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Development and Evaluation of Polyvinyl-Alcohol Blend Polymer Films as Battery Separators

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SUMMARY

This paper summarizes the work done with W. R. Grace a Co. under contract NAS3-22223, "The Development and Evaluation of Polyvinyl-Alcohol Blend Polymer Films as Battery Separators." The goal of this program was to identify, characterize, and commercially produce optimum variations of cross-linked films from water soluble polyvinyl alcohol. Several dialdehydes and epoxies were evaluated for their suitability as cross-linkers. Optimum concentrations of several cross-linking reagents were determined. A two-step method of cross-linking, which involves treatment of the film in an acid or acid periodate bath, was investigated and dropped in favor of a one-step method in which the acid catalyst, which initiates cross-linking, is added to the PVA - cross-linker solution before casting. The crosslinking was thus achieved during the drying step. This one-step method was much more adaptable to commercial processing. Cross-linked films were characterized as alkaline battery separators. Films were prepared in the lab and tested in cells in order to evaluate the effect of film composition and a number of processing parameters on cell performance. These tests were conducted in order to provide a broader data base from which to select optimum processing parameters. Results of the separator screening tests and the cell tests are discussed.

INTRODUCTION

The coulombic efficiency, cycle life, and power output of alkaline batteries are dependent upon effective separators. For long life the separator material must be stable in KOH and resistant to oxidation. Low ionic resisitivity is important for good cell performance (i.e., high voltages and ampere hour efficiencies on discharge). Along with low resistivity, high hydroxyl transport is required for batteries to have high rate capability. In addition, separators for batteries with zinc electrodes have further requirments. In alkaline electrolyte, the zinc forms a soluble species, zincate ($Zn(OH)_4^{=}$). This solubility leads to the growth of zinc dendrites which form on cycling from the dissolution and replating of the active material at the zinc electrode. Separators are required to be resistant to puncture from dendritic growth which could lead to failure by shorting. The solubility of the zinc in the alkaline electrolyte also leads to a loss of active material and eventual cell failure due to loss of capacity. Thus a separator that could effectively contain the zincate ions and retard their diffusion away from the vicinity of the zinc electrode might prove successful in extending cycle life.

A survey of materials that might provide these requirements for alkaline batteries with zinc electrodes resulted in the choice of polyvinyl alcohol (PVA) as a potential candidate for membrane separators in these systems. The use of PVA as a separator in various alkaline battery applications is well known (ref. 1). PVA is inexpensive, water soluble, and has minimal problems associated with its use and commercial production. The technology for commercial production and fabrication of PVA has been developed and is well established in U.S. industry. PVA films are insoluble and highly conductive in alkaline electrolyte. However, as with cellulose, PVA is prone to oxidative degradation. This results from the presence of a small percentage of 1,2-diol units formed in the predominately 1,3-diol structure of PVA during polymerization. These 1,2-diol units are susceptible to cleavage in an oxidative environment. Cleavage leads to breaks in the polymer backbone and eventual deterioration of the film.

The oxidation resistance of PVA films can be improved by cross-linking. Under certain oxidizing conditions, the carbon-carbon bonds of the 1,2-diol units can be cleaved, with each hydroxyl group subsequently oxidized to an aldehyde group. These aldehyde groups can then react with the hydroxyl groups of the normal PVA polymer forming cyclic acetals, or they can react with the hydroxyl groups on different polymer chains which results in cross-linking. Cross-linking can be achieved in-situ by treating a PVA film with an acid periodate solution. Alkaline battery separators produced in this way have increased mechanical strength and improved oxidation resistance, but have higher resistivity than uncross-linked PVA films (refs. 2 and 3).

Acid periodate can also be used to cross-link PVA films containing certain organic structures considered to be aldehyde precursors (ref. 4). Polysaccharides, such as sucrose or alginic acid, when treated with periodate, are converted to a aldehydes via cleavage of the C-C bonds of adjacent OH groups in the saccharide ring. In acid media the aldehydes undergo acetalization with the 1,3-diol units of PVA which results in cross-linking.

By a similar mechanism, PVA films containing aldehydes such as gluteraldehyde, terepthaldehyde, and the 2,5-dialdehyde of furan (DAF) can be cross-linked by in-situ immersion in an acid bath. While this method provides better control over the cross-linking reaction, it does not eliminate the weak 1,2-diol units of the PVA; as a result, these films are less resistant to oxidation (ref. 5).

Cross-linked films can be produced in one step by incorporating a small amount of a mineral acid or a reagent of the type of glyoxylic acid into the films before casting (ref. 6). Glyoxylic acid (GOA) is a reagent which contains both an aldehyde group and a carboxylic acid group, the acid catalyzes the cross-linking reaction and the aldehyde reacts with the 1,3-diol units to acetalyze or cross-link the PVA.

Screening of PVA cross-linked by the above methods with aldehydes, aldehyde precursors, and epoxies showed that cross-linked materials exhibit favorable properties as alkaline battery separators. They had low resistivities, low zincate diffusivities and high zinc dendrite penetration times.

The initial work on the cross-linked PVA was done at the NASA Lewis Research Center to identify suitable cross-linking methods, cross-linking reagents, and range of concentrations for the cross-linking reagents. Materials underwent limited development and testing. A cost-sharing contract was awarded to W. R. Grace and Co. to prepare and characterize a series of formulations for cross-linked seaparators, to identify optimum formulations, and to adapt the technology to a production process.

EXPERIMENTAL

Initially, several DuPont Elvanol PVA grades, spanning a range of molecular weights from high to low, were screened in an effort to identify the grade most suited to this application. The PVA's were all 99+ percent hydrolyzed. The 1,2-diol content of the various grades was determined by the method described in reference 7.

PVA solutions, 10 weight percent in water, were prepared in a Chemco high speed reactor. Films with cross-linkers were prepared by adding a quantity of dialdehyde or epoxy sufficient to achieve the theoretical amount of cross-linking desired, ranging from 2 to 40 percent, to the PVA solution. (The theoretical amount of cross-linker desired is the percentage of cross-linking reagent required to react with all of the hydroxyl groups present in the PVA, assuming one aldehyde group per two hydroxyl groups). The solutions were well mixed. Films were cast on glass or mylar, at thicknesses sufficient to achieve 2 to 7 mils when dry, and air dried.

Cross-linking was achieved by treatment of the dried films in an acid bath consisting of 200 ml H_2O, 20 ml concentrated H_2SO_4 and 200 grams Na_2SO_4. The bath was heated at 70° C to 90° C for 1 to 4 hrs. The cross-linked films were removed from the bath, washed and rinsed in cold tap water, and air dried to a constant weight

An alternate cross-linking method was also investigated. In this one-step method an acid "catalyst", 5 to 20 percent glyoxylic acid, sufficient to produce a pH below 5, was added to the PVA dialdehyde mixture before casting. Care was taken to cast the films before gellation began. The gellation was initiated by the addition of the catalyst. The films were cast as described above. The cast films were either dried in an oven or air dried, then heated. Oven residence times varied with the temperature. For films dried in the oven, the heat treatment ranged from 4 hours at 90° C to 4 min at 160° C. The air dried films were stripped from the plate on which they were cast then heated from 140° C for 5 min to 160° C for 2 min to achieve cross-linking.

The cross-linked films were subjected to a series of screening tests to determine their suitability as alkaline battery separators. Boiling water weight loss and weight loss after exposure to rapid oxidation (abbreviated ROX) were determined as measures of the extent and effectiveness of cross-linking. The test for solubility involves determination of percent weight loss following exposure to boiling water for 1 hr. In the test for weight loss after exposure to rapid oxidation, samples of know weight are exposed to nascent oxygen produced at 100 mA in a 45 weight percent solution of KOH for 96 hr, percent weight loss is determined. Additional preliminary screening involved tests for ionic resistivity, zinc dendrite penetration rate, tensile strength and percent elongation at failure. The two latter tests were run on samples before and after exposure to rapid oxidation. The retention of properties was monitored. These tests were run as described in Cooper and Fleischer (ref. 8).

Additional screening tests were run on the more promising materials and on those chosen for evaluation in cells. These tests include evaluation of zincate diffusion rates, oxygen diffusion rates, water and hydroxyl transport, water and hydroxyl content, and dimensional stability. These tests, with the exception of oxygen diffusion, were conducted according to the methods described in Cooper and Fleischer (ref. 8). Oxygen diffusion rates were determined in a cell similar to that used for zincate diffusion. One side of the cell was saturated with oxygen and sealed. The other side was degassed with prepurified nitrogen and sealed. Oxygen concentration was monitored as a function of time thus allowing a diffusion coeffient to be calculated.

In order to determine the effectiveness of the screening tests in predicting ultimate cell performance, a series of films was prepared in the lab to be tested in cells. The level of cross-linker, level and type of catalyst, the effects of wetting agents, film thickness and number of wraps were evaluated.

Separator performance was evaluated in 8-A hr nickel-zinc oxide (Ni/Zn) cells. Three cells with each separator were built and tested. The cells were positive limited and had a negative to positive plate capacity ratio of approximately 3.5:1. The zinc electrodes were wrapped in a U-fold of separator material. Separators were prepared in sheets 22.9 cm (9 in.) wide by 35.6, 50.8, or 66.0 cm (14,20, or 26 in.) long, with the lengths corresponding to the number of wraps around the zinc electrode; 2, 3, or 4. The nickel electrodes were placed in asbestos bags sealed with polyethylene foam tape. An 8-A hr cell consisted of 2-1/2 Ni plates, 1 full Ni and 2 Zn electrodes, the configuration was 1/2 Ni/Zn/Ni/Zn/1/2 Ni. The electrolyte was 35 percent KOH.

The cells usually leveled out in ampere hour efficiency after three to five formation cycles. Rate characterizations which involve evaluation of voltage and capacity performance at various rates (C/8, C/4, C/2, C, and 2C rate discharges) were run. (C represents the cell's nominal capacity, C/2 represents the current required to discharge the cells nominal capacity in 2 hr). Midpoint voltages and ampere hour capacities to 1.0 V were recorded. Following rate characterization the cells were cycled continuously at 50 percent or 80 percent depth of discharge, three 8-hr cycles/day consisting of 6 hr of charge and 2 hr of discharge. Overcharge was limited to 5-10 percent. Failure was defined as the point where the cell voltage dropped below 1.0 V at the end of discharge.

RESULTS AND DISCUSSION

PVA Optimization and Development of Cross-Linking Procedure

Three grades of DuPont Elvanol PVA were screened in order to determine which had properties most suited for use as the base polymer. The basic difference in the PVA's chosen was the molecular weight. Low, medium, and high molecular weight (or viscosity) polymers were screened. The high molecular weight Elvanol had a reduced 1,2-diol content when compared with the low and medium molecular weight grades, 2.68 versus 3.95-3.99 1,2-diol units/100 monomer units. This difference is probably insignificant when considering overall polymer stability.

In order to evaluate the PVA's suitablity for this application, films were prepared using gluteraldehyde (GLA) or the dialdehyde of furan (DAF) as the cross-linking reagent and each of the three grades of PVA. Initially films were cross-linked according to the two-step method described earlier. In this method the dried films were immersed in an acid bath at room temperature and slowly heated to 70° or 90° C over a period of 1 to 4 hr. The solution was heated slowly to minimize dissolution of the film before crosslinking occurs. The wet, cross-linked films were very weak and tore easily on handling. They were rinsed and air dried. The films wrinkled and shrunk upon drying. Thus it was difficult to obtain high quality, defect-free films with this cross-linking method.

It became evident early in the contract that this two-step method of cross-linking did not easily lend itself to continuous production methods. Film preparation posed no problem, but for a continuous operating process, greater wet film strength would be required during the cross-linking step to allow the film to be continuously pulled on production equipment. Efforts to improve the wet film strength by increasing cross-link density (i.e., increasing the percent dialdehyde from 10 percent to 20-30 percent) and increasing film thickness proved unsuccessful. The time required to achieve cross-linking (1 to 4 hr) and the requirement that the bath be heated slowly to prevent film dissolution before cross-linking were further barriers to developing a continuous production process. Batch processing was considered. A wound roll of uncross-linked PVA film would require a layer of material to separate the film to permit penetration of the acid catalyst and to prevent cross-linking between adjacent layers. Further, batch processing would lead to nonuniform cross-linking due to variations in the concentration and temperature of the bath, and the time required to achieve cross-linking is still prohibitive.

In general, films cross-linked with the two-step method showed good separator properties. Films where DAF was used as the cross-linking agent as opposed to GLA required more severe conditions, longer dwell times, and higher bath temperatures to achieve low boiling water weight loss. Films cross-linked with DAF had more wet strength than those cross-linked with GLA. Two step cross-linked films had volume resistivities less than 20 ohm-cm. Well cross-linked films had boiling water weight loss less than 10 percent.

Despite the fact that these membranes had good separator properties, the potential processing problems and poor film quality led to an investigation of a one-step method of cross-linking the films. In this method, as discussed in the Experimental section, 5 to 20 percent glyoxylic acid was used as the catalyst and incorporated into the film before casting. Initially the films were heated during the drying process to initiate cross-linking. Films produced in this way had defects from bubbles dried into them. Defect-free films were obtained by allowing the cast films to air dry then heating the dried films for 2 to 5 min at 120° to 160° C. The times and temperatures were representative of conditions that exist in the commercial processing of PVA.

Films were prepared with each of the PVA grades containing 3 percent DAF as the cross-linker and 10 percent GOA as the catalyst. The films were heated to achieve cross-linking from 2 to 5 min at temperatures of 120° to 160° C. Figure 1 illustrates the variation in the degree of cross-linking as measured by boiling water weight loss, with the temperature and oven dwell times of 2 and 5 min. Low boiling water weight loss was achieved with all three grades of Elvanol. Table I summarizes some of the data obtained in the evaluation of PVA grades for films cross-linked using the one-step method with 3 percent DAF and 10 percent GOA. These data show the one-step method of cross-linking yields films with acceptable separator properties. Films cross-linked in the lab under conditions chosen to simulate those on a production line had low boiling water weight loss, good separator properties, and were of good quality (i.e., were smooth and defect-free). This method seems easily adaptable to production processing. The success of the one-step method led to the decison to concentrate on developing it as the method of cross-linking the films rather than the two-step method.

The decision to abandon the two-step method of cross-linking did not come without its costs. Films prepared and cross-linked by the two-step method using acid periodate had better cycle life in cells than those cross-linked in an acid solution (ref. 9). Films cross-linked with periodate are more resistant to oxidation because the 1,2-diols in the PVA are oxidized during the cross-linking. This should lead to more stable films. There did not appear to be a way to incorporate the periodate treatment in a one-step method that allowed removal of residual iodine without an additional washing step which would lead to handling problems. As a result, the increased cycle life was sacrificed. In addition, cross-linkers classified as aldehyde precursors (i.e., polysaccharides, alginic acid, sucrose), which are cleaved by the action of the periodate to form dialdehydes for crosslinking, could no longer be used. The effects of acid vs acid periodate catalyzed cross-linking are further discussed in references 9 and 10. Details on the development of the one and two step cross-linking methods can also be found in those references.

Referring again to table I on the evaluation of PVA grades, we can see that there is not a great difference in the properties of films made with each of the PVA grades. The medium viscosity PVA, Elvanol 71-30 was chosen as offering the best compromise of properties and workability. It underwent the least weight loss after ROX and was the best at maintaining its tensile properties after ROX. The HV was very viscous and difficult to degas at the 10 to 12 weight percent level and the LV PVA was somewhat runny at the same concentration.

OPTIMIZATION OF LEVEL OF CROSS-LINKER

Dialdehyde of Furan

The optimization of film composition began with the DAF as the cross-linker. A series of films were prepared using DAF at 1, 3, 6, and 10 weight-percent concentration levels. The upper level of concentration was dictated by the solubility of the DAF in the PVA solution. The films were cross-linked by the one-step method described earlier. All films contained 10 percent GOA as the catalyst. The films were heated at 160° C for 2 or 5 min to achieve cross-linking. In general, the films that were heated for 5 min had better properties than those heated for only 2 min. Boiling water weight loss and the percent weight loss after rapid oxidation were lower, indicating that cross-linking was more extensive in the films heated for 5 min. The data in table II summarize the results of the screening tests run on the materials as a function of DAF concentration. The best compromise of film properties was achieved with 3 weight percent DAF. Films with 1 percent DAF had low resistivities and low boiling water weight loss but also showed greater weight loss after rapid oxidation and lower zinc dendrite penetration times. Those cross-linked with 6 and 10 percent DAF had low boiling water weight loss and comparable weight loss after rapid oxidation and higher zinc dendrite penetration times, but unacceptably high resistivities. In general, the boiling water weight loss and weight loss after rapid oxidation decrease with increased cross-link density. Film resistivity increases with the cross-link density.

Terepthaldehyde

The 2,5-dialdehyde of benzene, terepthaldehyde (TPA) was evaluated at the 1, 3 and 5 percent of theory levels. As with the DAF, the upper concentration was limited by the cross-linker's solubility in the aqueous solution. The films were cross-linked in one step with 10 percent GOA for 2 and 5 min at 160° C. There was little difference in resistivity between the two treatments; however, boiling water weight loss and weight loss after ROX were better for films heated for 5 min. Table III summarizes data for films with varying levels of TPA heated for 5 min at 160° C to achieve cross-linking. Again the 3 percent level of cross-linker seems to offer the best compromise of film properties. Films cross-linked with 3 percent TPA also had the best retention of tensile properties after ROX.

Dialdehyde of Starch

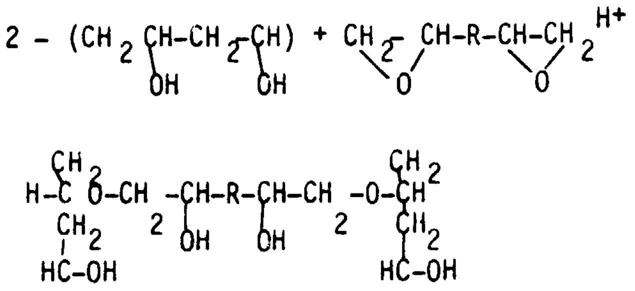
The dialdehyde of starch (DAS) was also investigated as a cross-linker for PVA. These films posed some processing problems. The DAS was hard to dissolve; it was necessary to heat the solution to 80° C to get the DAS to go into solution. Cast and dried films were unclear. Films cross-linked with DAS were inferior to those cross-linked with DAF or TPA as can be seen by the data in table IV. The percent weight loss after ROX ranged from 35 to 48 percent for DAS cross linked films as opposed to 18 to 22 percent to 14 to 21 percent for films cross-linked with TPA and DAF, respectively. Films were fragile after ROX. These films all had dendrite penetration times < 110 min compared with > 200 min for TPA and DAF cross-linked films. Since films cross-linked with DAS were inferior to those cross-linked with DAF or TPA and were difficult to process, DAS was not considered a candidate for production.

Gluteraldehyde

Gluteraldehyde (GLA) was the final dialdehyde evaluated as a cross-linker. Data on GLA cross-linked films is presented in table V. Films were prepared with 1, 3, 6, and 10 percent GLA. It seems that a higher degree of cross-linking is required to give low weight loss after ROX than was necessary with TPA or DAF. At the 10 percent level of cross-linking the film properties were comparable with DAFand TPA at the 3 percent levels. Based on the screening test, 10 percent was determined to be optimum for this cross-linking reagent. Gluteraldehyde is attractive for use as a cross-linker because it is inexpensive, easy to work with, and readily available.

Diepoxide - Ethylene glycol diglicidyl ether

Cross-linking with diepoxides was also investigated. It was postulated that using diepoxides would result in low resistivities at high cross-link density because the OH groups used up in dialdehyde cross-linking are regenerated when epoxides are used as cross-linkers. The cross-linking reaction with diepoxieds can be represented as follows:



$$2-(CH_2\underset{OH}{CH}-CH_2-\underset{OH}{CH}) + \underset{\diagdown O \diagup}{CH_2-CH}-R-\underset{\diagdown O \diagup}{CH-CH_2}\;^{H^+}$$

$$\overset{CH_2}{\underset{\underset{HC-OH}{CH_2}}{H-C}}\;O-CH_2-\underset{OH}{CH}-R-\underset{OH}{CH}-CH_2-O-\overset{CH_2}{\underset{\underset{HC-OH}{CH_2}}{CH}}$$

Cross-linking with diepoxides was erratic. The films required an initial low temperature treatment so that the epoxy was not immediately volatilized. Once cross-linking was initiated, the temperature could be increased to complete the reaction. An attempt was made at catalyzing the reaction with GOA. Films were successfully cross-linked with this method; however, cross-linking was most complete when the films were preliminarily treated at 90° C for 15 min then at 160° C for 5 min. Table VI summarizes results for films cross-linked with ethylene glycol diglicidyl ether (EGDGE). Films cross-linked with GOA as the catalyst had reasonable boiling water weight loss but excessive weight loss after rapid oxidation, which would tend to indicate a high degree of ester formation between the carboxylic acid of the GOA and the OH of the PVA. The ester linkage is then hydrolyzed in the KOH.

Films cross-linked with the EGDGE under the two-stage heat treatment were well cross-linked but had excessive resistivities. As the percent cross-linker was increased, the resistivity increased drastically. It appears that the addition of a hydrocarbon chain incorporates enough hydrophobicity into the PVA to make the films highly resistive.

An attempt at combining the addition of GOA with the two stage heat treatment resulted in films with lower resistivities (13 Ω-cm at 20 percent XL level); however, the ROX weight loss was still unacceptably high: >35 percent. In general, films cross-linked with the diepoxide EGDGE did not have acceptable properties for this appliction. As a result, it was dropped from further consideration.

Full Evaluation of Optimized Crosslinking Reagents

Films were prepared using the optimum levels of each of the three acceptable cross-linkers, 3 percent DAF, 3 percent TPA, and 10 percent GLA. The films were cross-linked in one step using 10 percent GOA. These films were put through a full series of screening tests. The results are reported in table VII. The values for resistivity and ROX in this table are higher than those previously reported. A wetting agent, Triton X-100, was used in preparation of these films. The presence of the wetting agent may have an effect on film properties.

In the full scale evaluation of these films, dimensional stability was monitored. The films swelled considerably with the area increasing 25 to 50 percent and the thickness increasing from 35 to 55 percent. This swelling will have to be controlled for these films to find application in batteries.

Correlation Studies

A series of films was prepared for cell testing to determine how data from the screening tests correlates with film performance in actual batteries. DAF was chosen as the cross-linking reagent. The percent cross-linker, percent GOA catalyst, film thickness, and number of wraps of a 2-mil film were varied in the initial group for cell tests. The film thickness and number of wraps were evaluated in an effort to eliminate the need of studying their effects with machine-made materials, and thus reducing the number of production runs. Table VIII contains a listing of the variations prepared for cell testing, 3 percent DAF, 10 percent GOA (earlier defined as optimum) was the baseline.

Since the quanitites of solution prepared for cell testing increased significantly over the amount used for initial screening, the solutions became more difficult to degas before casting. A small amount of Triton X-100 (less than 0.01 percent by weight) was added to aid release of the gas bubbles form the solution. There was some concern that the use of wetting agents might have a negative effect on film properties; as a result, an additional set of films with no wetting agent was prepared to serve as a control.

The data from the characterization screening of these films are summarized in table VIII. As the level of DAF, thus the cross-link density, is increased from 3 percent to 10 percent, the electrical resistivity increased, the weight loss after rapid oxidation and the zincate diffusion rate decreased, and the dimensional stability was improved. The properties change as expected. As cross-link density is increased, the number of OH groups decreases; a tighter film is produced with higher resistivity, greater resistance to oxidation and swelling, and a lower zincate diffusion rate.

With the concentration of DAF held constant at 3 percent, the level of GOA was varied from 5 to 20 percent. The volume resistivity decreased by a factor of 3, the zincate diffusion rate increased, and the OH diffusion rate doubled. As the concentration of GOA increased, the films exhibited a greater degree of swelling. In general, the incorporation of increased amounts of GOA led to more open films as seen by increased zincate and hydroxyl diffusion rates. The incorporation of increased amounts of carboxylic acid functionality led to less resistive films.

As film thickness was increased from 2 to 7 mils, the resistivity increased and percent weight loss after rapid oxidation decreased. The zincate diffusion rate, electrolyte diffusion, and dimensional stability remained constant as thickness increased. Although the volume resistivity decreased, the area resistivity increased as thickness increased. The area resistivity increased with thickness from 0.179 Ω-cm^2 at 2 mils and 0.247 Ω-cm^2 at 4 mils to 0.293 Ω-cm^2 at 7 mils. Assuming a constant cross-link density the volume resistivity should increase with increased film thickness. However, since all films were given the same cross-linking treatment (i.e., 5 min at 160° C), it is possible that the thicker films were not cross-linked to the same extent as the thinner ones.

Incroporation of Triton X-100 at <0.01 percent seems to have had little effect on film properties. The biggest difference is in percent weight loss after ROX, for the film without any wetting agent, the weight loss was 6.4 percent and with it, it increased to 27.7 percent.

The dimensional stability of these films needs to be improved before they can be used routinely in cells. With the area increasing from 38 to 76 percent when soaked in KOH, the films would wrinkle in the cell unless assembled with separators, wetted with KOH which is not feasible.

These membranes were further tested in cells. Three cells were constructed with each separator. The cells were run through a series of performance characterization tests. Midpoint voltages, watt hour output and ampere hours out to 1.0 V were monitored. The values reported are for the average of three cells.

The effect of DAF and GOA concentrations is shown in figure 2. As the level of DAF was increased from 3 percent to 7 percent, cell performance decreased slightly. At the C rate, the cell with the membrane with 3 percent DAF had a midpoint voltage of 1.41 V as opposed to 1.38 V for membranes with 7 and 10 percent levels of DAF. The decline in performance can probably be attributed to the increased resistance of the more highly cross-linked films.

As the level of GOA was increased from 5 to 20 percent, cell performance improved. The greatest improvement was in the midpoint voltages where a 10 mV increase was achieved between cells with membranes at the 5 percent and 20 percent level of GOA. The improved performance results from the decreased film resistivities and increased hydroxyl diffusion rates.

The effects of film thickness and number of wraps is shown in figure 3. As the number of wraps of a 2 mil film increased, the cell performance declined. This is expected since resistivity would increase with increased layers and the hydroxyl diffusion rate would decrease as the number of layers increased - both effects would tend to lead to poorer cell performance.

As the film thickness increased from 2 to 4 mils, cell performance decreased; when thickness increased from 4 to 7 mils, the performance improved. Multiple wraps of a 2 mil film (i.e., 4 wraps to yield 8 mils total) led to better performance than 2 wraps of a 4-mil film.

The low level of wetting agent in these films had essentially no effect on cell performance. This was expected as there was also no difference in film properties.

In general, the differences in cell performance correspond to resistivities with the exception of the thicker films.

Following the characterization, the cells were initially cycled at 80 percent DOD. Eighty percent DOD was chosen over the standard 50 percent DOD used on our separator tests as a means of running an accelerated test to rapidly differentiate between the membranes. However, these test conditions proved too severe. Within 30 cycles, all but four of the cells had fallen below 1.0V. The effect of the separators was masked by the poor performance of all the cells, including the standard control which had five wraps of cellophane as the separator. In order to salvage any available data, the cells were removed from test, reconditioned by several deep cycles with an overnight charge and C/2.5 rate discharge. The cells were then returned to cycle test at 50 percent DOD.

Figure 4 summarizes the cycle data. After reconditioning, on cycling at 50 percent DOD, the cells with multiple wraps or thicker films exhibited the greatest number of cycles before cell voltage dropped below 1.0 V. This is expected since the principal failure mode was loss of capacity and the thicker films had lower zincate diffusivities. Multiple wraps of a 2-mil film also effectively reduces zincate diffusivity.

As the cross-link density increased, the cycle life improved with the optimum being at 7 percent DAF. As the percent GOA was increased, cell performance improved as discussed earlier; however, cycle life decreased. Increasing the concentration of GOA led to films which were more open, thus less resistive, but also less selective with respect to zincate diffusivity.

From this study it is evident that a compromise must exist between cell performance and cell cycle life. Multiple wraps of a thinner film seem to yield the best cycle life without sacrificing performance to any great extent. Further study is required to determine the interactions of changes in the various processing parameters.

Evaluation of Wetting Agents

Wetting agents and release agents are commonly used in the commercial production of PVA films to aid in solution-degassing and release of the dried film from the stainless steel belt. They are commonly added at levels from 1.1 percent to 4 percent based on the weight of PVA. These levels are considerably higher than the .01 percent used in our initial evaluation, at the higher levels wetting agents may have a more pronounced effect. In preparation for scale up to production quantities, several wetting agents were evaluated to determine their effects on film properties and cell performance. The following wetting agents were evaluated: Triton X-100, the wetting agent used in preliminary work done at NASA; Emcol 5130, commonly used in commercial preparation of PVA films; and a proprietary wetting agent, used at W. R. Grace (GPWA) which had been identified as "non-foaming" and "non-interfering". A fourth wetting agent, Triton BG-10, a wetting agent known to cause foaming in cells, was included for comparison.

All of the wetting agents were evaluated at the 1.1 percent level in films cross-linked with 3 percent DAF and 10 percent GOA. The wetting agents were evaluated for their abilities to degas the solutions and aid release from stainless steel, as well as the amount of foaming, if any, which resulted when a 0.5 g film sample was shaken with 35 percent KOH. In addition, the films were characterized as separators. A film with no wetting agents was prepared and tested as a control. The results from the screening tests are summarized in table IX.

All of the wetting agents, except Triton BG-10, which was not tested, provided excellent release from stainless steel. The sample with no wetting agent did not release. All of the solutions were degassed sufficiently with the exception of the one with Triton X-100 as the wetting agent. This solution had some bubbles left in it; however, they broke when the solution was cast. When a 0.5 g sample of the film was shaken with KOH, the sample containing Triton BG-10 foamed excessively, Emcol 5130 produced a small amount of foam, the sample containing Triton X-100 foamed even less, and the samples with GPWA and no wetting agent did not foam at all.

The presence of wetting agents had little effect on film resistivity and boiling water weight loss. However, weight loss after rapid oxidation increased by 8 to 10 percent in films with wetting agents. The retention of tensile properties after ROX also seems to be adversely affected by the presence of wetting agents.

Films were prepared with each of the wetting agents and built into cells. The effect of the wetting agents on film performance is summarized in figure 5. Data from cells with no wetting agent and the low level of Triton X-100 are included for comparison. From this figure, it is evident that 1.1 percent of any wetting agent has a definite negative effect on cell performance. Ampere hour output, midpoint voltages, and watt hour output all decreased when wetting agents were used in the films. The two Tritons, BG-10 and X-100, seem to cause the greatest decline in performance. The Emcol 5130 would rank next and the GPWA has the least effect on cell performance. At the C rate, the presence of GPWA resulted in a 12 percent decrease in ampere hour capacity, a decrease in midpoint voltage from 1.42 to 1.36 V, and a decrease in watt-hour output from 7.1 WH to 6.66 WH. The differences in performance were greatest at the C rate.

The cells were cycled at 50 percent DOD, cycle life was reported to 1.0 V end of discharge voltage. Cycle life results follow the performance data very closely. The cycle life results are shown in figure 6. GPWA had the greatest cycle life with E-5130 and Triton X-100 following closely. Triton BG-10 had the poorest performance. The cells with no wetting agent and the low level of Triton X-100 were cycled on a different regime, thus that data is not available for comparison.

From this study, we conclude that the addition of wetting agents at the levels used in the commercial production of PVA should be avoided if at all possible because of the detrimental effect they have on cell performance.

Scale Up Efforts

PVA's other than Elvanol 71-30 are more commonly used in the commecial production of films. At Polymer Films, a subcontractor to W.R. Grace, Coval 9830 is the preferred grade. Fourteen weight percent solutions are commonly used. At this concentration Elvanol 71-30 does not release gas bubbles well enough to yield bubble-free films. At 14 weight percent, Elvanol 71-30 with 10 percent GOA tends to gel before casting. Coval 9830 was evaluated and found comparable to the Elvanol 71-30. Thus Coval 9830 was to be used in the production trials of the cross-linked films However, difficulties in obtaining the necessary quantitites of Coval 9830 led to another attempt at substitution. An appropriate substitute was not found. Vinol 325 resin from Air Products was evaluated and found inferior to the Elvanol 71-30 and Coval 9830. The difficulty in obtaining a suitable substitute for the PVA was a major factor which led to the decision to abandon the scale up effort.

CONCLUDING REMARKS

The contract was terminated without completing the efforts to produce commercial quantitites of the cross-linked materials. Several factors led to the decision not to proceed with commercial production. The first, mentioned earlier, was the fact that we were unable to identify an available PVA, with properties comparable to the Elvanol 71-30, used in the screening and optimization of the cross-linked materials. Substitution of a PVA or blend of PVA's which was not fully characterized could yield different results. Second was the necessity to add wetting agents at 1.1 to 4 weight percent level to provide sufficient release and degassing for production processing. The evaluation of wetting agents showed they have a definite negative effect on cell performance and possibly cycle life. The third factor was the swelling of the films. The cross-linked films swelled considerably when soaked with KOH. Films used as separators in cells wrinkled excessively. Further development would be required to miminize separator swelling. In addition, cells with cross-linked PVA separators had relatively poor cycle life when compared to the standard five wraps of cellphane and other systems we have worked with.

In conclusion, the PVA system shows promise for use as a separator in alkaline systems, namely Ni/Zn. However, further development is required before the system should be considered for commercial production. Program changes at NASA-Lewis have resulted in a focusing of our interest on electrochemical systems other than Ni/Zn, and as a result, work in this area has been terminated.

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TABLE I. - EVALUATION OF PVA ELVANOL GRADES

3 PERCENT DAF, 10 PERCENT GDA, ONE-STEP CROSS-LINKING

Elvanol grade	Thickness, mil	Boiling water weight loss, percent	Volume resistivity, Ω-cm	Weight loss after ROX, percent
High MW (HV)	3.9	+0.6	14.97	20.76
Medium MW (71-30)	3.97	2.5	15.47	14.57
Low MW (90-50)	3.86	3.9	14.27	17.43

TABLE II. - OPTIMIZATION OF CROSS-LINKING WITH DAF

ONE STEP TREATMENT - 160°C, 5 MIN

Percent DAF	Thickness, cm	Boiling water weight loss, percent	Volume resistivity, Ω-cm	Zinc dendrite penetration time, min	Weight loss after ROX, percent
1	9.9×10^{-3}	0.9	14.7	118	20.9
3	9.4×10^{-3}	2.5	15.5	>200	14.6
6	1.02×10^{-2}	1.2	35.7	>200	14.1
10	1.04×10^{-2}	1.1	53.8	>200	16.8

TABLE III. - OPTIMIZATION OF CROSS-LINKING WITH TPA

ONE STEP TREATMENT - 160°C, 5 MIN

Percent DAF	Thickness, cm	Boiling water weight loss, percent	Volume resistivity, Ω-cm	Zinc dendrite pentration time, min	Weight loss after ROX, percent
1	1.2×10^{-2}	+3.5	11.6	119	21.7
3	1.1×10^{-2}	-2.3	13.0	>200	16.4
5	9.6×10^{-3}	+0.8	19.7	Ω>200, 150	20.2

TABLE IV. - OPTIMIZATION OF CROSS-LINKING WITH DAS

ONE STEP TREATMENT - 160°C, 5 MIN

Percent DAF	Thickness, cm	Boiling water weight loss, percent	Volume resistivity, Ω-cm	Zinc dendrite pentration time, min	Weight loss after ROX, percent
1	8.8×10^{-3}	3.6	13.4	78	35.9
3	9.4×10^{-3}	4.3	13.3	102	37.7
6	8.6×10^{-3}	4.1	12.5	109	41.4
10	8.3×10^{-3}	5.2	10.6	82	48.2

TABLE V. - OPTIMIZATION OF CROSS-LINKING WITH GLA

ONE STEP TREATMENT - 160°C, 5 MIN

Percent DAF	Thickness, cm	Boiling water weight loss, percent	Volume resistivity, Ω-cm	Zinc dendrite pentration time, min	Weight loss after ROX, percent
1	1.0×10^{-2}	2.4	12.4	63	39.4
3	7.8×10^{-3}	2.4	12.3	>200	35.6
6	9.5×10^{-3}	1.5	11.9	>200	31.7
10	8.6×10^{-3}	0.9	18.1	>200	14.2

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TABLE VI. - CROSS-LINKING WITH DIEPOXIDE

ETHYLENE GLYCOL DIGLICIDYL ETHER (EGDGE)

Percent EGDGE	Cross-linking treatment	10 Percent GOA	Boiling water weight loss, percent	Volume resistivity, Ω-cm	Weight loss after ROX, percent
10	5 min at 160° C	Yes	13.2	12.9	41.8
20	5 min at 160° C	Yes	16.4	9.97	45.5
40	5 min at 160° C	Yes	23.5	6.53	47.5
10	15 min at 90° C 5 min at 160° C	No	3.1	95.4	25.2
20	15 min at 90° C 5 min at 160° C	No	[illegible]	193	20.7
40	15 min at 90° C 5 min at 160° C	No	20.0	332	17.3
10	15 min at [illegible] C 5 min at 160° C	Yes	4.4	12.7	37

TABLE VII. - FULL SCALE EVALUATION OF OPTIMUM CROSS-LINKERS

[0.01 Percent triton X-100 wetting agent present.]

Cross-linker	Thickness, cm	Boiling water weight loss, percent	ROX	Electrical resistivity, Ω-cm	Zinc dendrite pentration time, min	Zincate diffusion, moles/cm^2 min	Hydroxyl diffusion, moles/cm^2 min	Dimensional stability		
								Increase area, percent	Increase thickness, percent	Weight gain, percent
3Δ DAF	7.1x10^{-3}	6.7	27.7	25.3	>200	3.9x10^{-8}	4.19x10^{-4}	55	38.9	123
3Δ TPA	8.3x10^{-3}	1.0	19.6	16.7	>200	5.7x10^{-8}	4.4x10^{-4}	24	54.5	142
10Δ GLA	6.8x10^{-3}	2.0	20.3	36.3	>200	1.9x10^{-8}	3.5x10^{-4}	23	33.3	115

TABLE VIII. - SCREENING TEST RESULTS OF MATERIALS FOR CELL EVALUATION

Separator	Composition		Thickness, mil		Boiling water weight loss, percent	Weight loss after KOH, percent	Electrical resistivity, Ω-cm	Zincate diffusion, moles/cm² min	Hydroxyl diffusion, moles/cm² min	Dimensional stability		
	DAF, percent	GOA, percent	Wet	Dry						Area increase, percent	Thickness increase, percent	Weight gain, percent
WD03A2	3	10	2	2.8	6.7	27.7	25.3	3.9×10^{-8}	4.08×10^{-4}	55	38.9	123
WD07A2	7	10	2	2.2	18.3	17.1	50.4	1.1×10^{-8}	2.46×10^{-4}	39.2	30.8	90.2
WD10A2	10	10	2	3.1	17.8	11.5	52.8	2.9×10^{-9}	2.52×10^{-4}	38.5	25.5	80.1
WD03B2	3	5	2	3.2	6.6	21.5	28.5	4.8×10^{-9}	2.58×10^{-4}	42.4	32.0	98.8
WD03C2	3	20	2	3.6	3.0	14.0	9.87	1.0×10^{-7}	5.28×10^{-4}	76.4	36.4	155
WD03A4	3	10	4	5.9	1.0	10.7	16.5	9.6×10^{-9}	1.44×10^{-4}	60.9	30.6	135
WD03A6	3	10	7	10	1.1	6.4	11.53	9.6×10^{-9}	1.68×10^{-4}	60.9	43.5	125
CD01A2*	3	10	2	2.8	3.2	6.4	20.5	1.7×10^{-8}	3.66×10^{-4}	57.1	29.4	128

*No wetting agent.

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TABLE IX. - EVALUATION OF THE EFFECT OF VARIOUS WETTING AGENTS

(1.1 PERCENT) ON FILM PROPERTIES

Wetting agent	Release	Foaming	Degassing	Boiling water weight loss, percent	Thick-ness	Volume Resis-tivity, Ω-cm	Weight loss after ROX, percent
None	None	None	OK	2.0	2.8	24.5	18.8
EMCOL 5130	Excellent	Small amount	OK	1.0	2.5	28	27.7
GPWA	Excellent	None	OK	1.6	2.6	27.4	28.4
Triton X-100	Excellent	Some	Some bubbles left	.9	2.4	27.3	26.8
Triton BG-10	---------	Foamed badly	OK	.6	2.7	25.4	24.8

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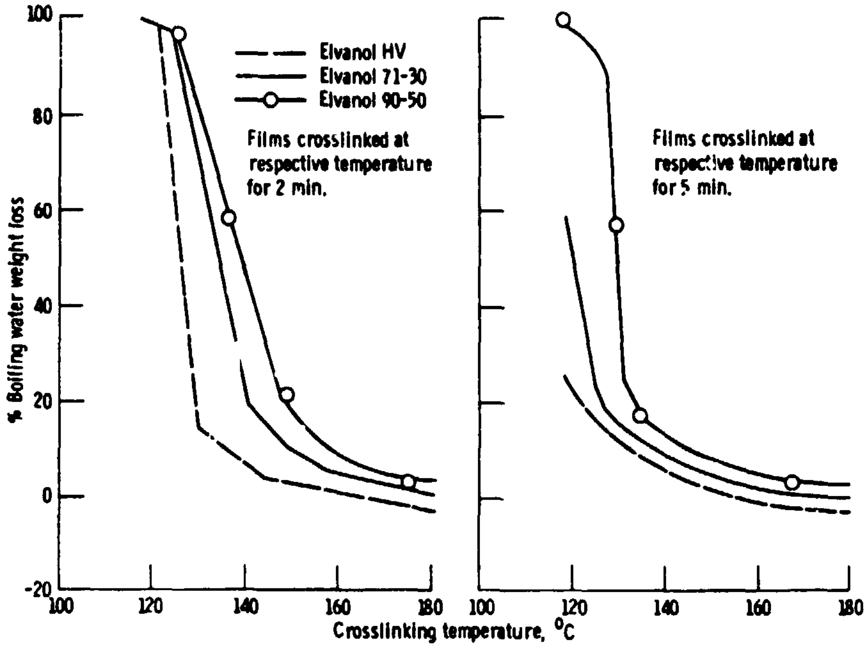
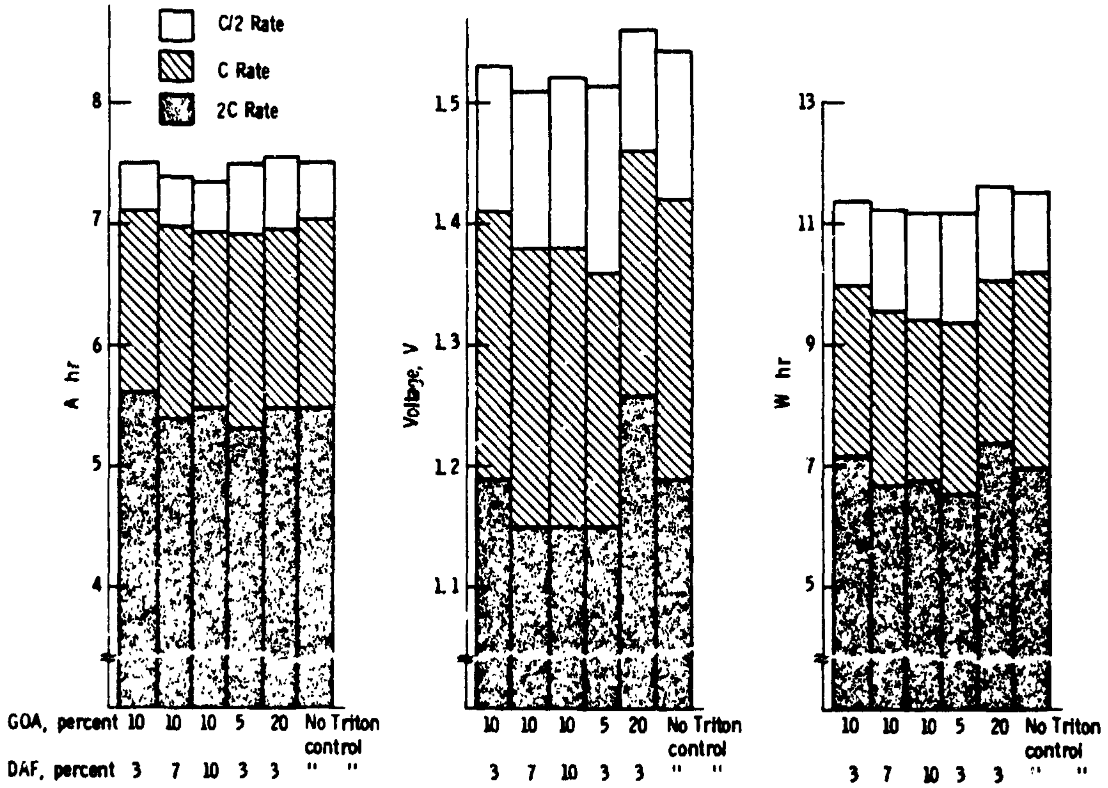
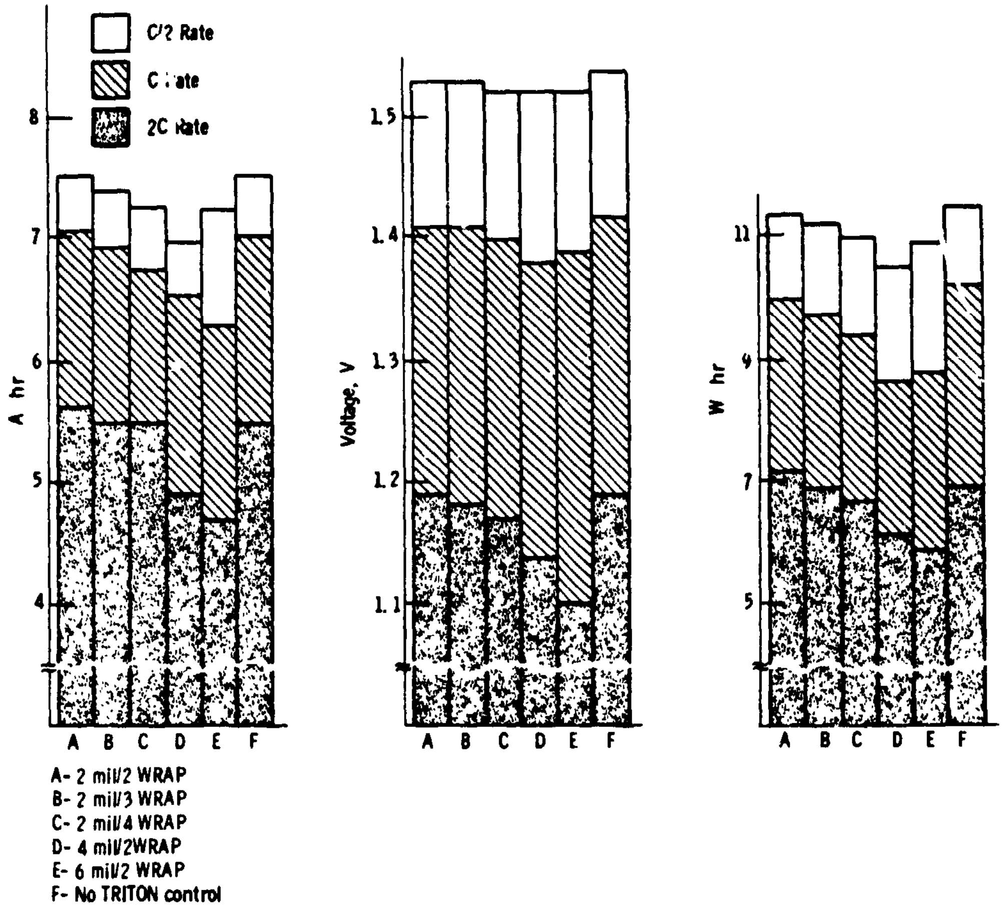


Figure 1. - Variation in amount of crosslinking as measured by boiling water weight loss with crosslinking temperature for PVA-Blend Membranes prepared by the "one step" method. All films contain 3% dialdehyde of furan and 10% glyoxylic acid.



(a) A hr output
(b) Midpoint V
(c) W hr output

Figure 2. - Performance vs DAF concentration & % GOA.



(a) A hr output
(b) Midpoint V
(c) W hr output

Figure 3. - Performance vs number of wraps.

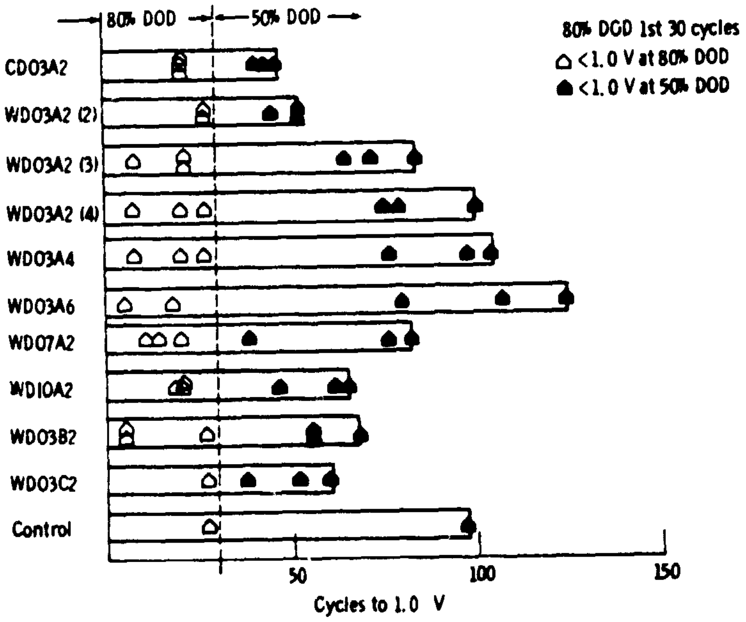
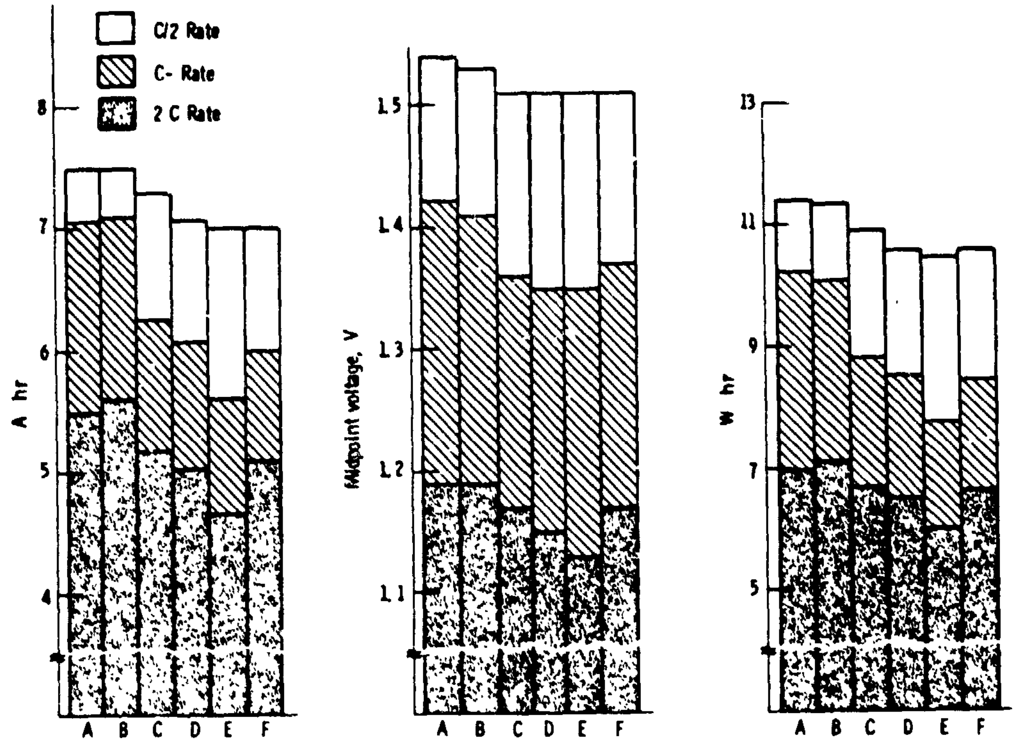


Figure 4. - Cycle life results-DAF films.



A- No wetting agent
B- Low TRITON X-100
C- GPWA
D- TRITON X-100
E- TRITON BG 10
F- EMCOL 5130

(a) A hr output
(b) Midpoint V
(c) W hr output

Figure 5. - Cell performance as a function of discharge rate and wetting agent.

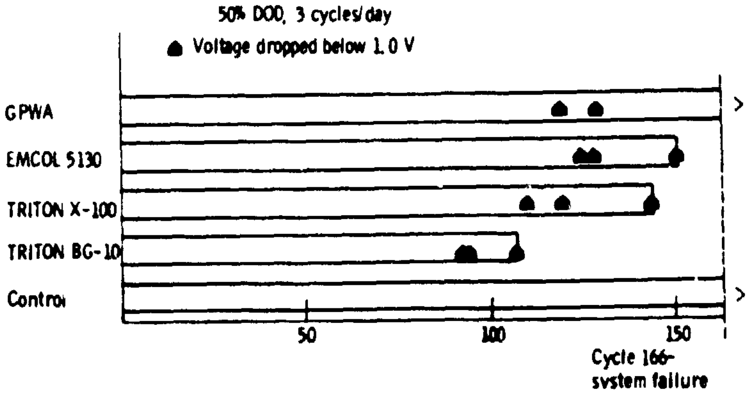


Figure 6. - Cycle results for cells with wetting agents.