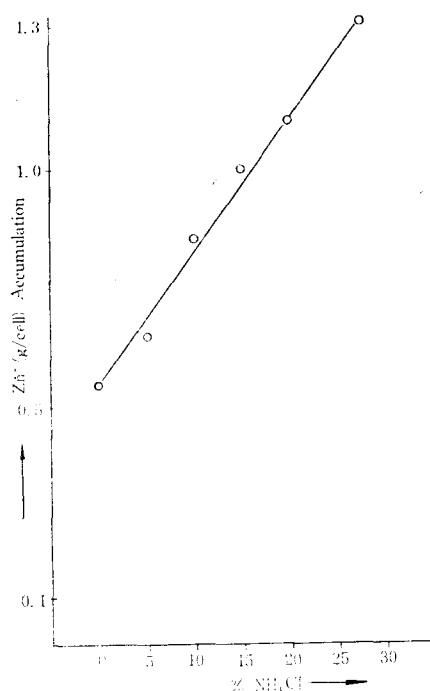


Fig. 5. Zn^{++} accumulated in separator and anode surface of said cells after constant discharge under 2 ohms load for 3 hours.

This result is in satisfactory agreement with that of phenomena in relation with concentration polarization behaviors. The concentration polarization behaviors as for sake of comparison were measured for "case A,D" type cells after their constant discharges under 2 ohms for 3 hours, and showed as much higher concentration polarization as with about three times superiority for the "case A" than "case D". Sharp increase of cell total polarization curve shown in those NH_4Cl -rich electrolytes is now attributed to accumulation of the Zn^{++} , and thus the concentration polarization pronounced at anode (Zn) side regulates the material flow slowing at the case of high power drain with constant 700mA. The least lower cell polarization was obtained from "case B"

therefore even to practical cells small fraction of NH_4Cl has been added to improve this polarization property.

2.2.2 NH_4^+ behaviors

As to find out supporting ideas on factors associating to the main discharging reaction, chemical analysis of NH_4^+ was carried on for those sample cells which discharged at 2 ohms-constant for 3 hours, and results appeared like in Fig. 6,

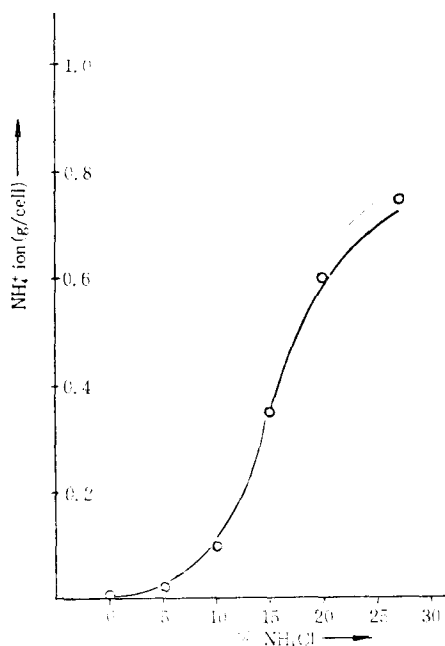


Fig. 6. NH_4^+ content in the precipitates of the cell concerned, discharged at 2 ohms-constant for 3 hours

NH_4^+ contents in the precipitate sharply increases from after the side of 5% NH_4Cl . With those lower concentration of NH_4Cl -contained-electrolytes, only small amount of NH_4^+ was detected, and this result is in good agreement with the fact of "D" zone appearance at the Fig. 3 in which showing $\text{Zn}(\text{NH}_3)_2\text{Cl}_2$ formation by an addition of small amounts of NH_3OH solution onto the electrolyte system containing of more above 10% NH_4Cl .

2.2.3 Moisture behaviors

Sample cells were also discharged at 20 ohms-constant for 3 hours to find something to be correlated between moisture consumption and pronounced electrochemical reaction (see Fig. 7) below,

Rasing up an argument theoretically against to that tested results appeared in the range of 5-27% NH_4Cl , which showing a discrepant assumption to electrochemical reaction formula (3) mentioned earlier in this paper, because this reaction seems not to involve any waters in its appearance but now we can see appreciable water consumption even at the electrolyte composing of 10% NH_4Cl .

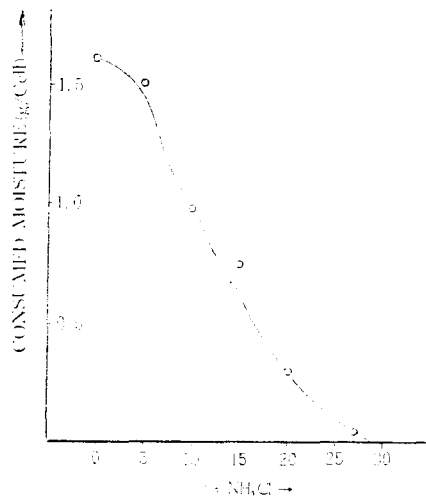


Fig. 7. Water consumption upon discharge reaction

In light of above tested results, Fig. 6 and Fig. 7, enough to speak a possible conclusion can be made on that those electrochemical reactions described as (2) and (3) take places at the same time but just with different speed, then its reaction rates each other depending on the concentration of NH_4Cl used in the electrolyte. The more NH_4Cl concentration turns up, the more the reaction (3) takes place, and therefore temporary conclusion on the prospectable reactions might be made up concerning those electrolytes as follow,

Electrolyte	Cathode (mix core)	Anode (zinc)
Below 10% NH_4Cl	$\text{ZnCl}_2 \cdot 4\text{Zn}(\text{OH})_2$	$\text{ZnCl}_2 \cdot 4\text{Zn}(\text{OH})_2$
10—25% NH_4Cl	$\text{Zn}(\text{NH}_3)_2\text{Cl}_2$	$\text{ZnCl}_2 \cdot 4\text{Zn}(\text{OH})_2$
Over 27% NH_4Cl	$\text{Zn}(\text{NH}_3)_2\text{Cl}_2$	$\text{Zn}(\text{NH}_3)_2\text{Cl}_2$

Of course, it should be different and varies depending on the discharge time, so the predominant reaction would be one either (2) or (3) or both of them (2)(3) with a same rate.

Lets make a study little more detail on the behaviors of the water in a cell in associating with the discharge reaction in the next succeeding section.

2.3. Relationship between moisture contents in the cathodic mix and its discharge property.

Various cathodic mixes were prepared for testing of moisture behaviors in the cathodic mix while setting down electrolyte composition alike ZnCl_2 20% + NH_4Cl 5% + H_2O 75% and the mix containing commercially available C— MnO_2 of which mixing ratios per one part of acetylene black (A.B) are 11.11, 7.14, and 4.17 part respectively. Sample cells were constructed after the figure of Fig. 1.

2.3.1 Discharge capacity upon the water contents

It was obvious that discharge capacity would be increased longer accordingly with increase of moisture contents in the mix upto a certain level of moisture contents, that is, of course, due to lower volume of active material of MnO_2 in a limited volume of cell package.

For to evaluate drain capacity as per unit weight of H_2O contained in unit weight of MnO_2 (assumed chemically pure), those sample cells were discharged at 2 ohms intermittent,

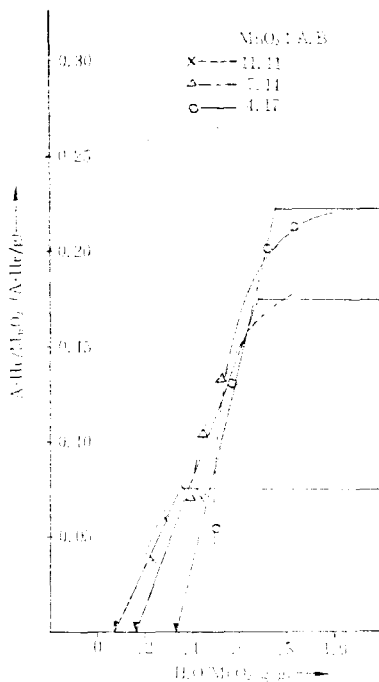


Fig. 8. Discharge capacity upon the variation of H_2O/MnO_2

As an interesting thing those values of $A \cdot hr / MnO_2$ (gr) decrease linearly with decrease of H_2O/MnO_2 up to some extent. Therefore, by extrapolating those straight lines down to base abscissa line, we can think of that moisture what being retained on even at the zero discharge capacity, and that which would not be related to a direct discharge reaction. And this water free from active reaction would depend on purity of $C-MnO_2$ concerned in. The meaning of those values of the reversed form of said slopes accounts for unit water contents useful directly for active discharging of pure MnO_2 1g and now they are all greater than value 1 which representing a molecular reaction ratio of H_2O versus MnO_2 as indicated in cell reaction formula (2).

According to the resultant indications of those values being greater than 1, we can say that water should be put more in practical cases in addition to the theoretical requirement for proper discharge reaction for sake of extra works, such transporting ions as an ionic carrier.

2.3.2. Relation between $A \cdot B/C-MnO_2$ and $H_2O/C-MnO_2$

Sample cells with variations of $A \cdot B/C-MnO_2$ were put into intermittent discharges at loads of 2 ohms, 10 ohms and 20 ohms, respectively. And the slopes obtained from the discharge

capacity (Fig.9) shall represent the unit water retained in unit A,B and the water is one sort of unuseable thing directly for generation of discharge reaction, and this water amount increases with increase of A,B/C-MnO₂ regardless its discharge conditions.

Since because the lines are straight lines as indicated by Fig.9, as mentioned earlier, this water plays important roles so as to resolve precipitates and transport ions as an ionic carrier.

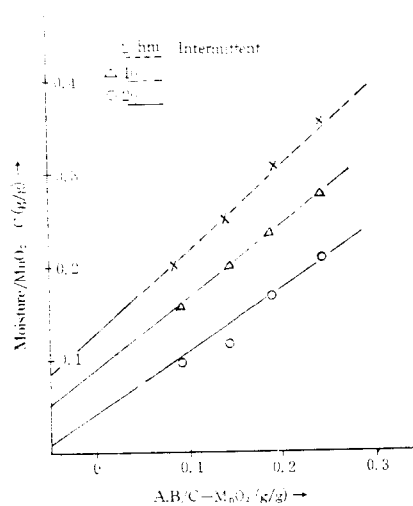


Fig.9. Water requirement for transportation of ions and the ratio of A,B/C-MnO₂

To drain high current from a cell, needless to say there should be required a plenty of water for sake of fast ionic migration. At higher current drains more water to be left as compared to cases of lower current drains, this phenomenon accounts for reaction characteristics in high drains what would not be of homogeneous and left not to be used properly on the reaction. As far as the value of A,B/C-MnO₂ goes downward, then expected worse non-homogeneous reaction would take place.

3. Conclusion

Recommendable electrolyte composition for Zinc chloride cell system should contain enough waters as for an ionic carrier, and slight amount of NH₄Cl necessary to reduce cell polarization which is very important factor in relation to obtain high powerful current drain. If we could improve the [H⁺] activity characteristics even from NH₄Cl-electrolyte system we may think about a dry cell which is powerful to discharges both at constant and inthemitant.

Reference

- ① Huber R. Metaloberflache, 24, 293 (1970)
- ② Cahoon N.C., The primary battery. John willey & Sons, 32 (1976)