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Cellulosic separator applications: new and improved separators for alkaline rechargeable cells

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Abstract

A study has been established at Naval Surface Warfare Center, Crane Division (NAVSURFWARCENDIV) and Rutgers University to obtain material analysis data on cellulosic separator properties such as tensile strength and swelling of alkaline-soaked film samples, degree of polymerization and crystallinity, cationic and anionic diffusion and penetration rates in alkaline media, and X-ray diffraction for crystallinity. These data are then related to cycle- and wet-life information from model electrochemical cells as a function of separator composition on an alkaline chemistry rechargeable cell set. The first examples used in this program are silver–zinc rechargeable cells of 28 Ah capacity, identical in every respect except for the separator composition, which are being tested in statistically significant numbers under identical temperature and relative humidity conditions, with 45% KOH as the electrolyte. The cycle-life test regime of continuous cycling is: $C/5$ discharge to 1.30 V, and $C/30$ and $C/60$ charge to 2.03 V, while the wet-life test regime includes a 30-day wet-stand at full charge between cycles. At the outset of the cell testing, a baseline cell was selected from each set in the matrix after the so-called formation cycling was complete, and the physical properties of crystallinity, tensile strength, and degree of polymerization were re-measured. Then, at intervals during cycle- and wet-life cycling, and as cells fail the life tests, these properties will be measured again for selected cells. In this way a correlation will be established between separator life under charge/discharge conditions in actual cells and the critical physical properties of each separator film. Eight separator compositions, all cellulose-based, are being evaluated. The purpose of the study is to utilize the cycle- and wet-life data which are a function of separator composition and physical properties in the alkaline chemistry rechargeable cell set, to designate a 'best' separator for incorporation into actual production cells by the manufacturing community for silver/zinc rechargeable cells. The recommendations will take the form of minimum separator physical properties which are beneficial to cell performance and long life, resulting in an improvement in the assets available for Fleet use in the US Navy. This paper discusses the data available to date on cycle- and wet-life, and their relationship to separator physical properties before and at several stages during cycling.

Keywords: Cellulosic separators; Separators; Alkaline rechargeable cells

1. History

About 60 years ago, the utility of regenerated cellulose film as a battery separator was recognized as a forward step which advanced the silver/zinc battery to a practical system. The French professor Henri André, who had been working with the silver–zinc system since the late 1920s, published a paper [1] in 1941 in which he stated "... that the short life of the system, could be considerably improved by the introduction of a suitable semipermeable separator". In this way the migration of silver colloid to the negative plate was prevented, as were short-circuits due to zinc 'trees' from the negative to the positive plate. Not until the introduction of such membranes could the great energy content per unit of weight and volume of the silver/zinc cell be utilized in a sufficiently reversible way.

André's previous experience in colloids in the mid 1920s made him believe that part of the trouble with the zinc and silver electrodes could be resolved by a regenerated cellulosic membrane. At first he made his own [2] by treating nitrocellulose and acetocellulose in order to obtain a semipermeable membrane; the first membrane patent was issued in 1932. An early US patent by André [3] specified a storage battery with semipermeable separation based on regenerated cellulose (cellophane) and special electrode arrangements. As stated by Fleischer [4]: ..." the requirements for preventing the diffusion of silver oxide (to the negative) and the growth of zinc in trails (towards the positive) are marginally met by

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the use of regenerated cellulosic film, usually cellophane or regenerated sausage casing in combination with porous electrolyte-absorbent separators. Generally, the cellulose film has been applied in multiple layers in the composite separator system ... it is generally recognized that regenerated cellulose lacks the desired chemical stability to withstand degradative effects during operation. The cellulose base is susceptible to oxidation and hydrolysis reactions which lead to structural changes. These changes ... permit an acceleration of the processes leading to cell failure (and short stand and cycle-life).''

Regenerated cellulose films are also commonly used in alkaline manganese cells, both primary and secondary, in nickel/cadmium industrial batteries, zinc/air cells, and silver/cadmium batteries, as well as in silver/zinc batteries. Although the electrolyte concentrations are somewhat different from one chemistry to another, the same fundamental properties and problems for separator films are commonly observed in these systems.

The nature of cellulosic films is affected by the source of the raw material stock, e.g. wood pulp versus cotton linters, and the chemistry and mechanics of the film forming process. Wood is, on average, 40–50% cellulose, the remainder being lignin and other non-cellulosic entities. Cotton is predominantly cellulose and may contain as little as 3% impurities [5]. Cellulose is polydisperse and the average polymer chain length depends on the source and the method of purification. In native cotton cellulose, the average chain length (DP, degree of polymerization) can be more than 3500, whereas it is commonly 700–1300 in wood pulps. In commercial regenerated cellulose from wood (by the viscose process), typical average chain length is 200–600. In the fabrication of films, a stretching step is included which increases the tensile properties in the direction of the stretch, usually the machine direction, although it is possible to stretch film in the transverse direction as well, to improve transverse properties.

2. Introduction

The separator currently used in silver/zinc rechargeable cells for a great many Navy applications is a cellophane film derived from wood pulp by a standard viscose process. The film is typically drawn to a thickness of 1 mil (0.025 mm), and usually five or six layers are used to wrap the cathode (silver plate) in the cells, to minimize silver migration and retard zinc dendrite growth. The film is slowly hydrolyzed in the strongly alkaline conditions of the cell chemistry, so it is also a sacrificial membrane. Thus, the maintenance of barrier properties and physical integrity are important to cycle- and wet-life of the cells.

Despite the history of testing and evaluation of cellophane films with the intent of improving this alkaline rechargeable cell performance, over the past ten years a substantial decrease in cell life has occurred in cells built for Navy use. In the historical efforts to understand how the physical and chemical properties of various cellulosic materials contribute to the manner in which these materials behave in real silver/zinc rechargeable cells [6–9], there has been an absence of coordination between measurement of separator properties and correlation of that data with cycle- and wet-stand life data from a matrix of rechargeable cell tests, followed by thorough failure analysis. Thus, a programme was initiated at the NAVSURFWARCENDIV Crane and Rutgers University, with financial support from a number of government entities, to study a set of properties for a variety of source-material and processing methods for cellophanes, and then to build a matrix of test cells which incorporated these cellophanes for evaluation by cycle- and wet-stand life testing.

The physical measurements on separator films included crystallinity, degree of polymerization, dry and wet thickness, dry and wet tensile strength, and silver and zinc migration rates. Subsequent to the determination of physical properties, a selection from the separator films currently available from various manufacturers were built into model cells for cycle- and wet-life testing. The separators were selected to represent a cross section of the previous property characteristics so that a correlation could be obtained between these properties and cell performance.

The test cells were built from a single stock of silver and zinc plates of identical thickness and loading, containing NAVSEC-1 composition [10] in place of mercury in the anodes, and filled with electrolytes of identical composition. The combined wet thickness of the separator for the cathode wrap was also constant. Therefore, the only variable from one cell set to another was the separator film used. A sufficient number of cells with each separator type was utilized in assembling a test matrix to provide statistical reliability for the data collected for cycle- and wet-life, and all cells were treated identically in the test programme. Finally, analyses were performed on the separators, plates and cells at intervals during the testing and at the conclusion of cell-life to determine the mechanisms for material and cell mechanical failure which resulted from the test procedures.

The final intention of this testing is to transmit the results to industry by writing a separator specification based on the separator physical properties and cell test data which will emphasize the use of cellophanes with optimal properties of resistance to silver ion migration and oxidation, resistance to zinc dendrite growth, and resistance to degradation effects of the alkaline environment. By defining those characteristics of cellophane which are responsible for the optimization of these properties, the specification will require manufacturers of cellophane separator to produce films with the desirable physical properties. By also writing the specification into contracts for cell manufacture, cells of optimum performance will be produced. The specification will also allow quality control of materials for consistent battery performance.

3. Test and analysis

A total of one hundred and three 30 Ah (nominal) low-rate cells, with unformed plates (i.e. uncharged), but filled

with electrolyte at manufacture, were divided into eight sets, based on the eight types of separator used to build the cells, as follows:
Set 1: 6 layers standard 1 mil wood pulp cellophane
Set 2: 6 layers 1 mil wood pulp silver-treated cellophane
Set 3: 6 layers 1 mil cotton cellophane
Set 4: 6 layers 1 mil wood pulp cellophane (alternative manufacturer to Set 1)
Set 5: 1 layer 1 mil wood pulp sausage casing + 2 layers 1.75 mil wood pulp sausage casing
Set 6: 1 layer 1 mil wood pulp sausage casing + 2 layers 3 mil fiber-reinforced wood pulp sausage casing
Set 7: 6 layers 1 mil PVA-coated wood pulp cellophane
Set 8: 1 layer of 1 mil wood pulp sausage casing + 2 layers 3 mil viscose-reinforced nonwoven polyamide fiber

These eight sets were further divided into three groups per set. Group 1 from each set consisted of one cell which was formed by charge–discharge cycling and then dissected and analyzed for baseline separator properties. Group 2 from each set consisted of five cells which were formed and then placed on wet-stand test, according to the procedure detailed below. Group 3 consisted of seven cells (except Set 3 which had only six cells) which were formed and placed on cycle-life test, again to the procedure detailed below.

3.1. Group 1

One cell from each set, which served as a baseline cell, was weighed, measured, and placed on 'formation' by charge–discharge cycling, at the $C/30$ (1 A) rate to 2.03 V followed by the $C/60$ (0.5 A) rate to 2.03 V for charge, and $C/15$ (2 A) rate to 1.30 V for discharge, with an equilibration time of 2 h between each charge and discharge cycle. The final discharge was at $C/5$ (16 A) rate to 1.30 V before dissection. These cells were re-weighed and re-measured and then dissected. Separator wet tensile strength, degree of polymerization, X-ray crystallinity, and silver migration into the separator layers were re-determined.

3.2. Group 2, wet-life testing

Five cells from each set were weighed, measured, and formed as above. At the completion of the formation cycling, a $C/5$ discharge was performed, the cells were recharged at the $C/15$ rate, and placed on a 30 day wet-stand at ambient temperature. After 29–31 days (depending on weekends and holidays), these cells were discharged at the $C/5$ rate to 1.30 V, allowed to equilibrate for 2 h, recharged at the $C/15$ rate to 2.03 V, and replaced on wet-stand. This cycle will continue for each cell in all sets until the discharge capacity for each cell on a given cycle drops below 50% of initial capacity, at which time that cell will be withdrawn from the test, discharged, and subjected to failure analysis. One cell from each set is also withdrawn from test for analysis at 6 and 12 months. Accurate logs of initial capacity and charge/discharge performance are maintained for each cell.

3.3. Group 3, cycle-life testing

Seven cells from each set were weighed, measured, and formed as before. The charge and discharge cycling procedure continues for each cell in all sets at the $C/15$ rate to 2.03 V for charging and the $C/15$ rate to 1. 30 V for discharge until the discharge capacity for each cell on a given cycle drops below 50% of initial capacity, at which time that cell is withdrawn from the test, discharged, and subjected to failure analysis. One cell from each set is also withdrawn for analysis at 50 and 100 cycles. Accurate logs of initial capacity and charge/discharge performance are maintained for each cell.

A second failure method was defined for all cycle- and wet-life charging, such that if a cell failed to accept at least 90% of the previous discharge capacity, the cell charge/discharge data would be examined to determine whether the cell should be withdrawn from the test and subjected to failure analysis.

3.4. Separator tests

The following tests are important for characterizing changes in separator properties as a function of cell life:

(i) X-ray diffraction spectroscopy to assist in determination of changes in separator crystallinity;

(ii) tensile strength testing to provide data on changes in the strength of the various separators as a function of cycle- and wet-life;

(iii) degree of polymerization measurements to provide data on oxidative and alkaline degradation rates for the various separators under actual cycle- and wet-stand conditions;

(iv) silver penetration through each separator layer to provide data on the extent of silver migration in each of the separator materials;

(v) zinc penetration to determine the resistance of the various separators to this physical process which leads to hard shorts.

4. Results and analysis

4.1. Physical testing

First, we examine the data for dry and wet thickness for the respective films, in Table 1. These data are from both the Navy and the Rutgers Laboratories; the dry and simple wet thicknesses from the former, the wet thicknesses under pressure from the latter, presented with their standard deviations. The dimensional changes which occur in cellulosic separators on wetting should be as small as possible because they can lead to increased large ion [$Ag(OH)^{2-}$] migration via increased pore size. There was good agreement between the two laboratories on dry thickness, while the data on wet thickness were at pressures intended to simulate internal cell conditions.

Table 1
Separator thicknesses before and after soaking in 45% potassium hydroxide, under zero, two or four psi. Thickness expressed in mil (0.025 mm)

Separator	Thickness, dry	Thickness, soaked	Soaked, 2 psi	Soaked, 4 psi
Set 1, WP film, 1 mil	1.19 + 0.04	3.01 + 0.03	2.41 + 0.07	2.36 ± 0.12
Set 2, WP film, 1 mil Ag treated	1.13 + 0.04	3.01 + 0.03	2.59 + 0,10	2.54 + 0.10
Set 3, cotton film, 1 mil	1.07 ± 0.02	2.28 + 0.10	2.15 + 0.10	2.13 ± 0.10
Set 4, WP film, 1 mil	1.14 + 0.07	2.94 + 0.12	2.98 + 0.08	2.94 + 0.04
Set 5, WP SC, 1.75 mil	2.29 + 0.00	7.24 + 0.02	6.43 + 0.18	6.32 + 0.14
Set 6, WP SC, 6 mil fiber-reinforced	5.91 + 0.71	7.81 + 0.09	6.81 + 0.24	6.66 + 0.27
Set 7, WP film, 1 mil PVA coated	1.19 + 0.04	3.01 + 0.03	no data	no data
Set 8, WP SC, 3 mil PA reinforced	4.59 ± 0.19	7.00 + 0.38	no data	no data

Table 2
Tensile strength data. Bulk values in pounds (454 g)

Separator	Dry, MD	Dry, TD	45% KOH, MD	45% KOH, TD
Set 1, WP film, 1 mil	5.35 + 0.18	3.25 ± 0.10	0.51 + 0.05	0.24 + 0.025
Set 2, WP film, 1 mil Ag treated	5.44 + 0.48	3.41 + 0.05	0.63 + 0.11	0.30 + 0.055
Set 3, cotton film, 1 mil	5.05 + 0.32	3.70 + 0.08	1.36 + 0.05	1.15 + 0.13
Set 4, WP film, 1 mil	4.97 + 0.10	3.54 + 0.09	0.40 + 0.02	0.24 + 0.01
Set 5, WP SC, 1.75 mil	5.24 + 0.41	3.19 + 0.09	1.22 + 0.06	0.32 + 0.05
Set 6, WP SC, 6 mil fiber-reinforced	4.54 + 0.15	2.85 + 0.15	1.54 + 0.12	1.09 + 0.09
Set 7, WP film, 1 mil, PVA coated	5.85 + 0.26	3.62 + 0.08	0.76 + 0.05	0.44 + 0.04
Set 8, WP SC, 3 mil, PA reinforced	7.27 + 0.16	4.32 + 0.18	4.34 + 0.14	1.68 + 0.21

Table 3
Tensile strength data, being normalized values in pounds

Separator	Dry, MD	Dry, TD	45% KOH, MD	45% KOH, TD
Set 1, WP film, 1 mil	4.18 + 0.14	2.54 + 0.08	0.17 + 0.02	0.08 ± 0.01
Set 2, WP film, 1 mil Ag treated	4.81 + 0.42	3.02 + 0.04	0.21 + 0.04	0.10 + 0.02
Set 3, Cotton film, 1 mil	4.72 + 0.30	3.46 + 0.07	0.60 + 0.025	0.50 ± 0.06
Set 4, WP film, 1 mil	4.36 + 0.10	3.10 + 0.08	0.14 + 0.01	0.08 + 0.002
Set 5, WP SC, 1.75 mil	2.29 + 0.18	1.39 + 0.03	0.17 + 0.01	0.04 + 0.00
Set 6, WP SC, 6 mil fiber-reinforced	2.30 + 0.08	1.45 + 0.08	0.59 + 0.05	0.42 + 0.03
Set 7, WP film, 1 mil PVA coated	3.81 + 0.22	3.04 + 0.07	0.25 + 0.02	0.15 + 0.01
Set 8, WP SC, 3 mil PA reinforced	1.58 + 0.04	0.94 + 0.05	0.62 + 0.02	0.24 + 0.03

As can be seen, the typical 1 mil wood pulp (WP) cellophane swelled approximately three-fold on soaking in 45% KOH for 24 h, while the cotton derived film swelled only two-fold. Under pressure, the swelling for all samples was reduced somewhat. The three sausage casing (SC) materials swelled quite differently, depending on the original thickness, whether they were reinforced, and the type of reinforcement. However, 1 mil sausage casing (not presented in Table 1) swells from 1.02 ± 0.02 to 2.95 ± 0.14 mil. All data are averages of eight measurements on the film samples. Once the films have been incorporated into actual cells, swollen thickness data are not relevant because of the incorporation of silver into the films, and alkaline degradation effects. The next set of data, in Table 2, are for tensile strengths (TS) for the films in the machine (MD) and transverse (TD) directions, on samples which were 1/4″ (6 mm) wide.

Again, measurements were performed in both laboratories as a check, and the results were very similar, and again the data are averages from eight measurements with standard deviations. The data in Table 2 are the bulk measurements, meaning that these are the actual sample strengths, while in Table 3, the data are presented in normalized form, with all values converted to a 'per mil thickness' value. The cotton-derived film appeared to retain the greatest strength in the KOH-soaked condition in both MD and TD directions, among the 1 mil films, while the two reinforced SC samples had tensile strengths about the same as the 1 mil cotton on a normalized basis.

The next set of data to consider are the degree of polymerization (DP) results. An ASTM method [11] was used which tests the kinematic viscosity of a cupro-ethylene diamine solution of the cellophane.

The data are presented in Table 4, based on two samples of each material and four measurements per sample. There are no data for the two reinforced SC materials because the reinforcing substances interfere with the measurement.

However, a measurement of 1 mil SC gave a value of 443 for the DP, which is within 6% of the value for the 1.75 mil

Table 4
Degree of polymerization

Sample	ASTM calculated
Set 1, WP film, 1 mil	278
Set 2, WP film, 1 mil Ag treated	245
Set 3, cotton film, 1 mil	482
Set 4, WP film, 1 mil	218
Set 5, WP SC, 1.75 mil	471
Set 7, WP film, 1 mil, PVA coated	237

Table 5
Degrees of polymerization (DP) of cotton fibers and wood pulps

Sample	ASTM calculated
Cotton fiber	905
Wood pulp (Flexel)	418
Wood pulp (Viskase)	535

(Set 5) value, and since the viscose solution used to make these two SC films is essentially the same, the DP of the coatings used on the fiber- and polyamide-reinforced is expected to be in the same range. Similarly, Set 7, which is a polyvinyl alcohol-coated 1 mil standard cellophane film, is expected to have about the same DP as the Set 1 film. The actual DP found was about 15% low, but the interference of PVA in the DP method is not understood, so the result may not be as 'deviant' as it appears. These results for DP complement the TS data in Table 3, because the Set 3 values for DP and TS were among the highest. In Table 5 are presented, for informational value, the DPs for cotton fiber and wood pulp supplied by film and sausage casing manufacturers.

One note of caution should also be added to the interpretation of the DP data, which is that the ASTM method depends on the weight of the sample used in the kinematic viscosity method, and these materials readily adsorb moisture. A 'dry' weight is obtained by thermogravimetric analysis (TGA), however, samples exhibited very different dehydration curves.

The last set of physical property data comes from X-ray diffraction (XRD) experiments. The degree of crystallinity [12] and the amount of included water [13] in the film are important to an understanding of film strength. The degree of crystallinity is substantially reduced by the viscose process; the greater the retained crystallinity, the stronger the film. The degree of water retention within a film is related to subsequent swelling in KOH, which affects porosity and is an indication of a film's effectiveness in preventing silver migration, because the greater the water retention, the less swelling will occur in KOH.

In cellophane, the degree of order determines the amount of swelling when an alkaline solution is absorbed [14], because interactions of OH^- and C–OH units aid in penetration of water into the structure, and $Ag(OH)_2^-$ absorption is also facilitated. Since the degree of swelling is also related to the degree of residual crystallinity, when the retained crystallinity is large, and retained water is also large, swelling is minimized and the primary penetration is by H_2O and OH^- (and K^+) as the lattice structure is maintained during separator life in a cell. In amorphous regions, the structure may be completely disrupted by water absorption so the polymer structure becomes a viscous solution with no distinct pore definition and penetration of large, destructive, silver species is facilitated. Thus, large residual crystallinity and retained water in the structure are desirable as barriers to chemical attack by Ag(II) and Ag(I) ions, which serve to oxidize (degrade) the cellophane structure. To assist natural barrier properties, metallic silver may be deposited in the cellophane, either from redox involving –C–OH and/or –CHO, or coated onto the cellophane before use, to inhibit reaction between Ag(II) species and the film.

In the diffraction spectra of cellophane, there are two principal 2θ regions of importance: one, at 212°, is a consequence of (101) plane interference, and a second, at $2\theta \approx 20$ and 22°, is a (101) + (002) doublet (Fig. 1). Spectra for cotton and wood pulp cellulose are shown in Fig. 2 (where the intensity differences are due only to sample size). A comparison of cellulose and cellophane spectra is shown in Fig. 3, and cellophane and cotton cellulose diffraction patterns from the literature [12] are presented in Fig. 4.

The relative intensities for the two peaks listed are given in Table 6. Now, (101) planes are preferentially oriented to the film sheet surface [13], and water is retained on the (101) surface of fibrils because most hydroxyl groups are located on the (101) planes. As a film dehydrates, uniplanar orientation of the (101) planes parallel to the film sheet surface occurs, and the value of $R = I_{(101)}/I_{[(101)+(002)]}$ increases.

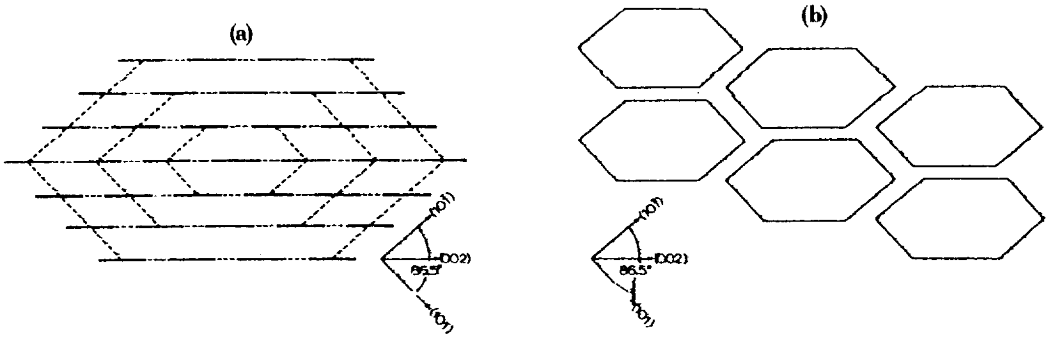

Fig. 1. Microstructures: (a) hexagonal unit microfibril configuration; (b) possible mode of hexagonal unit microfibril growth and layering.

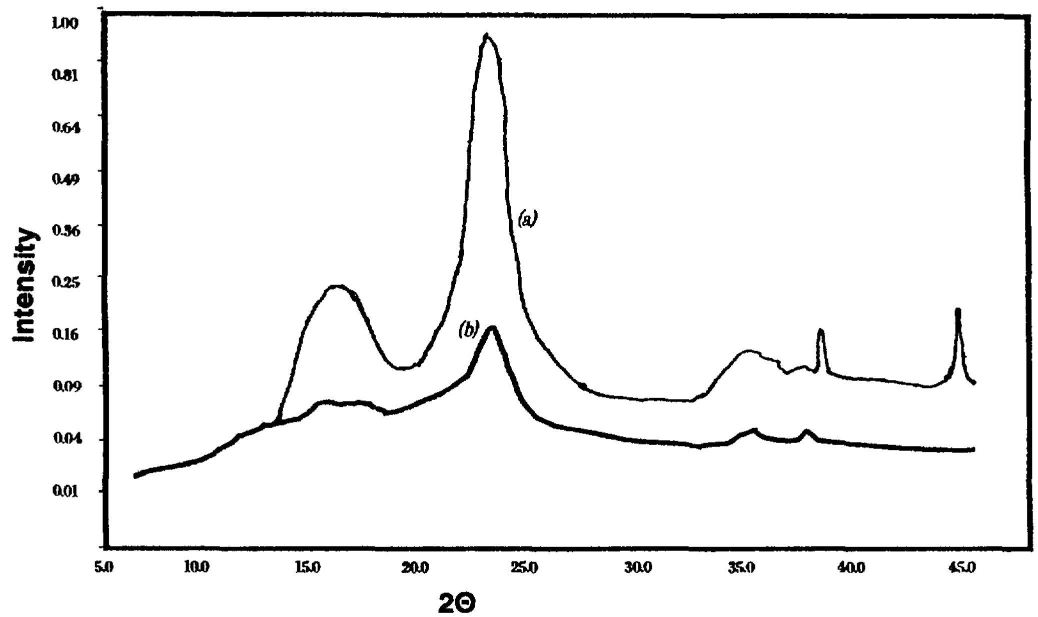

Fig. 2. X-ray diffraction spectra for wood pulp (a) and cotton (b) celluloses.

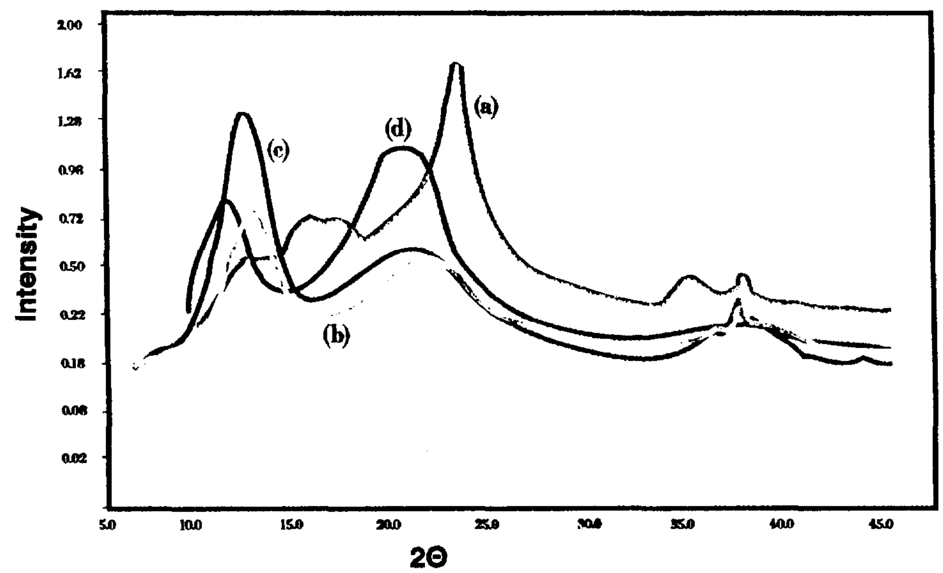

Fig. 3. X-ray diffraction spectra for cotton (a) and wood pulp (b) from Set 4, wood pulp (c) from Set 5, and cotton (d) from Set 3.

If the intensity ratio *R* is used as an indicator of retained water in a processed film, then the ratio for sample Set 1 corresponds to about 5% retained moisture while the cotton derived films (samples Set 3), at the other extreme, correspond to 25–30% [13], and the sausage casing sample was about the same as regular 1 mil wood pulp film. The data imply that Set 3 has the greatest retained crystallinity and retained moisture (H-bonded to glucose –OH groups) so this film should exhibit the greatest resistance to penetration by silver species, and consequently the greatest resistance to oxidative degradation. These results also conform to the swelling data in Table 1, the TS data in Table 3, and the DP data in Table 4.

4.2. Cell testing

When the life-cycle cell testing was begun, it soon became apparent that the test regime of a *C*/15 charge and *C*/5 discharge was giving very poor capacity performance, in comparison to that obtained during the cell formation cycling. Therefore, after several cycles, the regime was changed to a *C*/30 charge to 1.95 V, then a *C*/60 charge to 2.03 V, followed by the *C*/5 discharge. Immediately, the cells returned to their charge-capacity behavior observed during the formation process, so this was maintained for the remainder of both life- and wet-stand cycling.

The cells on cycle-life testing are approaching or at 50 cycles, and the following cycle-life plots are for Sets 1, 2, 4, 5 and 7. Problems arose with respect to the other cell sets, which will be explained subsequently. The following figures contain three sets of data plots. One set, represented by (+) marks, is the total capacity acceptance for each charge cycle. The second, represented by (●), is the total capacity on discharge. The third, represented by triangles, is the capacity

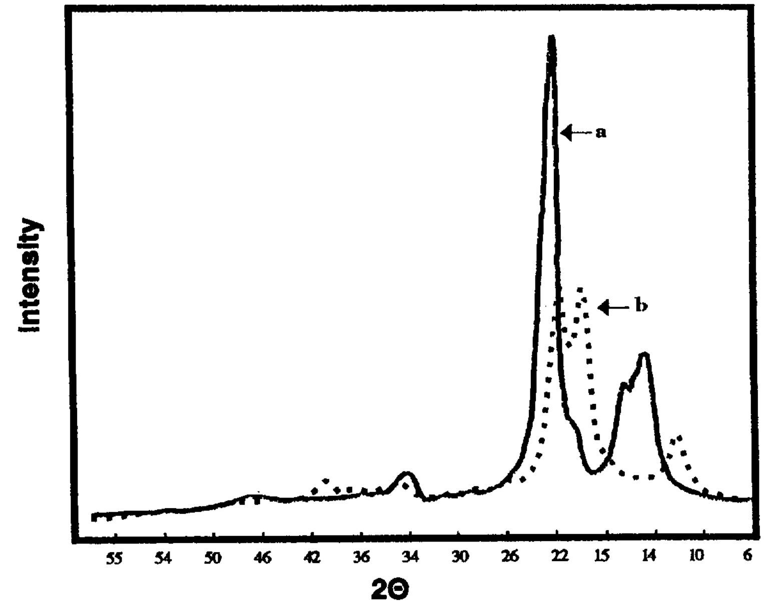

Fig. 4. X-ray diffraction spectra for cellulose (a) and cotton (b) cellophane. From Ref. [15].

Table 6
X-ray diffraction spectra data for films and celluloses

Sample	First peak (12°)	Second peak (22°)	Ratio (*R*)
Set 1, WP film, 1 mil	0.89×10^2	0.41×10^2	2.17
Set 2, WP film, 1 mil, Ag treated	1.08	0.44	2.44
Set 3, cotton film, 1 mil	0.58	0.81	0.72
Set 4, WP film, 1 mil	1.18	0.41	2.86
Sausage casing, 1.75 mil	1.78	0.79	2.26

acceptance at the 1 A charge rate, and this plot is discontinuous as, from the completion of formation to somewhere around the 15th to 20th cycle, the $C/15$ or 2 A charge rate was in use, before it was changed back to $C/30+C/60$.

Sets 1 and 2 (Figs. 5 and 6) differ only in that the separator, which comes from the same manufacturer, was untreated in Set 1, and coated with metallic silver in Set 2. The charge and discharge capacity data for the two sets compare well, although in the latter set, charge acceptance and discharge capacity in the 40–50 cycle region appear somewhat better. Both sets still contain five cells.

The separator DPs (Table 7) after baseline cycling and at 50 cycles are quite different, for although the DP for Set 1 appears to have decreased by 50% during the formation cycling, Set 2 showed little decrease. However, at the time of the 50-cycle teardowns, the two separators were exhibiting much closer DP values.

These data are averages of two samples per film, and two runs per sample, and the data values were generally within

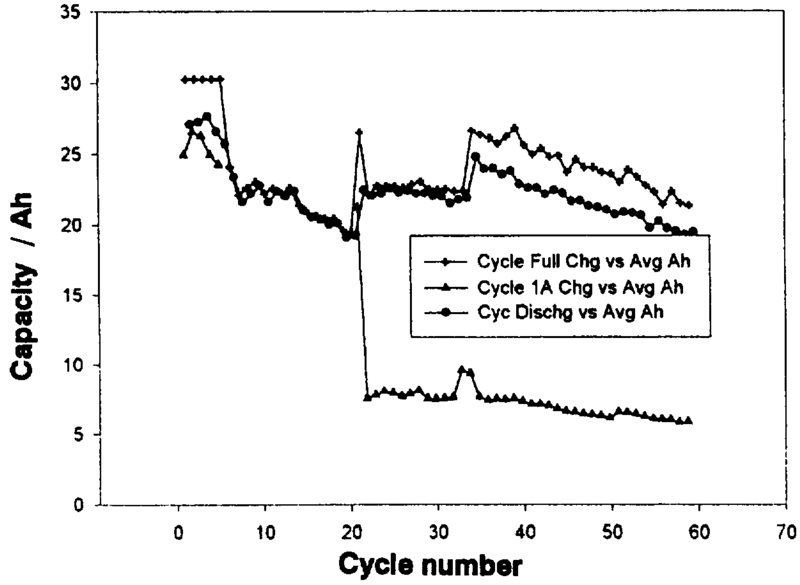

Fig. 5. Set 1 separator. Average charge and discharge capacities vs. cycle number.

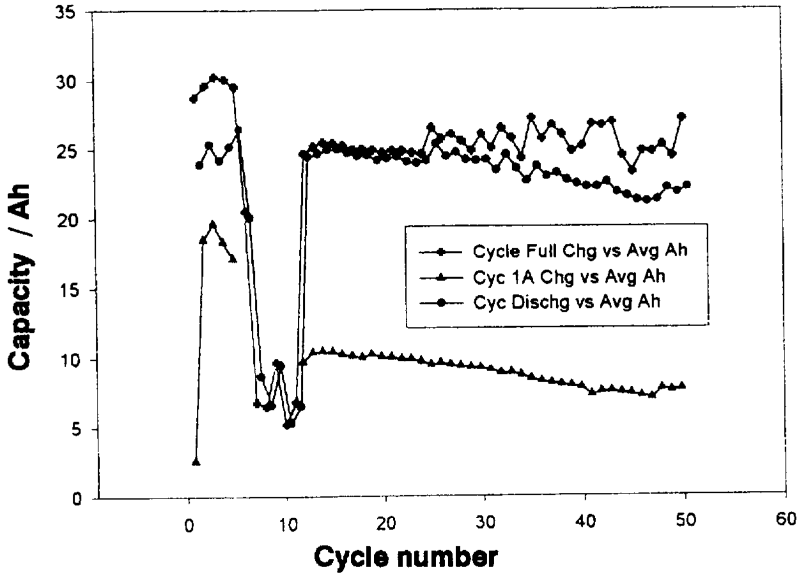

Fig. 6. Set 2 separator. Average charge and discharge capacities vs. cycle number.

Table 7
Degrees of polymerization (DP) after cell cycling

Sample	Original, dry	Baseline	50th cycle
Set 1, WP film, 1 mil	278	126	123
Set 2, WP film, 1 mil, Ag treated	248	219	93

5% of one another on the separate samples. An interesting observation regarding the separators from these two 50-cycle cells was that the untreated film was much less robust at this point than the silver-treated film, even though the DP values were close, so that cutting TS samples from Set 1 film was difficult, whereas the other film furnished samples readily. Based on the literature [7], the initial change in DP values in the formed cells could be attributed to the more facile oxidative degradation by Ag(II) ions on the untreated film, but after silver migration is established by longer cycling, alkaline degradation becomes the dominant cause of DP change. This hypothesis will be more extensively evaluated by continuing the analysis on cells at 100 cycles, and of any failures prior to that point.

For Set 4 (Fig. 7), only three of the original seven cells are still cycling, and the plotted data show a substantial drop-off in charge and discharge capacities in the 40–50 cycle region, compared to Sets 1 and 2. Cells from Set 4 have failed due to hot shorts at cycles 4 and 6 (during formation) and at cycle 14, and a fourth cell failed at cycle 12 due to low discharge capacity. Only preliminary analyses have been performed on these cells to date, and the cells have been frozen to preserve them until more detailed analyses can be performed. However, the cycle life performance appears to

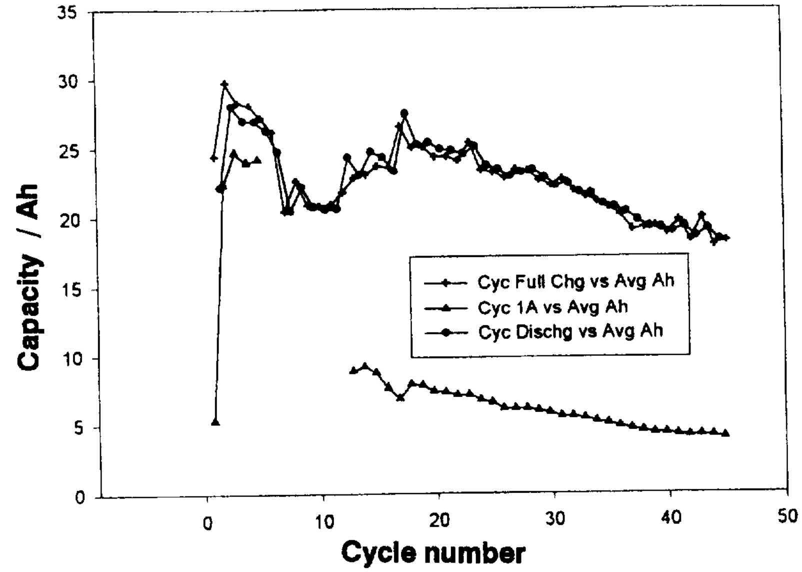

Fig. 7. Set 4 separator. Average charge and discharge capacities vs. cycle number.

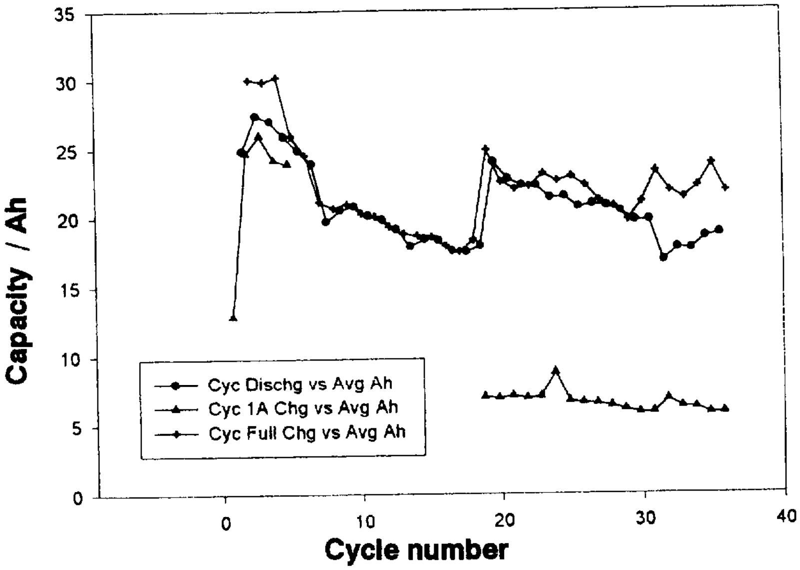

Fig. 8. Set 5 separator. Average charge and discharge capacities vs. cycle number.

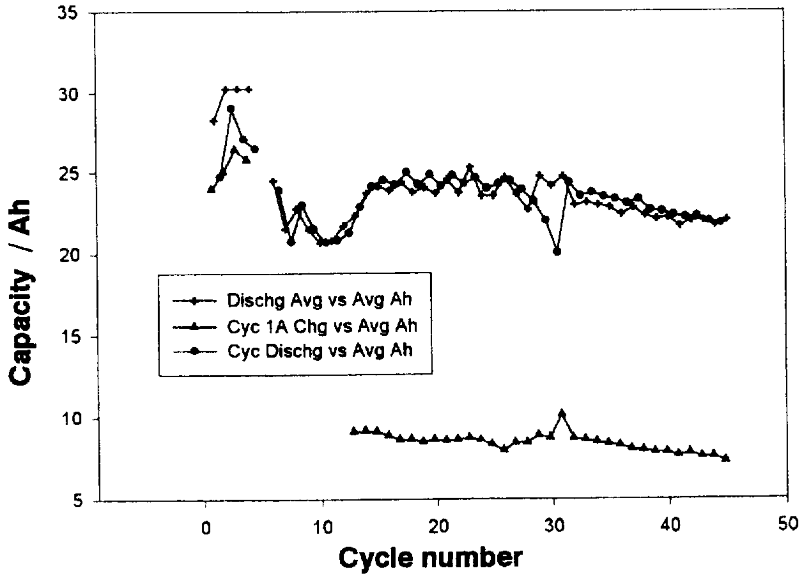

Fig. 9. Set 7 separator. Average charge and discharge capacities vs. cycle number.

reflect the poor TS, DP, and crystalline character of this separator film.

Set 5 (Fig. 8), which contains 1.75 mil SC, is performing well, although a divergence appeared between charge and discharge capacities at cycle 30. These cells are only at the 36th cycle, with no cell failures yet. However, one cell was removed at cycle 24 because the cell cases were bulging, and it was discovered that, because of a miscalculation when the cell design was established, three layers of SC were used instead of two, as required by wet thickness. Consequently, the internal stack pressure is about 20% greater than for Sets 1 and 2, and this is expected to be reflected in poor cycle- and wet-life performance.

Set 7 (Fig. 9) is exhibiting very consistent behavior, although two of the seven cells have been lost because of the generation of hot shorts. The capacity spread is quite tight and appears to be holding up well between 40 and 50 cycles, compared to Sets 1 and 2. This separator film was from the same manufacturer as that in Sets 1 and 2, but the film was coated with polyvinyl alcohol from solution, to reduce silver penetration. A cell is due for 50-cycle analysis soon, when the extent of silver migration through the separator layers will be determined for comparison to Sets 1, 2, 4 and 5.

Four sets of cells failed early in this study, for the following reasons.

(i) Set 3. This cell set was built with an internal plastic shim to provide matching internal stack pressure to Sets 1, 2 and 4. This shim has been found to dissolve in 45% KOH, leading to an excessively large internal impedance, and the cells accept charge very poorly.

(ii) Set 5. As already mentioned, this cell set is expected to exhibit poor performance because the internal stack pressure is about 20% too high, because one too many layers of separator were used.

(iii) Set 6. The separator cracked and split at the U-wrap corners because the folds at these points were stressed by the cell case constraints, leading to zinc intrusion into the cathodes and to hot shorts.

(iv) Set 8. The original separator was polyamide fiber coated on one side with viscose, and the cathode wrap was such that the uncoated side faced the anodes, allowing swift zinc dendrite penetration.

These four sets will be rebuilt with the following changes in the cell designs:

(i) Set 3: a cell case which will accommodate the less swollen separator without the need for shims;

(ii) Set 5: two layers of 1.75 mil SC instead of three;

(iii) Set 6: a cell case slightly wider than for Sets 1 and 2, to allow for the greater rigidity of 3 mil fiber-reinforced SC;

(iv) Set 8: polyamide fiber-reinforced SC coated on both sides with viscose will be used, to improve barrier properties to zinc dendrites.

5. Summary

These cell cycle-life studies are ongoing, and the wet-life cells have only 6 months of accumulated data, too little to draw any conclusions. Nevertheless, it is already apparent that the separator in Set 4 is failing prematurely, compared to Sets 1 and 2. This may be a reflection of the poor physical properties of the separator. Also, the behavior of cell Set 7 is remarkable, in spite of the loss of two cells to hot shorts, for the closeness of charge and discharge capacities, and also for the fact that these cells are showing a very narrow distribution of capacities over the cell set, 2 Ah, compared to both Sets 1 and 2 which are exhibiting distributions of 3–4 (Set 1) and 6 (Set 2) Ah.

Finally, Sets 1 and 2 are very close in average Ah performance through cycle 50, so that the expected differences due to silver coating of the separator film is not yet showing up in cell performance.

It is expected that this study will provide a 'best set' of separator physical properties for future silver/zinc cell design, and it will then be very informative to extend this work to other rechargeable alkaline cell chemistries.

In a separate study at Rutgers University and UMDNJ-Robert Wood Johnson Medical School, a sample of a new type of cellophane film, supplied by Courtaulds Corporate Technology, Coventry, UK, and cast by a solvent-spun process from *N*-methyl morpholine oxide, was evaluated for applications in alkaline batteries. A series of 5 Ah silver/zinc cells was fabricated with this separator along with cellophane control cells. The samples of solvent-spun material approached the properties of the cotton-based cellophane. Further studies are planned.

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References

[1] H. André, *Bull. Soc. Fr.. Electriciens, 1* (1941) 132.
[2] A.J. Salkind, Interview with H. André, quoted in S.U. Falk and A.J. Salkind (eds.), *Alkaline Storage Batteries*, Wiley, New York, 1969.
[3] H. André, *US Patent No. 2 317 711* (1943).
[4] A. Fleischer, in J.E. Cooper and A. Fleischer (eds.), *Characteristics of Separators for Alkaline Silver Oxide Zinc Secondary Batteries*, AF Aero Propulsion Laboratory, 300-sep-65-773-10-216, 1965.
[5] C. Hampel and G. Hawley (eds.), *The Encyclopedia of Chemistry*, 3rd edn.
[6] S.U. Falk and A.J. Salkind (eds.), *Alkaline Storage Batteries*, Wiley, New York, 1969, pp. 240–276.
[7] H.P. Gregor, in A. Fleischer and J.J. Lander (eds.), *Zinc–Silver Oxide Batteries*, The Electrochemical Society, Inc., Wiley, New York, 1971, pp. 219–232.
[8] A. Himy, *Silver–Zinc Battery — Phenomena and Design Principles*, Vantage Press, New York, 1995.
[9] J.E. Cooper and A. Fleischer (eds.), *Characteristics of Separators for Alkaline Silver Oxide Zinc Secondary Batteries*, AF Aero Propulsion Laboratory, 300-sep-65-773-10-216, 1965.
[10] A. Himy and O.C. Wagner, Substitutes for mercury in alkaline zinc batteries (11), *29th Power Sources Conf. Proc., Ft. Monmouth, NJ, 1978*, pp. 167–169.
[11] *ASTM Method D 4243-86*, American Society for Testing and Materials, Philadelphia, PA, 1986.
[12] M.A. Ivanov and A.L. Kosoy, *J. Appl. Polym. Sci., 19* (1975) 2353.
[13] H. Yokota, *J. Polym. Sci., Polym. Lett. Ed., 21* (1983) 285.
[14] R.E. Post, in A. Fleischer and J.J. Lander (eds.), *Zinc-Silver Oxide Batteries*, The Electrochemical Society, Inc., Wiley, New York, 1971, p. 263.