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Final Report

R.S. Yeo

December 1985
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RESEARCH ON SEPARATORS FOR

ALKALINE ZINC BATTERIES

Final Report

December 1985

by

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for

Technology Base Research Project
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SUMMARY

This project is concerned with the research and development of a hybrid separator as an improved battery separator in alkaline zinc secondary batteries. Particular emphasis has been directed toward increasing the cycle life of zinc electrodes by controlling the permselectivity of the separator.

Hybrid separators were synthesized and fabricated by Dr. J. Lee (RAI Research Corporation). These separators consist of a microporous film, radiation-grafted with monomer containing ion-exchange groups. The new separator incorporates the favorable aspects of both ion-exchange membranes and microporous separators. Such a hybrid separator should ideally be highly specific for fast transport of hydroxyl ion while inhibiting zincate diffusion.

Hybrid separators with a wide range of percent graft (0 to 60%) were made by varying the monomer concentration and radiation time. The grafting of ionic groups imparts the ion selectivity to the separators. The ion-exchange capacity of these hybrid separators increases with increasing percent graft. The fixed-ion concentration is as high as 8 mole/litre, while the zincate ion concentration in the hybrid separators is less than 0.1 mole/litre. This implies the ion selectivity of the hybrid separators is as effective as ion-exchange membranes.

The electrolyte uptake of hybrid separators is ca. 60 wt%. The higher the percent graft of the separator, the higher the water uptake and the lower the KOH uptake that are observed. The high electrolyte uptake suggests that hybrid separators can provide low cell internal resistance and high cell capacity. The electrolytic resistance of the hybrid separators ranges from 26 mΩ-cm² to 6.5 Ω-cm² depending on the percent graft, the prehistory of the film, KOH concentration, zincate concentration, and temperature.

In concentrated KOH solutions, t_ is 0.66 for microporous separators and t_ is 0.32-0.64 for cation exchange separators, whereas t_w is 0.76 for microporous separators and t_w is ca. 1.2 for cation-exchange separators. The cation transport number increases with decreasing electrolyte concentration due to the increase of Donnan exclusion effect. The water transport number increases with decreasing electrolyte concentration because of the greater degree of hydration of the cation. The permeability of hydroxyl ion in the hybrid separators is 1-3 x 10⁻⁶ mole/cm²/sec, corresponding to L_{OH} of 1-5 x 10⁻⁴ cm/sec. The L_{H₂O} for most separators in this study is found to be 1.35 x 10⁻⁸ cm/sec.
The zincate permeability for hybrid separator 229-3C is $9.6 \times 10^{-11}$ mole/cm$^2$/sec, while the permeability for ion-exchange membrane P2291 40/20 and microporous separator Celgard 3401 is $5.4 \times 10^{-9}$ and $2.5 \times 10^{-8}$ mole/cm$^2$/sec, respectively. Also, the diffusion coefficient of zincate ion in these separators can be described by the free volume theory. As expected, the tortuosity of the ion-exchange membranes is higher than that of the hybrid separators.

The hydraulic permeability of electrolyte in the hybrid separators varies from $1.74 \times 10^{-7}$ to $6.66 \times 10^{-7}$ ml.cm/sec.cm$^2$.atm. For comparison, the hydraulic permeability of Celgard 3401 and P2291 40/20 is $4.74 \times 10^{-7}$ and $1.16 \times 10^{-8}$ ml.cm/sec.cm$^2$.atm, respectively. The effective pore size of the hybrid separators is 45 to 63 Å while that of ion-exchange membranes is 4 to 15 Å, as estimated from the hydraulic permeability data.

Our results strongly suggest that the hybrid separators exhibit excellent selectivity against zincate ions, while the hydroxide ion and water transport through the hybrid separators are not altered by the presence of ion-exchange groups. These new separators show promise as potentially useful separators for alkaline zinc batteries.

A mathematical model that is based on the separator transport properties has been successfully formulated to analyze the change of the electrolyte concentration and volume during cell cycling. The measured active-material distribution over the zinc electrode, fluid flow rates across the separator and electrolyte concentration change during cell cycling are in close agreement with predicted values. The predicted cycle life based on various separator properties and cell operating conditions are in accord with experimental observations. The results of this modeling study could provide some direction for the future development of high performance alkaline zinc batteries. It has been clearly shown that cell separators play an important role in cycle life of these batteries.
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1. BACKGROUND

The alkaline zinc batteries have some unique properties. These batteries possess higher practical volumetric and gravimetric energy density, as well as being able to deliver higher specific power than other near-term batteries. However, the useful cell cycle life of present alkaline zinc batteries is relatively short. This is mainly due to the short cycle life of the zinc electrode (1). It has been generally agreed that one of the major factors for this failure is the cell separator (2,3). In this project, a new "hybrid" separator is developed to attempt to increase the cycle life of the zinc electrode by controlling the permselectivity of the cell separator. The "hybrid" separator is shown schematically in Figure 1. This separator embraces the advantages of both the microporous separator and the ion-exchange membrane. This thin, microporous, ion-exchange separator is new and unique in concept, and it can be tailor made to meet the specific requirements for application in alkaline zinc batteries.

2. TECHNICAL ACCOMPLISHMENTS

2.1 Synthesis and Fabrication of Separators

A series of hybrid separators have been made by the radiation grafting technique (4,5). A microporous sheet was soaked in the desired monomer solution. A chain transfer agent was then added to the solution, and the film was exposed to γ-radiation of a specific dose rate for a preset time. The "SC" process was employed because it is low cost, and it gives products with relatively short chain graft compared to the conventional "Permion" process. Short grafted chains offer less steric hinderance than long chains. The conversion of SC grafts can proceed more readily and this gives lower electrolytic resistance. It also gives much higher graft uniformity. The film produced by the SC process can generally be heat-sealed and has excellent mechanical strength.

The high energy γ-radiation causes cleavage of carbon-hydrogen bonds of the polymer and yields a highly reactive free radical, as illustrated in Figure 2. In the presence of olefinic monomers, the grafting process occurs preferentially. During the grafting reaction, little cross-linking or scission takes place since a small amount of radiation is used. Crosslinking produces a three-dimensional structure,
Figure 1. Schematic Diagram of Hybrid Separator.
\[
-\text{CH}-\text{CH}_2-(\text{CH} \ \text{CH}_2)_x- \xrightarrow{\gamma\text{-ray}} -\text{CH}-\text{CH}-(\text{CH} \ \text{CH}_2)_x- \\
\text{Polymer} \quad \text{Radical Formation}
\]

Crosslinks

\[
\text{Radical Degradation} \quad \rightarrow \text{C=CH}_2 + \text{CH}_3 (\text{CH} \ \text{CH}_2)_2 \text{CH}_2-
\]

Grafts

\[
\text{COOH} \quad \text{COOH}
\]

\[ R = \text{H or CH}_3 \]

Figure 2. Radiation Reactions.
while scission leads to molecular cleavage and polymer degradation. The mechanism and kinetics of radiation grafting are essentially the same as those of a standard polymerization reaction (6).

Hybrid separators with a wide range of percent graft were made by varying the monomer concentration and radiation time. The grafting of carboxylic acid groups imparts ion selectivity to the separators. Figure 3 shows a plot of ion exchange capacity versus percent graft for hybrid separators and ion-exchange membranes. The ion-exchange capacity of the separators increases with increasing percent graft.

2.2 Separator Stability

The ionic groups of the hybrid separators are chemically bonded onto the polymer backbone. These active groups are not leached out by the electrolyte, and they are not mechanically disintegrated during the separator wetting and dewetting processes. It is well known that polyolefin and fluoropolymer films are stable in strongly alkaline solutions. These polymers are also inert toward the electrochemical reactions of nickel and zinc electrodes. However, certain modifications of the polyolefin films are required for their use in batteries with strong oxidants, such as silver-zinc and zinc-ferricyanide cells.

The incorporation of ionic groups in the polymer chains has a drastic effect on the physical properties of hybrid separators. The thermal stability and tensile strength of the separator increase markedly (7). Figure 4 shows the thermal drying curves of the hybrid separators. It can be seen that the separators are thermally stable at temperatures up to 92°C.

2.3 Electrolyte Uptake

The permselectivity properties of separators and the operating characteristics of an alkaline zinc battery are strongly related to the electrolyte uptake of the separator. A maximum amount of absorbed electrolyte is desirable to achieve minimum cell internal resistance and to maximize capacity. However, the ion selectivity of the separator may be markedly reduced if the electrolyte uptake is too high.

The uptake of various components of the electrolyte by a separator can be described by the following relationships:

Electrolyte Uptake, \( Q_e = (W_e - W_o)/W_o \) [1]
Water Uptake, \( Q_{water} = (W_e - W_1)/W_o \) [2]
Salt Uptake, \( Q_s = Q_e - Q_{water} \) [3]
Figure 3. Ion exchange capacity for hybrid separators (Δ) and ion exchange membranes (o). Close symbols: RAI data; open symbols: PRI data.
Figure 4. Thermal drying curves of hybrid separators.
where $W_g$ is the total weight of the separator with the electrolyte; $W_0$ and $W_1$ are the dry weights of the separator before and after soaking in the electrolyte, respectively.

Figure 5 shows the water uptake and salt uptake of hybrid separators and ion-exchange membrane P2291 in 40% KOH solution. The water uptake increases with increasing percent graft because the degree of swelling is related to the ion-exchange capacity of the separator. The salt uptake of the hybrid separator decreases with increasing percent graft as dictated by the Donnan-exclusion principle. The maximum salt uptake at ca. 40% graft for the ion-exchange membranes is likely due to a decrease in membrane swelling at low percent graft and an increase in membrane ion-exchange capacity at high percent graft.

2.4 Sorption of Co-ions in Separators

Ions of charge similar to that of the charges bound to the ion-exchange polymer network are called co-ions. They are mostly, though not completely, excluded from the separator by electrostatic effect, often referred to as the Donnan-effect. When an ion-exchange separator is in equilibrium with an electrolyte solution, the following relationships are established:

$$Z_g \overline{m_g} + Z_n \overline{m_n} + \omega \overline{m_R} = 0 \quad [4]$$

$$\frac{|Z_g|}{a_n} \cdot \frac{|Z_n|}{a_g} = \frac{|Z_g|}{a_n} \cdot \frac{|Z_n|}{a_g} \quad [5]$$

where $\overline{m_R}$ and $\omega$ are the molality and valency of the fixed charges of the separator, respectively. For a cation exchanger with univalent fixed charges, i.e., $\omega = -1$, $a_g$ and $a_n$ are the activities of the cation and anion in the electrolyte, respectively, whereas $\overline{a_g}$ and $\overline{a_n}$ are the activities in the separator phase. $\overline{m_g}$ and $\overline{m_n}$ are the molalities in the separator phase. The valencies $Z_g$ and $Z_n$ have signs, positive for cations and negative for anions. Eq. [4] and [5] give information on the concentrations of co-ions (e.g. zincate ion) which are taken up by the ion-exchange separator from the surrounding solution.

The fixed-ion concentration of the separator can be calculated from the ion-exchange capacity and water uptake (8). Figure 6 shows a plot of fixed-ion concentration versus
Figure 5. Water Uptake (o, •) and salt uptake (Δ, ▲) as a function of percent graft for hybrid separators (open symbols) and ion exchange membranes (close symbols).
Figure 6. Plot of Concentration of fixed-ion versus percent graft for hybrid separators (o) and ion exchange membranes (Δ).
percent graft. The fixed-ion concentration reaches maximum for hybrid separator with ca. 22% graft. The presence of the maximum is due to a decrease in ionic group at low percent grafts and an increase in water content with increasing percent grafts. The latter effect "dilutes" the concentration of fixed-ions. Hybrid separators with more than 20% graft are designated as type II, whereas the others are regarded as type I because of the distinct difference in their transport properties.

2.5 Electric Resistivity

The electric resistivity of hybrid separators has been studied. Figure 7 shows a plot of the resistivity in 40% KOH of the hybrid separators with varying degrees of graft. The dashed line is for the case of ion exchange membranes. A decrease in resistivity was observed with increasing degrees of graft, and, in turn, with increasing ion-exchange capacity. For samples with low percent graft, the separator resistivity also changes drastically depending on the pre-history of the film. Table 1 shows the influence of pretreatments on the separator resistivity.

Figure 8 shows the separator conductivity in varying KOH concentrations for hybrid separators, ion exchange membrane and microporous separator. Data for KOH electrolyte is also included for comparison. It can be seen that the maximum conductivity for both Celgard 3400 and fiber-strengthened regenerated cellulose is at ca. 30% KOH, i.e., close to the concentration where one observes the conductivity maximum of the electrolyte. The maximum conductivity for hybrid separators and ion exchange membrane occurs at lower alkaline concentrations.

The separator resistivity at various temperatures has been measured. The separator conductivity increases at elevated temperatures, as shown in Table 2. It is attributed to both the increase of electrolyte conductivity and the increase in separator swelling.

The dependence of separator resistivity on zinicate ion in the electrolyte was studied. The results are listed in Table 3. The separator resistivity increases pronouncedly by the presence of the zinicate ion in the electrolyte. But, the dependence of resistivity on the zinicate concentration is rather small.
Figure 7. Areal resistance of separators with varying percent graft.
Figure 8. Conductivity of battery separators as a function of KOH concentration.

- △ cellulose
- □ Celgard 3400
- ○ 40/20
- ○ 196-3
- ○ 229-3C
- ... Electrolyte
TABLE 1.

EFFECT OF PRETREATMENT ON RESISTANCE OF HYBRID SEPARATORS

ELECTROLYTE: 40% KOH; TEMPERATURE: 25°C

<table>
<thead>
<tr>
<th>Sample</th>
<th>As Received</th>
<th>Leached in Acid</th>
<th>Leached in Acid and then boiled in dil. KOH</th>
</tr>
</thead>
<tbody>
<tr>
<td>191-1</td>
<td>0.097</td>
<td>163.7</td>
<td>2.50</td>
</tr>
<tr>
<td>191-2</td>
<td>0.097</td>
<td>233.5</td>
<td>7.46</td>
</tr>
<tr>
<td>191-3</td>
<td>0.097</td>
<td>224.2</td>
<td>2.95</td>
</tr>
<tr>
<td>191-4</td>
<td>0.097</td>
<td>3.7</td>
<td>3.60</td>
</tr>
</tbody>
</table>
TABLE 2
TEMPERATURE DEPENDENCE OF SEPARATOR CONDUCTIVITY
ELECTROLYTE: 30% KOH

Separator Areal Resistivity (mΩ·cm²)

<table>
<thead>
<tr>
<th>Sample</th>
<th>10°C</th>
<th>25°C</th>
<th>35°C</th>
<th>45°C</th>
<th>65°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>229-3C</td>
<td>103.2</td>
<td>83.9</td>
<td>71.0</td>
<td>64.5</td>
<td>51.5</td>
</tr>
<tr>
<td>229-4C</td>
<td>458.1</td>
<td>296.8</td>
<td>200.0</td>
<td>135.5</td>
<td>83.9</td>
</tr>
<tr>
<td>196-3</td>
<td>96.8</td>
<td>64.5</td>
<td>51.6</td>
<td>45.2</td>
<td>32.3</td>
</tr>
<tr>
<td>196-4</td>
<td>348.4</td>
<td>258.1</td>
<td>200.0</td>
<td>154.8</td>
<td>109.7</td>
</tr>
<tr>
<td>Celgard-3400</td>
<td>90.3</td>
<td>64.5</td>
<td>51.6</td>
<td>45.2</td>
<td>32.3</td>
</tr>
<tr>
<td>P2291-40/20</td>
<td>135.5</td>
<td>109.7</td>
<td>83.9</td>
<td>58.1</td>
<td>38.7</td>
</tr>
</tbody>
</table>
TABLE 3

ZINCATE CONCENTRATION DEPENDENCE OF SEPARATOR CONDUCTIVITY

ELECTROLYTE: 40% KOH  TEMPERATURE: 25°C

<table>
<thead>
<tr>
<th>Separator Type</th>
<th>0.0M</th>
<th>0.2M</th>
<th>0.4M</th>
<th>0.6M</th>
</tr>
</thead>
<tbody>
<tr>
<td>Celgard 3400</td>
<td>12</td>
<td>23</td>
<td>24</td>
<td>25</td>
</tr>
<tr>
<td>P2291 40/30</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hybrid Separator 229-4C</td>
<td>44</td>
<td>72</td>
<td>73</td>
<td>78</td>
</tr>
</tbody>
</table>
2.6 Zincate Permselectivity

Permeability of the membrane to electrolyte constituents is an important factor of separator performance. The permeability reflects the diffusivity of ionic species through the membrane matrix and any interaction between permeant and membrane. In conjunction with measurements such as electrical conductivity and electrolyte uptake, the effective ionic diffusivity can ultimately be used to correlate membrane microstructure and battery performance.

2.6.1 Zincate Permeability

The selectivity of the hybrid separators to zincate ions was measured in a two-compartment cell which was divided by a separator. Separators were presoaked in 40% KOH solution for 24 hours prior to use. The dilute solution in one side was rapidly stirred and the permeation of zincate ions into the dilute compartment was monitored by analysis of discrete samples removed at regular time intervals. At the start of a typical run, a step change of zinc concentration (0.7M ZnO in 40% KOH) was introduced into the concentrated compartment. The same volume of 40% KOH was replaced for each sample removed from the dilute compartment to maintain a constant chamber volume. The zincate concentration was determined by both ICP analysis and titration with 0.1 M EDTA using Erichrome Black T as an indicator.

Figure 9 is a plot of zincate ion permeability versus percent graft for various separators. The hybrid separators with ca. 25% graft exhibit excellent selectivity against zincate ion. It is related to the high fixed-ion concentration, as shown in Figure 10. For Type I hybrid separators the selectivity against zincate ion was not affected by the fixed-ion concentration because of the low percent graft.

The permeability is related to the diffusion coefficient by the following equation (9):

\[ P = \frac{DC}{\ell} \]  

[6]

where \( \ell \) is the separator thickness, \( C \) is the concentration in the separator, and \( D \) is the diffusion coefficient. The concentration of zincate ion in the separator in equilibrium with a 0.7 M zincate solution can be estimated from equations [4] and [5]. Table 4 summarizes the concentration and diffusion coefficient of zincate ion in the hybrid separators and ion-exchange membranes. It is noted that hybrid separators exhibit excellent zincate selectivity, as good as that for ion-exchange membranes.
Figure 9. Plot of zincate permeability versus percent graft for hybrid separators (o), microporous separator (●), and ion exchange membranes (△).
Figure 10. Plot of zincate permeability versus fixed-ion concentration for type I hybrid separators and microporous separators (●), type II hybrid separators (○) and ion exchange membranes (△).
<table>
<thead>
<tr>
<th></th>
<th>Co-Ion Concentration (mole/litre)</th>
<th>Zincate Diffusion Coefficient (cm²/sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Hybrid Separators</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>196-3</td>
<td>0.078</td>
<td>1.4 x 10⁻⁷</td>
</tr>
<tr>
<td>196-4</td>
<td>0.116</td>
<td>2.2 x 10⁻⁷</td>
</tr>
<tr>
<td>229-3C</td>
<td>0.067</td>
<td>3.6 x 10⁻⁹</td>
</tr>
<tr>
<td>229-4C</td>
<td>0.061</td>
<td>5.7 x 10⁻⁹</td>
</tr>
<tr>
<td><strong>Ion-Exchange Membranes</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>40/16</td>
<td>0.079</td>
<td>1.67 x 10⁻⁷</td>
</tr>
<tr>
<td>40/20</td>
<td>0.107</td>
<td>1.27 x 10⁻⁷</td>
</tr>
<tr>
<td>40/30</td>
<td>0.067</td>
<td>2.94 x 10⁻⁸</td>
</tr>
<tr>
<td>40/60</td>
<td>0.076</td>
<td>3.63 x 10⁻⁸</td>
</tr>
</tbody>
</table>
The function $V_p/(1-V_p)$, where $V_p$ is the volume fraction of polymer in a water swollen material, is plotted against log $D$ in Figure 11. The denominator of this term is therefore the volume fraction of water in the separator, calculated from sorption results. This function was developed by Yasuda and co-workers to treat diffusion in various hydrophilic polymers (10). Their equation:

$$D = A D^0 \exp \left[-b \frac{V_p}{1-V_p}\right]$$  \hspace{1cm} [7]

describes the relationship between the aqueous and the polymer diffusion coefficients of a species, $D^0$ and $D$, respectively. The pre-exponential term $A$ was found to depend on the electrostatic attraction of the counter-ion to fixed charge sites.

For a given water content, the diffusion coefficient of zincate ion decreases from microporous separators to type II hybrid separators to ion exchange membranes. The diffusion coefficient for type I hybrid separators resembles that for microporous separators. The diffusion coefficients for type II hybrid separators can be described by

$$\bar{D} = D^0 \exp \left[-1.8 \frac{V_p}{1-V_p}\right]$$  \hspace{1cm} [8]

whereas that for ion exchange membranes is given by

$$\bar{D} = 0.1 \ D^0 \exp \left[-1.5 \frac{V_p}{1-V_p}\right]$$  \hspace{1cm} [9]

The pre-exponential factor of 0.1 implies that tortuosity is lower in hybrid separators, compared to ion-exchange membranes, which have a more random distribution of ionic groups.

2.6.2 Zinc Penetration

When zinc is plated out of alkaline solution, the product is dendritic and spongy. In an alkaline cell, the spongy deposit grows rapidly across to the positive electrode to short-out the cell if it were not for the separator. A principal function of the separator is thus to retard the growth of the zinc sponge between the negative and positive electrodes.
Figure 11. Plot of log $D$ versus $V_p/(1-V_p)$ for microporous separator ($\bullet$), type I hybrid separators (o), type II hybrid separators (-o-), and ion exchange membranes ($\triangle$).
The main purpose of the zinc penetration test is to provide an accelerated test under controlled conditions of the rate at which zinc dendrites penetrate the separator. The approach is to determine the time for zinc dendrites to penetrate the separator and form a short circuit in the test cell. This method is commonly referred to as the Hull Test (11). The test equipment consists of a cell assembly which holds the separator sample between two zinc electrodes. Zincate-saturated 40% KOH solution was used as the electrolyte. One of the zinc electrodes serves as the anode and the other as the cathode. The zinc anode provides replenishment of the zincate as plating proceeds. Current is passed between the electrodes at a controlled current density until a zinc dendrite penetrates the separator. The test results for various separators are given in Table 5. The zinc penetration time for hybrid separators is generally the same as ion-exchange membranes, and is somewhat longer than that for microporous separators.

2.7 Transport Numbers

The concentration changes in the alkaline electrolyte are strongly related to the transport numbers of both the ions and water in the separator. The transport numbers of hydroxyl ion and water were determined by the EMF method (12) and Hittorf's method (13).

In the EMF method, a concentration cell was set up as follows:

\[
\text{Hg-HgO} / 0.9 \text{ N KOH} / \text{Separator} / 8.7 \text{ N KOH} / \text{Hg-HgO}
\]

\[\begin{array}{c}
a_1 \\
a_2
\end{array}\]

The potential, \(E\), for a cell with electrolyte solutions of activity \(a_1\) and \(a_2\) is given by the following equation:

\[
E = 2t_+ \left( \frac{RT}{F} \right) \ln \left( \frac{a_1}{a_2} \right)
\]

where \(R\), \(T\), and \(F\) have their usual significance. \(t_+\) is the apparent cation transport number, because in this type of measurement no correction has been applied for the transport of water occurring across the separator. Prior to the measurement, separators were thoroughly equilibrated in the solutions.
<table>
<thead>
<tr>
<th>Sample</th>
<th>Hull Test Time (min.)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Hybrid Separators</strong></td>
<td></td>
</tr>
<tr>
<td>191-1</td>
<td>40</td>
</tr>
<tr>
<td>191-4</td>
<td>30</td>
</tr>
<tr>
<td>191-5</td>
<td>30</td>
</tr>
<tr>
<td>191-8</td>
<td>40</td>
</tr>
<tr>
<td>196-3</td>
<td>30</td>
</tr>
<tr>
<td>196-4</td>
<td>30</td>
</tr>
<tr>
<td>229-3C</td>
<td>45</td>
</tr>
<tr>
<td>229-4C</td>
<td>20</td>
</tr>
<tr>
<td><strong>Celgard 3400</strong></td>
<td>10</td>
</tr>
<tr>
<td>P2291 40/16</td>
<td>20</td>
</tr>
<tr>
<td>P2291 40/20</td>
<td>30</td>
</tr>
</tbody>
</table>
In the Hittorf method, a cylindrical Teflon cell with platinum black electrodes was used. The pre-soaked separator was placed between the two compartments and the whole cell was pushed firmly together by a screw arrangement. Stirrers served to keep uniform concentrations throughout each compartment and reduce the formation of stagnant layers in the solution immediately adjacent to the separator. A constant current, which was maintained by a HP 6115A power supply, was measured by a digital coulometer (PAR 379).

Due to the possible volumetric error which could be introduced by the separator movement in the conventional capillary method, the weighing method (14,15) was used with some modifications. The pre-soaked separator along with the cells were surface dried and assembled. The dry weight of the cell was determined. The initial weights of the anolyte and catholyte were then obtained by determining the weight increase of the cell due to the additions of the anolyte, followed by the catholyte, to the cell. After the electrolysis process, the final weight of the anolyte was obtained by determining the weight decrease caused by the removal of anolyte and blotting dry the anode compartment. The weight of the catholyte was then determined by further emptying and blotting the cell dry. The initial and final concentrations of both the anolyte and catholyte were determined by titrating against standardized acids.

Figure 12 shows the transport number of cation versus percent graft. The transport numbers determined by EMF method and Hittorf method are in fairly good agreement. In general, cation selectivity is observed for the hybrid separators and the cation exchange membranes. The transport number for the hybrid separators reaches maximum at ca. 8% grafted. The cation transport number for the non-selective micro-porous separator is 0.29, in good agreement with the transport number of potassium ion (0.27) estimated from the ion mobilities of potassium ion (7.62 x 10^{-4} cm^2 volt^{-1} sec^{-1}) and hydroxyl ion (2.05 x 10^{-3} cm^2 volt^{-1} sec^{-1}). The novel feature is that hybrid separators exhibit excellent cation selectivity despite the microporosity. The ion exchange capacity of the hybrid separators increases with increasing grafting. The maximum cation transport number at ca. 8% graft results from the decrease of ion exchange group at low percent graft and the high swelling at high percent graft. As shown in Figure 13, the linear relationship between the counter-ion transport number and the fixed-ion concentration is observed for type II hybrid separators and ion exchange membranes. The behavior for type I hybrid separators does not obey ion exchange principle, primarily due to the low graft.
Figure 12. Cation transport number of hybrid separator (0) and ion exchange membrane (△). Open symbols: Hittorf method; closed symbols: EMF method.
Figure 13. Plot of cation transport number versus fixed-ion concentration for type I hybrid separators (●), type II hybrid separators (O), type II hybrid separators (O), and ion exchange membranes (△).
Figure 14 depicts the transport number of water versus percent graft. The water transport number exhibits a maximum value of 1.7 for samples with 8% graft.

Oda and Yawataya (16) assumed that the net transport of water (for monovalent ions and cation-exchange membranes) is given by

\[ t_w = n_+ t_+ - n_- t_- \]  

where \( n_+ \) and \( n_- \) are the number of moles of water associated with cations and anions, respectively. Accordingly they found, to a first approximation, \( t_w \) values to vary linearly with \( t_+ \). By inspecting the data of Figures 12 and 14, \( n_+ \) and \( n_- \) are found to be 4 and 1, respectively.

Figures 15 and 16 show the transport numbers of cation and water, respectively, of hybrid separator 229-4C for varying KOH concentrations. Data for Permiplex-30, a cation exchange membrane, (17), is also included for comparison. The cation transport number increases with decreasing electrolyte concentration due to the increase of Donnan exclusion effect. The water transport number increases with decreasing electrolyte concentration because of the greater degree of hydration of the cation.
Figure 14. Water transport number of hybrid separator (o) and ion exchange membranes (Δ). Open symbols: this study; closed symbols: ref. (15a).
Figure 15. Cation transport number of hybrid separator 229-4C and Permiplex-30 (dashed line) as a function of electrolyte concentration.
Figure 16. Water transport number of hybrid separators 229-4C and Permiplex-30 (dashed line) as a function of electrolyte concentration.
2.8 Hydroxyl-Ion Permeability

Two different cells were used in the measurements of hydroxyl-ion permeability. A concentration cell was set up using the cell that was used in the zincate permeability test. The amount of hydroxyl ion transported across the separator was monitored by measuring either the pH change or the conductivity change of the receiving solution. In addition, the cell used in the Hittorf experiments was also employed for the measurements of hydroxyl ion permeability. A concentration cell was set up and the changes in the electrolyte volume and concentration were determined in the similar manner as in the Hittorf experiments. The same experiments can also provide information on the transport of water (see Section 2.9).

The hydroxyl-ion permeability of a separator reflects the effect of the separator microstructure on the ionic migration, in perhaps the same manner as the separator affects the electrical resistance properties. It provides an additional means of characterizing separators. If one considers that the ionic mobility for diffusion is the same as that for conductance, then the ionic diffusivity can be related to the conductivity by the Nernst-Einstein equation (9,18):

\[
D_i = \frac{RT}{F^2} \frac{\lambda_i}{|Z_i|} \quad [12]
\]

and

\[
\lambda_i = t_i \Lambda \quad [13]
\]

where \( \lambda_i \) and \( \Lambda \) are the equivalent conductance of the ion and total equivalent conductance, respectively. \( |Z_i| \) is the valence of the ion, \( t_i \) is the transport number of the ion, and \( R, T, \) and \( F \) have their usual meanings. Table 6 lists the permeability of hydroxyl ion in various separators.

The fundamental theory of nonequilibrium thermodynamics is that the forces and the fluxes are so chosen as to conform to the following relations:

\[
J_{OH} = L_{OH} \Delta C = D \Delta C / t \quad [14]
\]

where \( L_{OH} \) is the phenomenological coefficient, and \( t \) is the separator thickness.

Figure 17 shows the phenomenological coefficients for \( OH^- \) ion as a function of percent graft of the separators. In general, a high hydroxyl-ion transport rate is observed for these separators. The \( L_{OH} \) reaches a minimum value of \( 1.5 \times 10^{-4} \) cm/sec at ca. 15% graft for the hybrid separators. As expected, the \( L_{OH} \) increase with increasing percent graft for the cation exchange membranes.
Figure 17. Plot of $L_{OH}$ versus percent graft for hybrid separators (o), microporous separators (●), and ion exchange membranes (Δ).
2.9 Transport of Solvent

The incentive for obtaining a better understanding of the electrochemical-pumping effect in these separators is to determine the relationship between the structure and the solvent transport rate. With this in mind, the hydraulic permeability of electrolyte through various separators was measured. These measurements can be used to estimate the effective pore diameter, \( D_p \). The hydraulic permeability was analyzed according to the expression (19):

\[
D_p = (128 \ell \eta L_p d^2 / \pi)^{1/4}
\]  

where \( \ell \) is the thickness of the separator, \( \eta \) is the viscosity of the electrolyte, and \( L_p \) is the hydraulic permeability coefficient. Table 6 lists the hydraulic permeability and effective pore diameter for various separators. It is clear that the effective pore diameter for hybrid separators is ca. 60Å. The dimension for Celgard 3400 is 20Å x 200Å. This pore size is equivalent to a circular pore with a diameter of 70Å.

The transport of water due to a concentration gradient was measured from the dialysis experiment, as described in Section 2.8. According to irreversible thermodynamics (20), the flux of water is given by

\[
J_{H_2O} = L_{H_2O} \Delta C
\]  

The \( L_{H_2O} \) coefficients versus percent graft is shown in Figure 18. The \( L_{H_2O} \) for most separators is ca. \( 1.35 \times 10^{-3} \) cm/sec.
<table>
<thead>
<tr>
<th>Sample</th>
<th>Hydraulic Permeability ml/cm(^2)/sec/cm(^2).atm (\times 10^9)</th>
<th>Effective Pore Size (Å)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hybrid Separators</td>
<td>174 - 666 (#)</td>
<td>45 - 63</td>
<td>This work</td>
</tr>
<tr>
<td>Celgard 3400</td>
<td>474 (#)</td>
<td>57</td>
<td></td>
</tr>
<tr>
<td>Ion-Exchange Membranes</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>P 2291</td>
<td>1.16 - 1.25 (#)</td>
<td>4</td>
<td></td>
</tr>
<tr>
<td>Nafion-120 (E-form)</td>
<td>19 (*)</td>
<td>19</td>
<td>21</td>
</tr>
<tr>
<td>Nafion-117 (N-form)</td>
<td>6 (†)</td>
<td>14</td>
<td>22</td>
</tr>
<tr>
<td>Nafion-120 (N-form)</td>
<td>3.7 (*)</td>
<td>13</td>
<td>23</td>
</tr>
<tr>
<td>Nafion-125 (N-form)</td>
<td>8.1 (*)</td>
<td>15</td>
<td>24</td>
</tr>
<tr>
<td>Nafion-117 (N-form)</td>
<td>4.6 (*)</td>
<td>13</td>
<td>24</td>
</tr>
</tbody>
</table>

Electrolyte - (#) 40 wt% KOH; (*) \(\text{H}_2\text{O}\); (†) \(\text{l.\,ON\,NaCl}\).
Figure 18. Plot of $L_{H_2O}$ versus percent graft for hybrid separators (o), microporous separator (●), and ion exchange membranes (△).
3. THEORETICAL ANALYSIS OF CYCLE LIFE OF ALKALINE ZINC CELLS

The purpose of this analysis is to correlate the cycle life of zinc-nickel oxide cells to the transport properties of the separator, the behavior of alkaline zincate solution, and the current distribution on the zinc electrode. The model describes cell failure due to shape change of the zinc electrode. Dendritic shorting could be controlled by the ion selectivity of the separator or by additives to the zinc electrode.

3.1 Electrode Reactions

The electrode reactions at or near the anode are:

**Charge-transfer reaction**

\[
\text{Zn} + 2\text{OH}^- \xrightarrow{\text{charge}} \text{Zn(OH)}_2 + 2\text{e}^- \tag{17}
\]

**Solution reaction**

\[
\text{Zn(OH)}_2 + 2\text{OH}^- \rightarrow \text{Zn(OH)}_4^{=} \tag{18}
\]

**Precipitation**

\[
\text{Zn(OH)}_4^{=} \rightarrow \text{ZnO} + \text{H}_2\text{O} + 2\text{OH}^- \tag{19}
\]

The overall reaction for the anode becomes

\[
\text{Zn} + 2\text{OH}^- \xrightarrow{\text{discharge}} \text{ZnO} + \text{H}_2\text{O} + 2\text{e}^- \tag{20}
\]

The electrode reaction at the cathode is

\[
2\text{NiOOH} + 2\text{H}_2\text{O} + 2\text{e}^- \xrightarrow{\text{discharge}} 2\text{Ni(OH)}_2 + 2\text{OH}^- \tag{21}
\]

Experimental evidence (25,26) indicates that potassium ions are taken up by nickel-oxide electrodes during the charge cycle, and released during the discharge cycle.
If one assumes a hydration number of 4 for the K⁺ ion (27), and 4 for the OH⁻ ion (28), then equation [21] can be written as:

\[
\frac{x}{2} \text{NiOOH} (-\text{KOH, }4\text{H}_2\text{O}) + (2 - 8x)\text{H}_2\text{O} + 2e^- \\
\text{discharge} \quad \rightarrow \quad 2\text{Ni(OH)}_2 + (2+x)\text{OH}^- + x\text{KOH} \quad [22]
\]

A recent study by Barnard et al (26), indicates that the take-up/release of potassium ions depends on the crystal structure of the nickel oxide electrode: 0.102 mol per 2e⁻ for β-NiOOH and 0.47 mol per 2e⁻ for γ-NiOOH. If \( x = 0.1 \) is assumed, then equation [22] becomes:

\[
2\text{NiOOH} \cdot (0.05\text{KOH, }0.8\text{H}_2\text{O}) + 1.2\text{H}_2\text{O} + 2e^- \\
\text{discharge} \quad \rightarrow \quad 2\text{Ni(OH)}_2 + 2.1\text{OH}^- + 0.1\text{K}^+ \quad [23]
\]

Eq. [23] was used instead of eq. [21] since there is no change in the total electrolyte volume during cell cycling. There will be no change of OH⁻ and H₂O in the cell without a separator during cell charge/discharge process.

3.2 Concentration Change in Zinc Compartment

There are three ionic species responsible for the charge transfer between the two electrodes, namely, K⁺, OH⁻ and zincate ions.

The concentration of anolyte in an alkaline zinc cell changes during discharge as a result of the following events:

(a) depletion of OH⁻ by electrochemical reaction;
(b) replenishment of OH⁻ by migration from the catholyte under electric field.
(c) replenishment of OH⁻ by diffusion across the concentration gradient.
(d) transport of water including electroosmotic and osmotic movements, and depletion or replenishment by electrochemical reaction.
These events are given by the following rate equations:

\[
d(OH^-)/dt = -I/nF = - I/F \tag{24}
\]

\[
d(OH^-)/dt = \frac{It_-}{F} \tag{25}
\]

\[
d(OH^-)/dt = L_{OH} (C_C - C_a) \cdot A \tag{26}
\]

\[
d(H_2O)/dt = I/2F \tag{27}
\]

\[
d(H_2O)/dt = -It_w/F \tag{28}
\]

\[
d(H_2O)/dt = L_{H_2O} (C_C - C_a) \cdot A \tag{29}
\]

\[
I = i \cdot A \tag{30}
\]

where \(L_{OH}\) and \(L_{H_2O}\) are the phenomenological coefficients of \(OH^-\) ion and water, respectively; \(t_-\) and \(t_w\) are the transport number of the \(OH^-\) ion and water, respectively; \(C_C\) and \(C_a\) are the concentrations of KOH in the catholyte and anolyte, respectively; \(A\) is the membrane area, and \(i\), \(n\), and \(F\) have their usual meanings.

Combining equations [24] to [26] yields

\[
d(OH^-)/dt = (t_-1)I/F + L_{OH} (C_C - C_a) \cdot A \tag{31}
\]

whereas combining equations [27] to [29] yields

\[
d(H_2O)/dt = (0.5-t_w)I/F + L_{H_2O}(C_C - C_a) \cdot A \tag{32}
\]

Equations [31] and [32] imply that the \(OH^-\) in concentration will not change if \(t_- = 1\) and \(t_w = 0.5\). \(C_C\) and \(C_a\) change only if the concentration of \(OH^-\) ion is changed. Figure 19 shows the concentration change during cycling of a cell using two layers of P2291 40/30. The KOH concentration increases during charge and decreases during discharge. The volumetric flow of water across the separator for the same cell is illustrated in Figure 20. Water flows from the zinc compartment to the nickel-oxide compartment during discharge, and the flow reverses direction during charge. The results reported by Hamby et al (29) are in close agreement with the calculated values (shown in Figures 19 and 20) from the present mathematical model. The same experimental conditions given by Hamby et al were used in the mathematical calculation.
Figure 19. KOH concentration of the anolyte as a function of cycling.

--- predicted results from this modeling;

experimental values of Hamby (29).
Figure 20. Volumetric flow rate across the separator as a function of cycling.
---, predicted results from this modeling;
---, results reported by Hamby (29).
3.3. Irreversible Dissolution of Zincate Solution

Zincate solutions may be prepared by dissolving ZnO in aqueous KOH, and the ZnO solubility increases with increasing KOH concentration. The most common of the complex ions in this solution is $\text{Zn(OH)}_4^{2-}$ (30). When zinc is dissolved anodically in KOH solutions, the product of the charge transfer reaction is $\text{Zn(OH)}_2^- \ (31)$. As shown in Figure 21, the extent to which $\text{Zn(OH)}_2^-$ dissolves in the electrolyte is 2-3 times higher than the equilibrium solubility of ZnO in the KOH solutions and is usually referred as supersaturated solution (32). These solutions have a fair degree of stability but the excess zincate is eventually precipitated as ZnO (33).

As the KOH concentration decreases during cell discharge, part of the zincate ion will be precipitated out as ZnO, according to equation [19], and deposited on the lower portion of the electrode, and, perhaps, in the separator and cell bottom. The concentration of zincate will be reduced to reach the solubility limited (point B). The amount of ZnO loss can thus be given by:

$$W_{\text{ZnO}} = K \cdot (C_1 - C_2) \quad [33]$$

where $C_1$ and $C_2$ are initial and final, KOH concentration, respectively. $K$ is the concentration coefficient of zincate solubility. In this study, $K = 0.28$ mole ZnO/mole KOH is used.

As the KOH concentration increases to concentration $C_1$ during cell charging, the ZnO precipitated previously cannot re-dissolve into the solution due to the solubility limit of ZnO, point C. However, the solution is available for further dissolution of the anodic product and the amount of $\text{Zn(OH)}_2^-$ dissolved from the electrode would be equal to $W_{\text{ZnO}}$. Another amount, $W_{\text{ZnO}}'$ of ZnO would be again precipitated from the solution during the next discharge cycle, because of lower KOH concentration. Thus, the degree of zinc active material loss from the electrode at N th cycle can be given by:

$$\% \text{ Loss} = N \frac{W_{\text{ZnO}}}{W_0} \quad [34]$$

where $W_0$ is initial weight of ZnO.

3.4 Current Distribution

Equations [31] and [32] suggest that the concentration change will be higher with higher current density. The loss of ZnO will be higher and the cycle life will be shorter for higher current density, as shown in Figure 22. The amount of electrolyte transferred decreases with increasing current density. An opposite trend will occur if $t_w < 0.5$. 

-41-
Figure 21. Solubility curves of ZnO and Zn(OH)$_2$ in KOH.
Figure 22. Cycle reaching 60% capacity and percent electrolyte transferred as a function of current density. Conditions: ZnO capacity = 2, electrolyte stoichiometric ratio = 1, KOH concentration 8.6 M, \( t_e = 0.5 \), \( t_w = 1.2 \), \( L_{OH} = 3 \times 10^{-4} \) cm/sec, \( L_w = 10^{-3} \) cm/sec, \( L_{w} = 10^{-3} \) cm/sec. 4-hr. charge and 4-hr. discharge.
Figure 23 shows a cross section of the zinc-nickel oxide cell with electrolyte reservoirs that are present above the electrodes. The x direction is parallel to the direction of the electric current and the y direction is in the direction perpendicular to the electric current. One end of the electrode compartment at $y = 0$ is closed, and the other end of the electrode at $y = L$ is next to the electrolyte reservoirs. The current density is infinite at the top ($y = L$) of the electrodes since the current can flow through the electrolyte reservoirs. The electrodes meet the cell bottom casting (an insulator) at a right angle at $y = 0$, and the current density would not be affected by the edge effect. The primary current distribution with both electrode edges open and the inter-electrode distance is half of the electrode length can be described by the equation (34).

$$\frac{i_y}{i_{avg}} = \frac{\pi}{K} \cosh \frac{\pi}{K} \left( \frac{\sinh^2 \pi}{2} - \sinh^2 \left( \frac{2y}{L} \right) \right)^{-1/2}$$

where \(L\) is the electrode length, \(y\) is measured from the center of the electrode, and \(K\) is the complete elliptic integral of the first kind. In this study, the primary current distribution is first calculated from equation [35] for the top to the electrode. The value of \(y\) is then doubled and \(y\) is now measured from the "closed" bottom of the electrodes.

Due to the nonuniform current distribution, a higher current density at the top of the electrodes will occur. A higher concentration change at the top of the electrode than that at the rest of the electrode is expected as illustrated in the upper part of Figure 24. It follows that the loss of zinc oxide at the top would be higher than that at the rest of the electrode, as shown in the lower part of Figure 24. The calculated result agrees well with the data reported by Hamby et al (29).

### 3.5 Cycle Life Analysis

#### 3.5.1 Effect of Electrolyte Concentration

Figure 25 shows the cycle life and electrolyte transferred as a function of electrolyte concentration. The cycle life increases with increasing KOH concentration. Pemsler (35) has reported that the cycle life is higher for more concentrated KOH electrolyte. As shown in Table 7, this theoretical model predicts the cycle life very well with the results obtained by Pemsler. Due to the presence of limited (stoichiometric) electrolyte, ca. 55% of electrolyte will be transferred across the separator during the discharge cycle and the same amount will be transferred back during the charge cycle. It is worth mentioning that an opposite concentration dependence on cycle life may result if the separator properties and cell operations conditions (such as current density) are different.
Figure 23. Schematic cell cross section and flow pattern on discharge.
Figure 24. Upper part. KOH concentration distribution of the zinc compartment after 3-hr. discharge. Average current density = 15 mA/cm². Lower part. Normalized ZnO distribution.

---, predicted results from the modeling.

○ experimental results of Hamby (29).
Figure 25. Cycle reaching 60% capacity and percent electrolyte transferred as a function of electrolyte concentration. Conditions: ZnO capacity = 2, electrolyte stoichiometric ratio = 1, current density = 15 mA/cm², t₁ = 0.5, t₂ = 1.2, L₀H = 3 x 10⁻⁴ cm/sec, L₆ = 10⁻³ cm/sec. 4-hr charge and 4-hr discharge.
TABLE 7

EFFECT OF ELECTROLYTE CONCENTRATION ON CYCLE LIFE

<table>
<thead>
<tr>
<th>Concentration</th>
<th>Experimental</th>
<th>Model Prediction</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.0 M</td>
<td>255</td>
<td>242</td>
</tr>
<tr>
<td>8.3 M</td>
<td>375</td>
<td>446</td>
</tr>
</tbody>
</table>

Conditions:
3 layers Celgard 3501
ZnO capacity is 3.
4-hr. charge at 5.5 mA/cm$^2$ and 2-hr. discharge at 11 mA/cm$^2$. 
3.5.2 Effect of Electrolyte Additive

Several modified electrolytes to reduce the zinc species concentration in KOH electrolyte have been used in order to improve the cycle life of alkaline zinc cells. Nichols et al(36) have shown that the rate of zinc material redistribution in zinc-nickel oxide cells is substantially reduced by using electrolyte additive to reduce ZnO solubility. Equation [33] suggests that the ZnO loss will be reduced for a lower zincate solubility, or a smaller K. As shown in Table 8, the cycle life increases several times when an electrolyte with zinc-species solubility, approximately one-fourth of that in standard alkaline electrolyte is used.

TABLE 8

EFFECT OF ADDITIVES ON CYCLE LIFE

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>% Loss per Cycle</th>
<th>Experimental</th>
<th>Model Prediction</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.4 M KOH</td>
<td>0.46</td>
<td>261</td>
<td>264</td>
</tr>
<tr>
<td>7.4 M KOH + Additives</td>
<td>0.09-0.14</td>
<td>857-1333</td>
<td>1056</td>
</tr>
</tbody>
</table>

Conditions:

3 layers Celgard 3401

Zn-active material capacity: 3

6-hr charge at 5.16 mA/cm² and 2.5-hr discharge at 12.4 mA/cm²
3.5.3 Effect of Electrolyte Volume

Figure 26 shows the influence of electrolyte volume on the cycle life of alkaline zinc cells. The cycle life decreases as the electrolyte volume increases. The amount of electrolyte transferred across the separator is constant so that the percentage of electrolyte transferred decreases with increasing electrolyte volume.

3.5.4 Effect of Separator Thickness

Figure 27 illustrates the influence of separator thickness on cycle life. The cycle life decreases drastically with increasing separator thickness and number of layers of separator. It is because the $L_{OH}$ coefficient decreases as the separator thickness increased. The amount of electrolyte transferred across the separator is ca. 53% and changes insignificantly with separator thickness. This model prediction is consistent with the results reported by Pemsler (35). As shown in Table 9, the cycle life is higher for a cell using two layers of Celgard than that for the cell with three layers of Celgard. It is worth noting that an opposite trend could occur because the dendritic shorting for a cell using Celgard increases with decreasing separator thickness and/or number of layers employed.
Figure 26. Cycle reaching 60% capacity and percent electrolyte transferred as a function of electrolyte stoichiometric ratio. Conditions: ZnO capacity = 2, KOH concentration = 8.6N, current density = 15 mA/cm², \( t_0 = 0.5 \), \( t_w = 1.2 \), \( L_{OH} = 3 \times 10^{-4} \) cm/sec, \( L_{dW} = 10^{-3} \) cm/sec. 4-hr charge and 4-hr discharge.
Figure 27. Cycle reaching 60% capacity and percent electrolyte transferred as a function of separator thickness. Conditions: ZnO capacity = 2, electrolyte stoichiometric ratio = 1, KOH concentration = 8.6 N, current density = 15 mA/cm², t₀ = 0.5, t₁ = 1.2, L₀H = 3 x 10⁻⁴ cm/sec, Lₙ = 10⁻³ cm/sec. 4-hr charge and 4-hr discharge.
## TABLE 9

**EFFECT OF NUMBER OF LAYERS OF SEPARATOR ON CYCLE LIFE**

<table>
<thead>
<tr>
<th>Number of Layers</th>
<th>Experimental</th>
<th>Model Prediction</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>62</td>
<td>104</td>
</tr>
<tr>
<td>3</td>
<td>20</td>
<td>70</td>
</tr>
</tbody>
</table>

**Conditions:**

- KOH concentration: 5 M
- ZnO capacity: 1
- 5-hr charge and 3-hr discharge at 12 mA/cm².
- Separators: 1 mil Celgard 3501
3.5.5 Effect of Electrolyte Permeability

Figure 28 shows the cell cycle life for varying phenomenological coefficients. The cycle life increases drastically for separators with $L_{OH}$ greater than $10^{-4}$ cm/sec. The effect of $L_{H_2O}$ on cycle life is relatively small. Since $L_{OH}$ is related to the separator resistance, cells with high resistance separators will yield short cycle life. This observation is consistent with the results reported previously (37).

3.5.6 Effect of Transport Numbers

Figure 29 shows a plot of cycle life versus $t_\perp$. A maximum cycle life occurs at high $t_\perp$ values. The position of the maximum depends on the $t_w$ value and the relationship can be described by

$$(t_\perp)_n^{\infty} = 1 - 0.18 (t_w - 0.5)$$

Results suggest that the cycle life decreases with increasing cation selectivity. An anion exchange separator is favorable for reducing the electrode shape change problem. However, dendritic shorting would increase when the cation selectivity decreases.

Figure 30 shows the amount of electrolyte transferred across the separator. The percent of electrolyte transferred can be given by

$$\% = 74.8 (1-t_\perp) + 22.7 (t_w - 0.5)$$

A complete loss of electrolyte will occur for a cell using separators with $t_w$ greater than 1.5 and $t_\perp = 0$. The loss decreases with increasing $t_\perp$ and decreasing $t_w$. A high electrolyte loss would cause cell dry-out and shorten the cell cycle life.

3.5.7 Performance of Commercial Separators

Table 10 summarizes the calculated cycle life of alkaline zinc batteries using various separators. In general, the cycle life is higher for microporous-type separators than for membrane-type separators. The tendency for dendritic shorting for microporous separators is higher than for hybrid separators (see Table 5 and Figure 10). It is clear that the best cell cycle life can be realized for cells using hybrid separators.
Figure 28. Cycle reaching 60% capacity and percent electrolyte transferred as a function of $L_{OH}$ and $L_{H_2O}$. Conditions: ZnO capacity = 2, electrolyte stoichiometric ratio = 1, KOH concentration = 8.6 N, current density = 15 mA/cm², $t_-$ = 0.5, $t_w$ = 1.2. 4-hr charge and 4-hr discharge.
Figure 29. Cycle reaching 60% capacity as a function of $t_-$ and $t_w$. ---, $t_w = 0.5$; ..., $t_w = 1.0$; ---, $t_w = 1.5$; ---, $t_w = 2.0$.
Conditions: ZnO capacity = 2, electrolyte stoichiometric ratio = 1, KOH concentration = 8.6 N, current density = 15 mA/cm$^2$, $I_{OH} = 3 \times 10^{-4}$ cm/sec, $I_{H2O} = 10^{-3}$ cm/sec. 4-hr charge and 4-hr discharge.
Figure 30. Percent electrolyte transferred as a function of $t_-$ and $t_w$. Conditions same as that given in Figure 29. The dashed line represents the $t_-$ values where the cycle life is maximum.
TABLE 10

CYCLE REACHING 60% CAPACITY FOR CELLS WITH VARIOUS SEPARATORS
(1 LAYER SEPARATOR, 1 MIL THICK)

<table>
<thead>
<tr>
<th>Separator</th>
<th>Number of Cycles</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hybrid Separators</td>
<td></td>
</tr>
<tr>
<td>196-4</td>
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<tr>
<td>Microporous Separators</td>
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<td>3401</td>
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<tr>
<td>Ion Exchange Membranes</td>
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<td>40/60</td>
<td>212</td>
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<tr>
<td>40/100</td>
<td>112</td>
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4. TECHNICAL FEASIBILITY

An ideal separator for alkaline zinc battery should have excellent selectivity against zincate ion while allowing fast hydroxyl-ion transport. The ratio of hydroxyl ion permeability to zincate permeability is plotted against percent graft for hybrid separators and ion-exchange membranes in Figure 31. It is obvious that the permeability ratio for hybrid separators can be as high as four orders of magnitude.

Figure 32 depicts the zincate permeability and hydraulic permeability for hybrid separators, microporous separators, and ion-exchange membranes. An ideal separator should have low zincate permeability, high hydraulic permeability, and low electric resistivity (or high hydroxyl-ion permeability). The zincate permeability for microporous separators is higher than that of both the hybrid separators and ion-exchange membranes. On the other hand, the hydraulic permeability of the ion-exchange membrane is two orders of magnitude lower than that of the microporous separator and hybrid separator.

Table 11 summarizes all the advantages of hybrid separators. It is clearly shown that hybrid separators possess all the desirable properties for use in secondary alkaline zinc batteries.

A mathematical model based on the separator transport properties has been successfully formulated to analyze the change of the electrolyte concentration and volume during cell cycling. Measured active material distribution over the zinc electrode, volume average fluid flow rates across the separator, and electrolyte concentration change are in agreement with predicted values. The predicted cycle lives based on various separator properties and cell operating conditions are in accord with the experimental observations. The results of this modeling study could provide some direction for the future development of high performance alkaline zinc batteries. It has been clearly shown that the cell separator does play an important role in cycle life of these batteries.
Figure 31. Plot of permeability ratio of hydroxyl ion over zincate ion as a function of percent graft for hybrid separators (o) and ion exchange membranes (△).
Figure 32. Plot of zincate permeability versus hydraulic permeability for hybrid separators (o), ion exchange membranes (△), and microporous separators (●).
TABLE 11

ADVANTAGES OF HYBRID SEPARATORS

A. Hybrid separator combines the advantages of both the microporous and the ion-exchange membraneous separators:

1. Cationic selectivity slows down the tendency for dendrite shorting.
2. Microporous properties allow easier electrolyte flow, reducing shape change problems.
3. Permanent water/electrolyte wettability.
4. Excellent chemical stability.

B. Best separator can be achieved by optimizing separator properties, such as electrolytic resistivity, ionic selectivity, pore size, crosslinking and fixed charge density.

C. Material cost and manufacturing cost are low (<$1/ft²).

D. Fabrication and handling techniques are easy.
5. ACKNOWLEDGEMENT

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6. REFERENCES


PUBLICATIONS


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