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THE SILVER OXIDE-ZINC
ALKALINE PRIMARY CELL

PART V - COMPARISON OF POTASSIUM HYDROXIDE,
CESIUM HYDROXIDE, AND
RUBIDIUM HYDROXIDE ELECTROLYTES

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ABSTRACT

Preliminary work has been done on determining the capacities of the silver oxide-zinc alkaline cell when using CsOH or RbOH solution as an electrolyte. These two compounds have just recently become commercially available.

All the discharges were made using high-purity, sheet-zinc negative electrodes. It was found that the cell capacity, within limits, is directly proportional to electrolyte volume, to electrolyte concentration, and to the amount of CsOH or RbOH present in the electrolyte.

At a given set of discharge conditions, the maximum capacity that could be obtained using CsOH or RbOH electrolytes was considerably less than could be obtained from KOH when compared on a weight basis. On a volume basis KOH was slightly better than CsOH or RbOH.

PROBLEM STATUS

This is an interim report; work on this problem is continuing.

AUTHORIZATION

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THE SILVER OXIDE-ZINC ALKALINE PRIMARY CELL

PART V COMPARISON OF POTASSIUM HYDROXIDE, CESIUM HYDROXIDE, AND RUBIDIUM HYDROXIDE ELECTROLYTES

INTRODUCTION

The silver oxide-zinc alkaline cell is in considerable demand because of its many desirable characteristics. This cell has a very high capacity in watt-hours per unit weight and is capable of delivering this power at very high current densities. Another outstanding characteristic of this cell is the nearly constant voltage maintained under certain operating conditions. Moderate changes in temperature, current density, and electrolyte concentration have only a slight affect on its emf.

Whenever the demand for the cell is based on a minimization of weight or volume, a separate design will generally be needed for each set of discharge conditions. Such a design will require considerably more data than is necessary for the construction of ordinary batteries (1).

The basic data necessary for the design of a primary cell using high-purity, sheet-zinc negative electrodes and a potassium hydroxide electrolyte has already been published (2). It was found that cell capacity is directly proportional to electrolyte volume, to electrolyte concentration, and to the amount of potassium hydroxide present in the electrolyte, within certain limits which cover almost all cell designs. It has been shown that this information is applicable to many other types of zinc electrodes (3). This data was subjected to a mathematical analysis and presented graphically in a manner that could be readily utilized to design a cell having certain specific characteristics (1). This analysis makes it possible to minimize weight or volume or to maximize the output of a given cell weight or volume for a particular set of discharge conditions.

The cell consists of a negative electrode of zinc, a positive electrode of silver (II) oxide, $\text{AgO}_2$, and an alkaline electrolyte which in the past has invariably been potassium hydroxide. During the discharge the $\text{AgO}_2$ is reduced to metallic silver in a two-step process which is capable of operating at very high current densities with little polarization. The lower oxide of silver, $\text{Ag}_2\text{O}$ is also highly effective as a cathode material but has less capacity per unit weight than the $\text{AgO}_2$.

From an analysis of the equilibrium potentials measured at different activities of the components, Dirkse has shown the zinc-containing ion in a strongly alkaline solution to be $\text{Zn(OH)}_4^{2-}$ (4).

It seems probable that

\[ \text{Zn} + 4\text{OH}^- \rightarrow \text{Zn(OH)}_4^{2-} + 2e \]  

(1)

is the major reaction that occurs during cell discharge. Under certain conditions one of the following reactions may also occur:

\[ \text{Zn} + 2(\text{OH})^- \rightarrow \text{ZnO} + \text{H}_2\text{O} + 2e \]  

(2)

\[ \text{Zn} + 2(\text{OH})^- \rightarrow \text{Zn(OH)}_2 + 2e. \]  

(3)
The AgO is reduced to silver according to the following general reaction

$$\text{AgO} + \text{H}_2\text{O} + 2e \rightarrow \text{Ag} + 2\text{OH}^- \quad (4)$$

which generally takes place in two steps. As long as sufficient AgO is present, this electrode does not limit the cell capacity. Equation (4) may be combined with Eqs. (1)-(3) to give the following overall cell reactions:

$$\text{Zn} + \text{AgO} + 2\text{OH}^- \rightarrow \text{Ag} + \text{Zn(OH)}_2^- \quad (5)$$

$$\text{Zn} + \text{AgO} \rightarrow \text{Ag} + \text{ZnO} \quad (6)$$

$$\text{Zn} + \text{AgO} + \text{H}_2\text{O} \rightarrow \text{Ag} + \text{Zn(OH)}_2^- \quad (7)$$

Measurements made with a reference electrode show that cell failure always occurs at the zinc electrode as long as a sufficient amount of silver oxide is present. Consequently, the cell capacity is determined by the components of either Eq. (1), (2), or (3) or both and also by any factors that may have an effect on these components. Since zinc and hydroxyl ion are the only reactants in the anode reaction, the electrolyte must contain some compound that ionizes to give hydroxyl ion and a suitable cation. Although this cation does not enter into the cell reactions, it can have a considerable effect upon it and upon the cell characteristics by affecting such factors as solubility of electrolyte, solubility of reaction products, viscosity, conductivity of electrolyte, and many others. Changes in these factors will affect the extent to which the above reactions are polarized during a cell discharge.

Organic compounds, that will ionize to furnish hydroxyl ion, are generally unsatisfactory because they will react chemically with the silver oxide. The only metallic hydroxides that are sufficiently soluble are the hydroxides of the alkali metals, namely lithium, sodium, potassium, rubidium, and cesium. Lithium hydroxide gives very little cell capacity. Sodium hydroxide is somewhat better. Potassium hydroxide is excellent, giving a cell with very high capacity and excellent cell characteristics (2). Since the cell capacity here increases with increase in molecular weight of the cation, one might wonder if this trend would continue, thus obtaining even higher capacities with rubidium and cesium hydroxides. Such hypothesis must be verified experimentally because an extrapolation of this type is not theoretically justified.

Until a short time ago the price of cesium and rubidium compounds was so high that it was not even feasible to test any cells using their hydroxides as electrolytes. Prices on cesium and rubidium were quoted as high as $15.00 a gram. American Potash and Chemical Corporation has recently developed a commercial method of producing cesium and rubidium compounds which makes them available in appreciable quantities at greatly reduced prices. If either of these hydroxides would give sufficiently better characteristics than potassium hydroxide, then their use today in a silver oxide-zinc alkaline cell could be economically feasible.

A research program on this problem should have two main objectives. First, it should determine the feasibility of replacing potassium hydroxide with cesium or rubidium hydroxide in various cell applications. Secondly, because of the different cations involved, it should give added information on the discharge reactions and other cell phenomena. A study is being made of this problem and some of the preliminary results are given in this report.
EXPERIMENTAL METHODS

Since the AgO electrode does not polarize much, cell failure always occurs at the zinc electrode if an excess of AgO is present in the cell. To insure this excess, an assembly was made using two positive electrodes and one negative electrode, each 3.8 centimeters square. For the positive plates a grid of 40 × 30 mesh silver screen was pasted with a mixture of 5 grams of silver chloride and a few drops of potassium hydroxide, and then oxidized anodically in a solution of 15 percent potassium hydroxide at 0.25 amperes for 24 hours or until no brown spots of Ag₂O were showing. After washing and air drying, the plates contained only a few milligrams of potassium hydroxide and would analyze over 90 percent AgO, the remainder being Ag₂O.

The zinc electrode was cut from high-purity, sheet-zinc 0.020 inch thick or thicker if necessary. Even though other types of zinc electrodes give higher capacities, sheet zinc was used because it gives basic data that is easy to analyze and because its use simplifies the comparison of results obtained from various electrolytes. No separators were used in the cell assembly for the same reasons.

Two polystyrene spacers 0.15 centimeter wide, 3.8 centimeters long, and of the desired thickness were cemented to each side of the zinc sheet electrode. The total area for both sides of the electrode was 27.5 square centimeters (4.26 sq in.) after deduction of the area covered by the spacers. The electrodes were assembled in a tight fitting cell case.

Just before the start of the discharge, the electrolyte was added until its level was slightly above the top of the electrodes. All discharges were made at a constant current and a constant ambient temperature of 20° C. At the end of the discharge the emf drops very rapidly and the discharge was considered complete when the emf had dropped to 1.0 volt.

DATA AND DISCUSSION OF RESULTS

Densities of RbOH and CsOH Solutions

In analyzing the battery discharge data it was necessary to know the approximate density of the electrolyte. The available information in the literature gives the densities of CsOH solutions up to 10.5 percent and of RbOH solutions up to 28 percent (5-8). Since the batteries were discharged at concentrations of 30 percent or greater, it was necessary to determine the density curves in this region. Ten solutions of RbOH varying in concentration from 29 to 63 percent and twelve solutions of CsOH varying from 30 to 75 percent were prepared from commercial solutions having the analysis shown in Table 1.

Solutions were concentrated, when necessary, by evaporation at room temperature under vacuum. The specific gravities were measured at 0° C and 25° C by means of a Westphal balance and the data was used to calculate the densities at 20° C. The total hydroxide content for each of these solutions was determined by titration. The content of solutions prepared from commercial RbOH was calculated on the basis of the assumption that all of the hydroxide content was present as RbOH. The CsOH analyses were computed in the same manner. These data and data from the literature were used in plotting the density curves shown in Figs. 1 and 2.
Table 1
Analysis of CsOH and RbOH Solutions

<table>
<thead>
<tr>
<th>Sample</th>
<th>Analysis (wt-%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>RbOH</td>
</tr>
<tr>
<td>CsOH</td>
<td>0.21</td>
</tr>
<tr>
<td>RbOH</td>
<td>54.21</td>
</tr>
<tr>
<td>KOH</td>
<td>0.16</td>
</tr>
<tr>
<td>K₂CO₃</td>
<td>0.24</td>
</tr>
<tr>
<td>Na₂CO₃</td>
<td>0.09</td>
</tr>
<tr>
<td>H₂O (by difference)</td>
<td>45.09</td>
</tr>
</tbody>
</table>

Fig. 1 - Density of RbOH at 20°C
The density of aqueous RbOH solutions can be calculated from the equation

\[ d_{\text{RbOH}} = 0.977 + 1.222 p_1 - 0.465 p_1^2 + 1.725 p_1^3 + 0.0006(20 - t)(p_1 + 0.7) \]  \hspace{1cm} (8)

where \( d_{\text{RbOH}} \) is the density of the RbOH solution, \( p_1 \) is the fraction of the solution weight that is RbOH, and \( t \) is the temperature in degrees centigrade. The equation holds within 0.003 on Fig. 1 from \( p_1 = 0.06 \) or 6 percent up to \( p_1 = 0.63 \) or 63 percent RbOH.

The density of aqueous CsOH solutions can be calculated from the equation

\[ d_{\text{CsOH}} = 0.971 + 1.18 p_2 - 0.35 p_2^2 + 2.16 p_2^3 + 0.001(20 - t)(p_2 + 0.2) \]  \hspace{1cm} (9)

where \( d_{\text{CsOH}} \) is the density of the CsOH, \( p_2 \) is the fraction of the solution weight that is CsOH, and \( t \) is the temperature in degrees centigrade. The equation holds within 0.003 on Fig. 2 from \( p_2 = 0.09 \) or 9 percent up to \( p_2 = 0.73 \) or 73 percent CsOH. The total error in Eqs. (8) and (9) due to measurement and calculation probably averages less than 0.003.

Because of the presence of impurities, the data obtained here are slightly different from what would have been obtained with pure materials. The method of calculating the hydroxide concentration by including the other hydroxides present, would lower the corresponding densities a small amount, probably not more than 0.007. The presence of carbonates would increase the observed densities by a value that probably does not exceed 0.003. The average difference between the densities of pure RbOH and CsOH solutions and the values obtained from Figs. 1 and 2 and Eqs. (1) and (2) should be considerably less than 0.005. If any appreciable variation does occur, it would be at the high densities.
Effect of Electrolyte Volume

The reactions shown in Eqs. (6) and (7) do not consume hydroxyl ion, and if they can take place, the cell capacity would not be dependent to any great extent on the volume of electrolyte present, as long as there was enough to cover the electrodes. The reaction given in Eq. (5) consumes hydroxyl ion and its concentration drops during discharge. Assume that failure occurs when the hydroxyl ion concentration drops to a certain level $C_e$ in the double layer at the electrode surface. This value of $C_e$ should correspond to a molar concentration $C_a$ in the main body of the electrolyte. $C_a$ is a function of the current density $i$ and is independent of electrolyte volume. If $C_i$ is the initial molar concentration

$$1/60,000 (C_i - C_a) VnF = iT,$$

where $V$ is the volume of electrolyte in cc per unit area, $n$ is the valence change, $F$ is the Faraday, and $T$ is the discharge time in minutes. At a given current density and initial concentration $C_i$, all the above factors are constant except $V$ and $T$. Consequently Eq. (10) can be written in the form

$$T = kV,$$

where $k$ is a constant equal to

$$(C_i - C_a) nF/60,000 i.$$

By similar reasoning it can be shown that Eq. (11) would also hold if we had assumed that cell failure occurs whenever the zinc concentration becomes high enough to cause a high resistance film of some insoluble zinc compound such as ZnO to form on the electrode surface. Actually Eq. (11) would apply wherever electrolyte is consumed in the cell reaction as it is in Eq. (5). A large number of measurements have been made over a wide range of temperatures, electrolyte concentrations, electrolyte volumes, and current densities using sheet-zinc electrodes and potassium hydroxide electrolyte. Electrolyte volumes from 0.1 to 0.8 cc/cm$^2$ were obtained by varying the spacer thickness. In nearly all cases the cell capacity in minutes $T$ was found to be proportional to $V$, the electrolyte volume per unit area, and consequently in agreement with Eq. (11). Examples of these results are shown in Fig. 3, curve A, and Fig. 4, curves A and C.

At large values of $V$ the relationship between cell capacity and volume is no longer linear. A typical example is shown in Fig. 3, curve A, where the maximum electrolyte volume at which the linear relationship holds is approximately 0.5 cc/cm$^2$. Since this value of $V$ is considerably larger than any that may generally be encountered in an ordinary cell, it is safe to use the straight line relationship in cell design.

Since the cation does not enter into the electrode reaction, Eq. (11) would be expected to hold for cells using sheet-zinc electrodes with cesium hydroxide and rubidium hydroxide electrolytes. A number of discharges were made at 20°C and the cell capacity was determined as a function of the electrolyte volume for a number of electrolyte concentrations and current densities. In nearly every case the relationship was found to be linear. Typical examples have been plotted in Figs. 3 and 4.

Electrolyte Concentration

The variation of cell capacity with electrolyte concentration is shown in Fig. 5. The curves are characterized by a sharp increase in cell capacity with increase in electrolyte concentration, followed by an equally sharp decline. That Eq. (11) still holds in this area of declining capacity, is illustrated in Fig. 4, curve A. Thus, it is unlikely that the decline is due to a change in the electrode reaction.
Fig. 3 - Variation of cell capacity with electrolyte volume
Fig. 4 - Variation of cell capacity with electrolyte volume

Fig. 5 - Variation of cell capacity with electrolyte concentration
Viscosity and solubility effects may be of more importance here. Data of Dirkse (9) on the composition and viscosity of saturated solutions of zinc oxide in potassium hydroxide have been plotted in Fig. 6. If cell failure is considered to be due to film formation, then a capacity curve such as the one shown in Fig. 5, curve A, should be similar in nature to the solubility curve shown in Fig. 6, curve B. The curves are similar. As the potassium hydroxide content is increased, both curves rise to a maximum point and then decline rapidly. However, the maximum solubility occurs at 36 percent K, which corresponds to approximately 760 g/l KOH whereas the maximum capacity was obtained at 500 g/l KOH. The concentration of electrolyte that gives maximum capacity is known to increase as the current density decreases (2). Thus it is possible at low current densities that the concentration of electrolyte giving maximum solubility may also give maximum capacity. During a cell discharge, the zinc dissolves electrochemically and it is possible to obtain a more saturated solution than that shown in Fig. 6, which was prepared by saturating potassium hydroxide with zinc oxide. This new solubility curve is probably similar in shape to the one in Fig. 6. At this point it seems certain that the decline in cell capacity that occurs above a certain electrolyte concentration is tied closely to the solubility of the zinc oxidation products in the electrolyte.

In Fig. 6 it can be seen that the viscosity of a saturated solution is increasing very rapidly above 25 percent K (490 g/l KOH). This increase would cause a rapid decrease in the diffusion coefficient and an increase in the thickness of the diffusion layer. Consequently, the limiting current would decrease rapidly and a decline in capacity at a given current density would result. More data is needed to clarify the effects of viscosity and solubility.

If the data in Fig. 5 is replotted against molarity instead of concentration, the curves lie much closer together, as can be seen in Fig. 7. The variation among the curves is due to the effects that the different cations have on such factors as solubility and viscosity.

From approximately one third of the peak value up to the peak value, the cell capacity $T$ is directly proportional to the electrolyte concentration $C$ in grams per liter and can be expressed between these limits by

$$T = kC.$$  (12)
Figures 5 and 7 illustrate this relationship, which holds true over a moderately wide range of current densities, electrolyte concentrations, and temperatures.

At this set of conditions potassium hydroxide gives a higher cell capacity than cesium hydroxide or rubidium hydroxide and is also lighter in weight.

Equations (11) and (12) can be combined to give

\[ T = k_w CV \]

(13)

However, the volume of the electrolyte times its concentration is equal to the amount of alkaline metal hydroxide present in the electrolyte. The equation for cell capacity then becomes

\[ T = k_w W \]

(14)

where \( K \) is a function of the temperature, current density, and electrolyte material, and \( W \) is the weight of alkaline metal hydroxide in the electrolyte per unit electrode area. Within the limits of electrolyte volume and concentration previously mentioned, the cell capacity is directly proportional to the weight of hydroxide per unit area. This is illustrated in Figs. 8 to 10, where the capacity has been plotted against grams of hydroxide.
Fig. 8 - Variation of cell capacity with hydroxide content

Fig. 9 - Variation of cell capacity with hydroxide content
per square centimeter and in Figs. 11 to 13, where the same data has been plotted against milliequivalents per square centimeter. In each of these last three curves the slopes are nearly the same, potassium hydroxide being slightly the best. As the current density decreases the slopes become more nearly equal for each of the three hydroxides. The silver oxide electrode operates at high efficiency and would not be affected to any extent by a change in the cation. Under this condition, the first step in the minimization of battery weight would be the minimization of electrolyte weights. In Fig. 14, the capacities of the most effective electrolyte have been plotted as a function of the current density. The capacity is expressed in minutes per gram of electrolyte per square centimeter of electrode area. This is the maximum capacity that can be obtained under the conditions previously described. The potassium hydroxide is much more effective. It is at least 30 percent better than the rubidium hydroxide and 50 percent better than the cesium hydroxide.
Fig. 12 - Variation of cell capacity with hydroxide content

Fig. 13 - Variation of cell capacity with hydroxide content
The most effective electrolytes have been plotted on a basis of volume in Fig. 15. Potassium hydroxide has a slightly higher capacity than an equal volume of rubidium or cesium hydroxide.

CONCLUSIONS

Capacities of silver oxide-zinc alkaline cells using sheet negative electrodes were measured at various electrolyte concentrations and current densities at 20°C. Under these conditions a KOH electrolyte is much more effective than one using CsOH or RbOH. It is highly probable that KOH will be the most effective electrolyte on a weight basis wherever the negative electrode reaction consumes hydroxyl ion as it does in Eq. (1). On a volume basis, there should not be much difference among the three electrolytes.

Under certain conditions the reaction in Eq. (2) or in Eq. (3) may take place and electrolyte will not be consumed during the discharge. This will occur mainly in porous grids and at extremes of temperature and current density. It may also occur after the cell has discharged for some time according to the reaction in Eq. (1). Under these conditions, the cell capacities tend to fluctuate considerably and it may be possible that there are areas where a CsOH or RbOH electrolyte is superior to KOH.

In the area covered by this work KOH is superior to CsOH or RbOH electrolytes on the basis of weight, volume, cost, and availability.
Fig. 15 - Capacity of electrolyte in minutes per cc of electrolyte per square centimeter at 20°C

REFERENCES


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Naval Research Laboratory. Report 5635.

Preliminary work has been done on determining the capacities of the silver oxide-zinc alkaline cell when using CsOH or RbOH solution as an electrolyte. These two compounds have just recently become commercially available.

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