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Advanced membranes for alkaline primary and rechargeable alkaline cells with zinc anodes

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Abstract

Several advanced cellulosic and radiation grafted polypropylene membrane materials are currently under evaluation in the laboratories at Navsea Crane and Rutgers University, for application to alkaline primary and rechargeable cell chemistries which employ zinc as the anode material. A portion of these tests involve model cell evaluations of cellulosic membranes for silver migration rates through the membranes as a function of separation layers and changes in the degree of polymerisation (DP), wet tensile strength (WTS) and voltage changes at both electrodes as a function of model rechargeable cell life cycle. Other testing on the actual membranes is generating data for both cellulosic and polypropylene materials on impedance, swelling properties, and silver and zinc penetration rates. The overall goal of these investigations is to obtain candidate separation membranes which will reduce zinc anode shape change and shedding and resist alkaline oxidative degradation to extend the active wet life in primary cells and both wet and life cycle in rechargeable cells.

Keywords: Silver/zinc rechargeable cells; Separators/cellulosic; Separators/graft copolymer

1. Introduction

In previous papers [1–7] several of the authors developed concepts relating to the improvement of separations used in alkaline cells, particularly as they are applied to the rechargeable silver–zinc chemistry.

The standard separation for over 60 years has been cellulosic, because of its resistance to zinc dendrite growth, to alkaline and oxidative degradation, and because it is very inexpensive. However, its limitations which impact useful cell life are its gradual loss of tensile strength and degree of polymerisation (DP) under the alkaline oxidative effects of AgO and concentrated KOH, and the loss of volumetric energy density and large internal impedance which result from the required multiple layering.

This report presents the results of model cell studies with cellulosic membrane separations for changes in voltage at the plates, separation wet tensile strength (WTS) and DP, loss of discharge capacity, and rates of silver migration, all at intervals in life cycle. In these studies, Viskase sausage casing and UCB cellophane films of an experimental nature were evaluated.

2. Experimental

The cell sets are identified as follows (five sets of seven rechargeable silver/zinc cells of nominal 26 Ah capacity were constructed at Eagle-Picher Industries on 21 September 1999):

Set 1 — Standard 1 mil (dry) Flexel film (Lot 139013 from 04/06/98, EPI no. 40330020): Cathode/1 × 3 mil Pellon/6 × 1 mil Flexel (U-wrap) Anode/1 × 3 mil Pellon.

Set 2 — New 1 mil (dry) UCB, Bridgwater, UK film (Lot 161602 from 02/24/99, EPI no. 40330020): Cathode/1 × 3 mil Pellon/6 × 1 mil UCB (U-wrap) Anode/1 × 3 mil Pellon.

Set 3 — PVA film with Viskase fibre-reinforced tubular sausage casing (FRSC), (1 month old, special preparation, Chicago plant): Cathode/1 × 3 mil Pellon/1 × 2 mil PVA/1 × 5.9 mil FRSC (tube wrap) Anode/1 × 3 mil Pellon and 10 × 10 mil Vinylite shims.

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Set 4 — PVA film with Viskase unreinforced tubular sausage casing (USC), (2 weeks old, special preparation, Spain plant): Cathode/1 × 3 mil Pellon/1 × 2 mil PVA/ 1 × 2.3 mil USC (tube wrap) Anode/1 × 3 mil Pellon and 3 × 30 mil Plexiglass shims + 1 × 10 mil Vinylite shim.

Set 5 — New 1.75 mil (dry) UCB, Wigton, UK film (02/ 98, special preparation): Cathode/1 × 3 mil Pellon/ 3 × 1.75 mil UCB (U-wrap) Anode/1 × 3 mil Pellon and 1 × 30 mil Plexiglass shim + 2 × 10 mil Vinylite shims.

These five sets of seven cells each were all designated for life cycle study. All cells were filled to the red mark with 45% KOH in a standard filling procedure with vacuum application. All cells were charged at *C*/30 rate to 2.02 V + *C*/60 rate top-off to 2.04 V and discharged at *C*/6 rate to 1.20 V. The first three were ''formation'' cycles, which were counted towards life cycle. After 3 cycles one cell was withdrawn from each Set in a discharged state and dissected for baseline silver migration, DP and WTS for the separation. Additional cells were to be withdrawn at 25, 50, and 75 cycles for similar dissection evaluations. Failed cells were also dissected for failure mode and evaluation of properties.

The intent was to establish the degradation and failure processes and their rates. These data were to be compared to standard 1 mil (25 μm) cellophane degradation and failure rates (Set 1).

Cells were fitted with a third reference electrode consisting of a silver wire amalgamated with mercury to provide for anode potential versus the mercury electrode to obtain data on anode performance and cell impedance during testing.

Data evaluations included discharge Ah, silver migration, DP and WTS, all versus life cycle (in number of cycles) and state-of-health during testing from the plate voltage measurements.

3. Results and discussion

3.1. Tensile strength measurements

Fig. 1 presents the comparison between 1 mil Flexel cellophane (Set 1) and 1 mil UCB cellophane (Set 2). A fourth datum point was available for Flexel for layer 6 because one cell failed at 12 cycles. This value, 1 × 10 lb, was right on line with the other layer 6 data. (layer 1 is the closest to the cathode.) Loss of tensile strength for the innermost layer in both cellophanes is greater with life cycle than for the outermost layer. Overall, the Flexel cellophane started with greater tensile strength and retained greater tensile strength with life cycle. All three layers of UCB cellophane were too weak for measurement at 50 cycles.

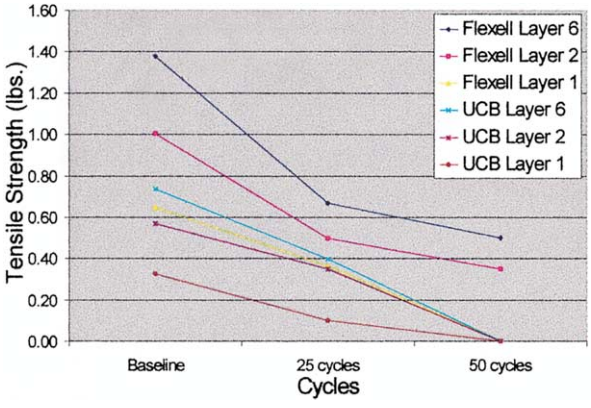

Fig. 1. Flexel vs. UCB tensile strength.

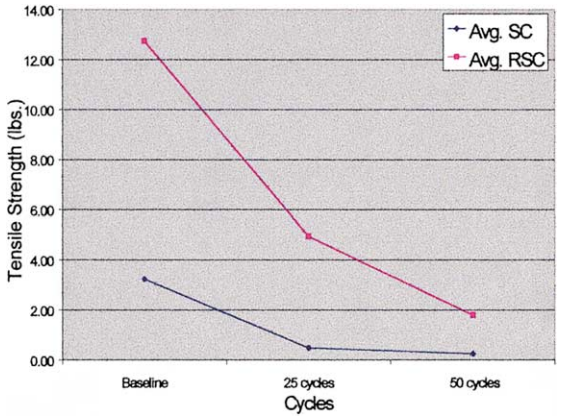

Fig. 2. RSC vs. USC tensile strength.

Fig. 2 shows the comparison between 1.75 mil USC (Set 3) and 5.9 mil FRSC (Set 4). The FRSC showed overall greater tensile strength, but its rate of degradation was much greater.

Fig. 3 presents data for the UCB single ply (1 mil, Set 2) versus double ply (1.75 mil, Set 5) cellophane.

Data for the double ply are problematical because in the baseline measurements the material showed two peaks, one for each layer, with the second break point at about twice the value for the first, and at 25 cycles, about 4×. The average values are plotted. At 50 cycles, both materials were too weak for measurement, as the cellophane fell apart during dissection. From the data, it appears that initially and through 25 cycles, the single layer film was stronger than the double.

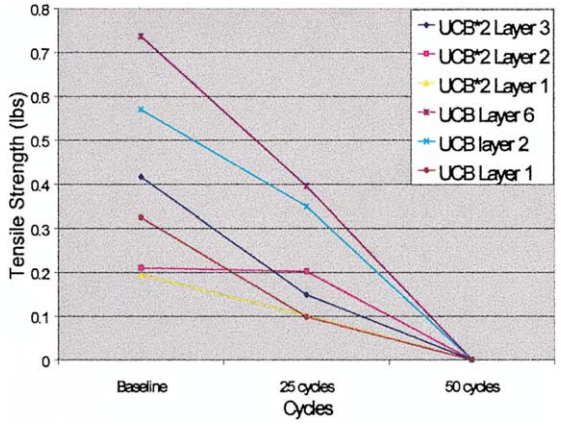

Fig. 3. UCB vs. UCB*2 tensile strength.

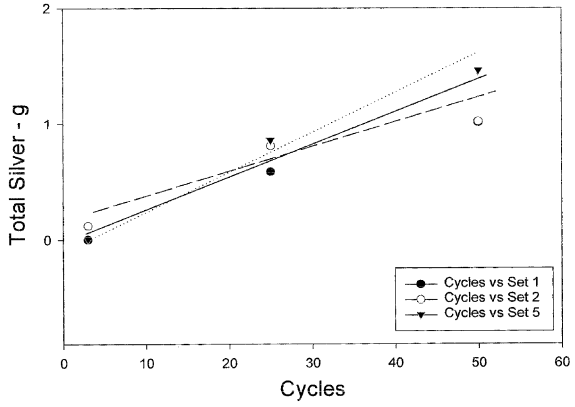

Fig. 4. Flexel vs. UCB silver migration.

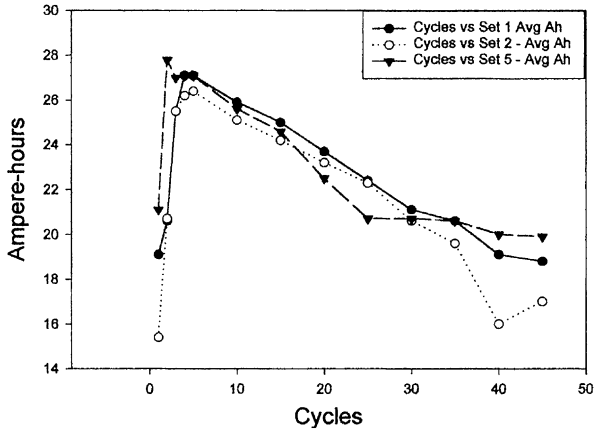

Fig. 6. Flexel vs. UCB discharge capacities.

3.2. Silver migration data

In Fig. 4, total silver migration data from Sets 1 (Viskase), 2 (UCB single ply), and 5 (UCB double ply) are plotted for life cycle. There appears to be no significant difference in the amounts of silver accumulating in the separations.

In Fig. 5, the same data for Sets 1, 3 (FRSC) and 4 (USC) are plotted, and here, there appears to be very little difference between the cellophane and the FRSC, however the USC separation exhibited a consistently higher rate of silver migration. But this did not influence performance because the silver was trapped in the PVA layer and did not appear in the SC layers.

3.2.1. Discharge capacity data

In Fig. 6 are plotted the data for Flexel cellophane (Set 1) versus UCB (Sets 2 and 5), both single and double ply. The data plots for all three separations are about the same, with only a small advantage for the Flexel material. In Fig. 7 the data for Flexel (Set 1) versus the two SC separations (Sets 3 and 4) are plotted, and again there is very little difference, with a small advantage to Flexel out to 30 cycles, after which both SC materials exceed cellophane in discharge capacity.

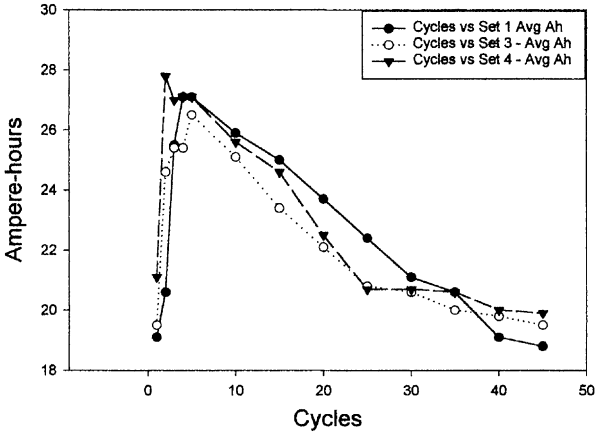

Fig. 7. Flexel vs. SC discharge capacities.

3.2.2. Degree of polymerisation data

In Fig. 8 the data are plotted for DP changes with life cycle. The method of measurement is by an ASTM technique [8]. From the data plots, it is obvious that the DP decreases drastically in just the first few cycles and then

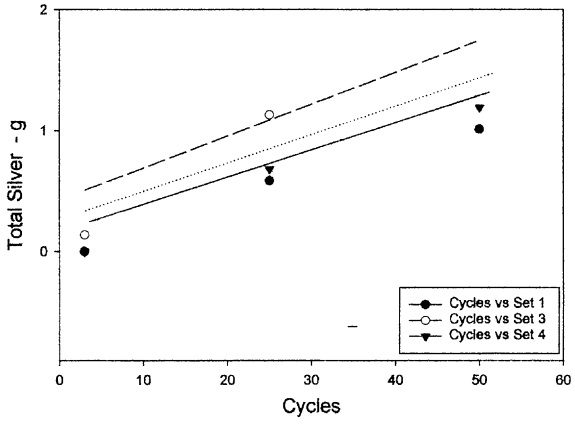

Fig. 5. Viskase vs. SC silver migration.

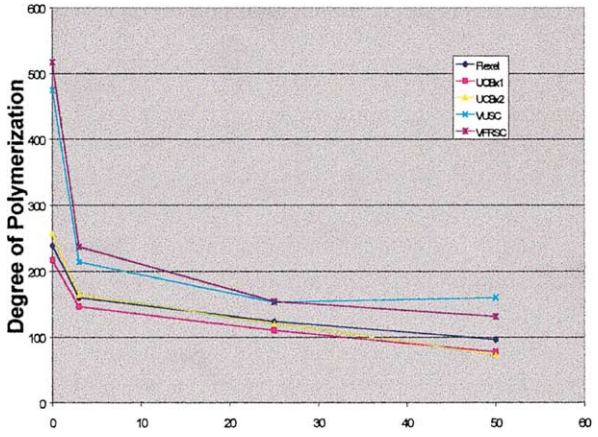

Fig. 8. Change in DP with cycling.

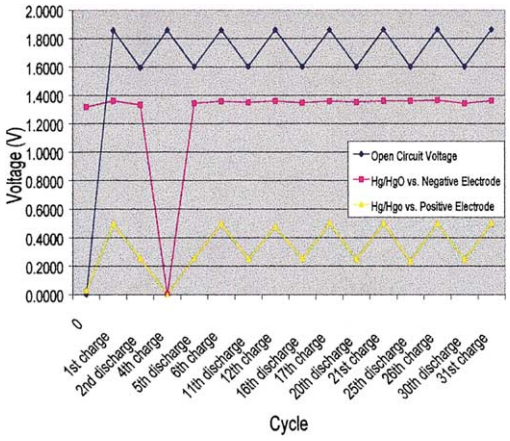

Fig. 9. Voltage measurement data for Set 1 cell 5.

decreases more slowly with cycling. All the plots appear to be trending toward a common minimum with cycling.

3.3. Voltage measurement data

The data for the voltage measurements with a third electrode are plotted for a single set in Fig. 9.

Voltages were only determined for Set 1 (Flexel cellophane) cells because the intent was to see if the anode voltage would change as it underwent shape change. No change in the voltage profiles was observed for any of the cells, and the data for cell 5 in Set 1 are representative of all the cells in this set. It was not possible to obtain voltage measurements beyond the 31st cycle because of zinc shedding in the cells.

4. Conclusions

4.1. Wet tensile strength and degree of polymerisation

From the WTS data (Figs. 1–3), it seems that both the UCB films and the USC tubing lose their tensile strength by the 50th cycle. The outermost layers of Flexel cellophane retained some strength, as did the FRSC tubing. The gradual alkaline hydrolysis and silver oxidation of cellulosic separations are the major contributors to loss of strength, and this loss is generally accompanied by shorting failure as the separations become more amorphous in character [9]. The loss of strength is also reflected in the DP data (Fig. 8), to a lesser extent, because all the separations, although the two SC maintained about 50% greater DP at 50 cycles than the cellophane films.

4.2. Silver migration rates

These data show that for the cellophane films (Fig. 4) the total silver accumulation in the respective films is constant with life cycle. Layer-by-layer data for the two 1 mil films (Flexel and UCB) show that the migration beyond layer 3 was very small at 50 cycles, while for the 2 mil UCB film, the migration stopped at layer 2.

For the two SC materials versus Flexel (Fig. 5) the migration rates were about the same, while the layer-by-layer data show no silver beyond the PVA film layer at 50 cycles. So one layer of either SC in combination with the PVA film served as an effective silver barrier an also prevents zinc dendrite formation.

4.3. Discharge capacities

These data show identical behaviour (Fig. 6) for both UCB films versus Flexel, out to 40 cycles, after which the 1 mil UCB set cells began shorting. However, the double layer (2 mil, Set 5) cells were performing as well as the Flexel cells (Set 1) at 50 cycles.

The SC data in comparison to Flexel (Fig. 7) are especially interesting, because both SC separations tracked the Flexel performance out to 50 cycles, with no cells lost to shorting. The importance of these data is in the available volume generated by the reduction in separation wet swollen thickness (ca. 30 mil total for VUSC versus 48 mil total for Flexel) for energy density increases through the use of just one layer of tubular SC with PVA.

4.4. Reference voltage data

These measurements, in the way in which we performed them, did not provide useful data for evaluation of shape change in the anode in any of the Flexel cells used. There was no evident variation in anode voltage out to 31 cycles, where measurements were discontinued because the reference electrode shorted against the shed zinc.

5. Recommendations

The substitution of double-ply UCB cellophane film for UCB single-ply (which is the current film available for silver–zinc rechargeable cells) is a definite advantage, for at least two reasons:

1. it is much less subject to dendritic hard shorting by zinc and retains some DP after long cycling;
2. it may be possible to combine one or two layers of this separation with a layer of PVA film, yielding a volumetric savings which could be used to increase the energy density.

The substitution of a single tubular layer of either VUSC or VFRSC with a layer of PVA film for cellophane film is definitely an advantage in that:

1. the discharge capacity life is equally good;
2. the tubular sausage casings retain WTS and DP during cycling to as greater degree;

3. the additional volume available in the cell case will allow at least a 25% increase in volumetric energy density, which is very significant for mission capabilities in Navy undersea platform applications.

Acknowledgements

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