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ABSTRACT

Polyvinyl alcohol (PVA) cross-linked with aldehyde reagents yields membranes that demonstrate properties that make them suitable for use as alkaline battery separators. Film properties can be controlled by the choice of cross-linker, cross-link density and the method of cross-linking. Three methods of cross-linking and their effects on film properties are discussed. Film properties can also be modified by using a copolymer of vinyl alcohol and acrylic acid as the base for the separator and cross-linking it similarly to the PVA. Fillers can be incorporated into the films to further modify film properties. Results of separator screening tests and cell tests for several variations of PVA films 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 resistivity 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 requirements. In alkaline electrolyte the zinc forms a soluble species, zincate ($Zn(OH)_4^{2-}$). 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 zincate 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.

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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 (Ref. 2, 3).

Acid periodate solution can also be used to cross-link PVA films containing certain organic structures considered to be aldehyde precursors, such as polysaccharides (Ref. 4). Cross-linking with polysaccharides can be used to incorporate carboxylic acid groups to the cross-link structure and thus significantly reduce resistivity. The use of glyoxylic acid (GOA), a reagent which contains both an aldehyde and a carboxylic acid group, in PVA films cross-linked in-situ using periodic acid solution allows control of ionic conductivity.

PVA films containing dialdehydes such as gluteraldehyde, terephthaldehyde, and the 2,5-dialdehyde of furan can be cross-linked by in-situ immersion in a sulfuric acid solution saturated with sodium sulfate. While this method provides better control over the cross-linking reaction it does not eliminate the weak 1,2-diol units of the PVA and as a result these films are less resistant to oxidation (Ref. 5). When glyoxylic acid is incorporated into these films before casting, a cross-linked film is produced in one step (Ref. 6). This one-step method appears most favorable for the development of a commercial production process as it eliminates the handling of weak films with acid solution.

PVA can also be irradiation cross-linked under certain conditions (Ref. 7). In addition to self cross-linking, PVA cross-links with other polymers such as polyacrylic acid (PAA), and polyethylene oxide (PEO). The mechanism proposed by Philipp and Hsu (Ref. 8) involves hydrogen abstraction in an aqueous acid medium. These films exhibit very low resistivity in alkaline electrolyte.

The incorporation of carboxylic acid functionality in PVA films leads to more conductive separators. As discussed above, this functionality has been added by using cross-linkers which contain carboxylic acid groups and by forming blends of PVA and polymers which contain the desired functionality (e.g. PAA). Another method of adding this functionality is copolymerizing vinyl acetate (VA) with the acrylic acid (AA) which yields a vinyl alcohol acrylic acid copolymer upon hydrolysis. The ratio of VA:AA can be controlled in the copolymer. Ratios ranging from 3:1 to 7:1 VA:AA appear to possess optimum properties for alkaline batteries with zinc electrodes. These films can be cross-linked similar to PVA films. (Ref. 9)

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The PVA system seems to be very versatile. Film properties can be controlled by the choice of cross-linker, cross-link density, and cross-linking method. Fillers can be incorporated into the films to further modify film properties. The addition of fillers to the films yields increased cycle life in Ni/Zn cells. (Ref. 10)

Experimental

Materials - The sources and grades of commercially available PVA used in this study are shown in Table I. PVA designated LV represents a low viscosity grade, MV represents a medium viscosity grade, while HV represents the high viscosity grade. All grades used were 99 percent hydrolyzed polyvinyl acetate.

Categories of aldehydes evaluated and their sources are shown in Table II. The oligoaldehydes and polycarboxyaldehydes as represented by sucrose and alginate are considered aldehyde precursors, since the aldehyde functional groups are generated in-situ in the PVA films upon treatment with acid periodate solution.

The filler combinations, their compositions and sources are identified in Table III.

General Procedure for the Preparation of Crosslinked PVA Films

Film Preparation Procedure - PVA films were cast from a 10 percent solution of the desired grade of PVA in water. The copolymer films (Ref. 8) were cast from a 5 percent aqueous solution and the films of PVA-PAA blends were cast from solutions mixed in the proper proportions to achieve the desired ratio between the polymers.

Films with cross-linkers were made by adding a quantity of dialdehyde or dialdehyde precursor to achieve the theoretical amount of cross-linking desired, usually 2 to 10 percent assuming one aldehyde group per two hydroxyl groups.

The solutions were well mixed. If the films contained fillers, 5-20 weight percent of the filler mixture was added. Entrapped air bubbles were removed by placing the solution in a bell jar under vacuum. The solutions were then cast on a smooth, clean glass or teflon surface using a Gardner blade. Films were cast to achieve a dry thickness ranging from 2 to 5 mils. The cast films were air dried at room temperature overnight, unless otherwise specified.

Crosslinking Methods - The dried films produced as described above were cross-linked by one of the following methods:

Two-Step Crosslinking - Films containing dialdehyde cross-linking reagents were cross-linked by immersing the dried film in a solution containing 20 ml of sulfuric acid saturated with 200 g sodium sulfate, in 1 liter of water. The solution was gradually heated to 90° C in an oven, usually overnight. The films were rinsed to remove the sodium sulfate, then air

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dried. For films containing an aldehyde precursor as the cross-linking agent and/or where cleavage of the 1,2-diol units of the PVA was desired, cross-linking was achieved by immersing the dried film in an acid periodate solution containing 30 g KIO_4 , 50 ml H_2SO_4 and 200 g Na_2SO_4 in 1 liter of water. The heat treatment, rinsing, and drying steps described above were also performed on these films.

One-Step Crosslinking - To achieve cross-linking in one step (i.e., during the initial drying of the film) a specified amount of an acid-aldehyde reagent, glyoxylic acid (GOA) was added to the solution PVA or PVA + dialdehyde before casting. The same method was used to cross-link the copolymer or copolymer + dialdehyde. The amount added was sufficient to produce a pH below 5. The addition of the acid catalyst initiated gelation. Care was taken to cast these films before gelation occurs. The cast films were dried in an oven. Oven residence time varied with the temperature. Times ranged from 4 hours at $90^\circ C$ to 5 min. at $160^\circ C$. The films could also be air dried then heated appropriately to achieve cross-linking.

Radiation Crosslinking - PVA films and films made from blends of PVA and PAA solutions were radiation cross-linked. The dried films were soaked in a solution consisting of 1 liter of water, 20 ml concentrated H_2SO_4 , and 200 grams of Na_2SO_4 prior to irradiation. The wetted film was placed in a round dish and covered with the aforementioned solution. The submerged film was then irradiated for a specified time with 2 MeV electrons from a linear accelerator (Dynamitron) at a beam current density of 10^{-7} A-cm². The irradiation time ranged from 5 to 20 minutes. The total dose ranged from 5 to 25 megarads. The irradiated polyvinyl alcohol films were washed with water, then with dilute sodium bicarbonate solution, and finally with water. The films were then air dried at room temperature. To prevent tearing, care was taken in handling wet cross-linked films containing polyacrylic acid. No treatment with sodium bicarbonate solution was used on these films because the films swollen by the formation of sodium polyacrylate were particularly weak.

Films cast from solution with a slightly acidic pH, resulting from the incorporation of the carboxylic acid groups in the film, could be irradiated immediately after casting. These films did not require immersion in an acid solution.

Screening Tests of Crosslinked PVA Separators

The cross-linked PVA films, the PVA copolymer films and the PVA-PAA blends were evaluated by determining their ionic resistivity (d.c. method), zinc dendrite penetration rate, and zincate ion diffusivity according to methods described by Cooper and Fleischer (Ref. 11).

Cell Test Evaluation of Crosslinked PVA Separators

Cell test evaluation of cross-linked PVA film separators was performed in 7.2 ampere-hour (A-hr) nickel oxide-zinc (Ni/Zn) cells and 8 AH silver oxide-zinc (Ag-Zn) cells. The electrode configuration for the Ni/Zn cells was

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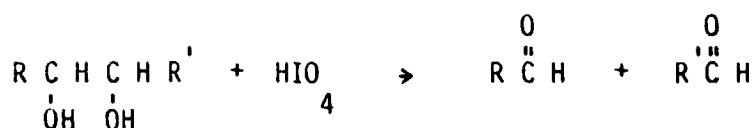
Ni/Zn/2 Ni/Zn/Ni. The nickel electrodes were placed in asbestos absorber bags while the zinc electrodes were either wrapped with 2 wraps of the cross-linked separator or placed in bags made from the cross-linked material. In the silver-zinc cells the electrode configuration was Zn/Ag/Zn. Both silver and zinc electrodes were placed in bags made from the cross-linked PVA. The electrodes were 7.3 cm x 9.4 cm, the silver and nickel electrodes were .075 cm thick and the zinc electrodes were .225 cm thick. Both Ni/Zn and Ag/Zn cells had a negative to positive ratio of approximately 4:1. The electrolyte used in the cells was 35 percent KOH for Ni/Zn and 45 percent KOH for Ag/Zn.

The cells were given three formation cycles after which ampere hour efficiencies usually reached 95 percent. Overcharge was limited to 10 percent of the nominal capacity. Performance was characterized at discharge rates of C/8 (C represents the nominal capacity, C/8 represents the current required to discharge the cell's nominal capacity in 8 hours), C/4, C/2, C, and 2C. Midpoint voltages (i.e., the voltage when half of the nominal ampere hour capacity has been removed from the cell), and ampere hour capacities to 1.0 volt were recorded.

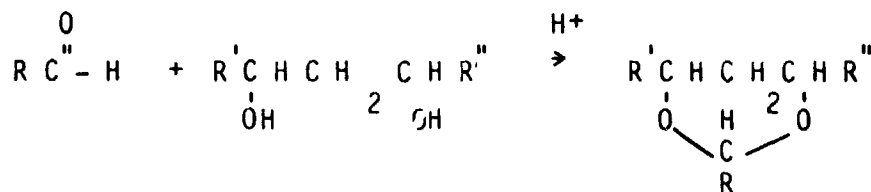
The cells were cycled continuously, the cycle regime consisted of 3 8-hour cycles per day (6 hours of charge at the C/12 rate and 2 hours of discharge at the C/4 rate). The cells were cycled at 50 percent depth of discharge. Failure was defined as the point where the cell could no longer deliver 40 percent of its nominal capacity above 1.0 volt.

Results and Discussion

In order to improve the oxidation resistance of the PVA membranes a method of cross-linking using an acid periodate solution was developed to cross-link PVA to itself. This is accomplished through oxidative cleavage of the 1,2-diol units of the PVA to form aldehyde groups which then react with the secondary alcohol groups of the PVA. The cleavage reaction is represented as follows:

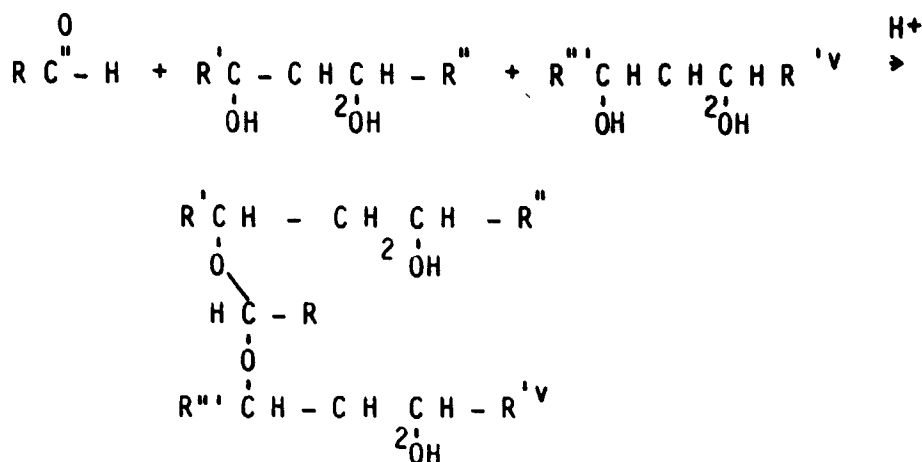


In acid media the aldehydes undergo acetalization with the 1,3 diol units of PVA which results in reformed polymer chains and cross-linking. This may be illustrated as follows:



Or -

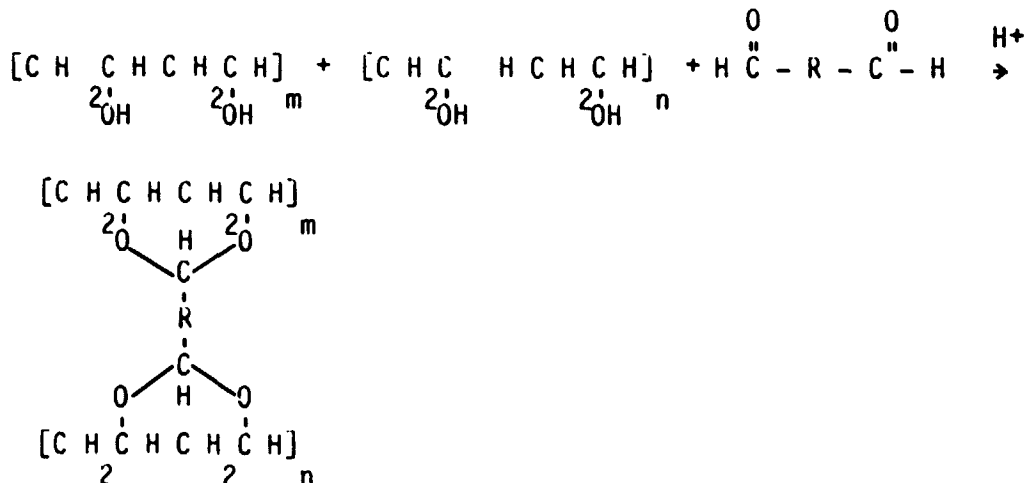
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The degree of cross-linking in periodic acid treated films is dependent on the proportion of 1,2-diol units in the 1,3-diol structure of polyvinyl alcohol. This proportion is related to the proportion of head-to-head units to head-to-tail units in the original starting material, polyvinyl acetate from which polyvinyl alcohol is made by hydrolysis. Head-to-head units in polyvinyl acetate lead to 1,2-diol units.

PVA films treated with periodic acid were tough and resisted tearing. Practically no swelling was observed after a 24-hour exposure to 45 percent KOH. A comparison of resistivities for treated versus untreated films given in Table IV shows that the resistivity doubled for the cross-linked films. This indicates a higher degree of cross-linking than is desired for good ionic conduction. Since the degree of cross-linking is dependent upon the 1,2-diol content of the PVA, the resistivity of the membrane cannot be controlled with this method.

The degree of cross-linking can be controlled by introducing controlled amounts of dialdehydes as cross-linking reagents. PVA films with dialdehydes can be cross-linked with an acid solution. The acid catalyzes the acetalization reaction leading to cross-linking. The reaction can be described as follows:



Resistivity data for gluteraldehyde cross-linked PVA films are shown in Table V. These data show that the resistivity increases as the degree of cross-linking increases. Where cross-linking is extensive the films become hard and brittle. The poor conductivity of highly cross-linked films is probably due to the poor electrolyte absorption in the membrane that arises from the rigidity of the cross-linked structure and from the decreased OH group concentration resulting from extensive acetalization. Sufficient cross-linking was obtained at 2 1/2 percent gluteraldehyde to give tough, water insoluble films with little swelling when immersed in aqueous KOH and little increase in film resistivity. As with the periodate treatment, the incorporation of cross-linking with hydroxyl or carboxylic acid functionality can be used as a method to reduce resistivity.

Table VI compares the two-step method using either acid or acid periodate and two cross-linking reagents, furfuryl dialdehyde (DAF) and terephthaldehyde (TPA) in medium viscosity PVA (MVPVA). Properties measured were volume resistivity, zinc dendrite penetration rate, and zincate diffusivity. The data show that resistivity is increased by use of acid periodate treatment. However, periodate treatment results in a longer time for zinc dendrite penetration and a lower zincate diffusion rate. Uncross-linked PVA has a generally higher resistivity and zinc dendrite penetration rate, but the unaltered PVA structure shows the lowest zincate diffusion rate. From these data it appears that the cross-linked films generally represent an improvement in PVA used as an alkaline separator.

However, resistivity can be lowered by incorporating cross-linkers with hydroxyl or carboxylic acid functionality in the films. For this purpose dialdehyde precursors, polysaccharides such as sucrose or alginic acid, which contain the desired functional groups were added as cross-linking agents. Films containing dialdehyde precursors were treated with periodic acid to cleave the carbon-carbon bonds of adjacent hydroxyl groups in the saccharide ring which leads to the formation of aldehydes used to cross-link the PVA.

The effect on resistance of an aldehyde precursor cross-linking agent which contains carboxylic acid functionality is shown in Table VII. The data shows that with a periodate cross-linking treatment, the carboxylic acid group significantly reduces resistivity when the alginic acid content is increased from 2 percent to 10 percent by weight. This is expected since the carboxylate ion is formed in the alkaline electrolyte and is more hydrophilic than hydroxyl groups.

The data presented in Table VIII show the effect of incorporating GOA into the PVA films. The reagent contains both an aldehyde and carboxylic acid group. The carboxylic acid group affects the resistivity and zincate diffusivity. The reaction of the aldehyde with PVA can follow two routes, either form the cyclic acetal with PVA (the intramolecular reaction) and/or cross-link it (the intermolecular reaction). The extent of cross-linking versus cyclic acetal formation with the GOA is not known. The percent GOA shown in Table VIII represents the percent of theoretical amount needed to cross-link all of the OH groups of the PVA.

As the amount of GOA in the film increases, the volume resistivity decreases with a corresponding increase in zincate diffusion rate. Between 10 percent

and 50 percent GOA, the resistivity is halved (24 ohm-cm to 13 ohm-cm) while the zincate diffusion rate increases approximately 10 percent. The use of smaller amounts of GOA appears to represent a method of resistivity control with minimal change in zincate diffusion.

The effect of GOA on lowering resistivity is very pronounced in the data shown in Table IX. The films contained 2 percent (by weight) sucrose in MVPVA with the amounts of GOA required to achieve the percent of the theoretical amount to react with all the PVA. Films were cross-linked with periodic acid.

The resistivity is decreased significantly (approximately 90 percent) over the range from 10 percent to 35 percent GOA. However, zincate diffusivity increases approximately 20 times over the same range. But the zincate diffusivity does not approach the 2×10^{-6} moles/cm² - min value of commercially available film separators (Ref. 12) until about 70 percent GOA in the film is reached.

A series of films using different cross-linkers over a range of concentrations from 2 - 10 percent and both cross-linking methods were prepared for cell testing.

The PVA films used in these tests for performance characterization and cycle life testing were made and cross-linked in the laboratory according to the procedure described earlier. The films were carefully selected to avoid pin holes, cracks, or other defects. The objective was to correlate the differences in performance and cycle life resulting from cross-linking treatment (periodate or acid) and concentration of cross-linker. Films containing 2 and 7 percent DAF, 2 and 10 percent dialdehyde starch (DAS), and 2 and 10 percent sugar were evaluated in Ni/Zn cells. The results of performance characterization showed that higher concentrations of cross-linker resulted in lower ampere-hour (10 - 15 percent) capacity and lower mid-point voltages (5 to 10 percent) at the 2C and C discharge rates. Typical C rate (1 hour) discharge curves for voltage vs. ampere-hour capacity for PVA-DAF are shown in Figure 1.

Figure 2 contains cycle life data on Ni/Zn cells containing LVPVA-dialdehyde membranes. The cycle life information is represented in bar graph form. The principal mode of failure was loss of capacity from the zinc electrode which resulted in the cell's inability to deliver the required AH capacity above 1.0V. In all tests with these membranes, the periodate treated films with 2 percent cross-linker exhibited the greater cycle life.

The results of cycle life tests in Ag/Zn cells showed that the periodate cross-linked films at the higher concentration of cross-linker exhibited better cycle life. All the Ag/Zn cells eventually failed by shorting. In Figure 3 cycle life data comparisons are shown only for the higher cross-linker content, for 10 percent sucrose, 10 percent alginic acid and 7 percent DAF. Figure 4 also shows results of a film made from high viscosity PVA with 7 percent DAF which was cross-linked by acid treatment. This one exhibited good cycle life presumably due to the lower 1,2-diol content of the HVPVA.

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Both Ag/Zn and Ni/Zn cells showed better cycle life when a periodate cross-linking method was used in LVPVA but they differed in the amount of cross-linker necessary. Ag/Zn cells needed a high cross-linker content while Ni/Zn cells needed a lower amount for better performance. One can conclude that the effect of the method of cross-linking is significant as well as the concentration of cross-linker in the films for better performance of the cells.

The two-step methods of cross-linking yield films with acceptable properties that seem promising for use in alkaline batteries with zinc electrodes. The films can be tailored for their respective uses by controlling the type of cross-linker and the percent cross-linking as well as the cross-linking treatment. However, the two-step methods of cross-linking are not commercially desirable because the dry films lost much of their strength when immersed in the acid solutions. They tore easily when handled. Therefore, machine-processing appeared very unlikely. An evaluation of a batch processing method to achieve cross-linking showed that a wound roll of uncross-linked PVA film required a layer of material to separate the PVA films to permit penetration of the acid treating solution and to prevent "adhesion" of adjacent film layers of PVA due to the cross-linking reaction. Further, batch processing would lead to non-uniform cross-linking due to varying concentration and temperature of solution. In addition, films cross-linked by the two step methods curled and wrinkled, when dried, in such a way that handling was very difficult. The dried films also swelled considerably when immersed in KOH.

An apparent manufacturing method was found when the one-step cross-linking method was worked out. This method involves the incorporation of an acid catalyst, usually GOA, into the solution of PVA-dialdehyde before casting the film. Heating the film either during the drying step or after the film has dried initiates the cross-linking reaction. Glyoxylic acid was chosen as the model reagent. The GOA contains the necessary acid to catalyze the cross-linking reactions, and since GOA reacts chemically with PVA, it leaves no residual products in the film which need to be rinsed out. The only constraints on the film casting process are time and temperature. The film had to be cast before gellation started to prevent casting a film containing domains of cross-linked product. As temperature was lowered, the time to start of gellation increased.

The acid periodate cross-linking treatment does not appear easily adaptable to the one-step method of cross-linking. The oxidation-reduction reaction involving the hydroxyl and the periodate leaves an iodine reaction product in the membrane. This residue can be removed but requires an additional washing procedure. This washing would probably lead to handling problems similar to those encountered with two-step films and as a result, this approach was not pursued. Thus, it appears that the increased cycle life of cells with PVA films treated with periodic acid must be sacrificed to obtain a commercially producible cross-linked film.

In Table X the effect of the cross-linking methods (two-step vs. one-step) on resistivity and zincate diffusivity is measured for two cross-linking reagents, DAF and TPA, and on films with 2 percent DAF and 5 percent fillers. The one-step method generally results in a cross-linked film having higher (but acceptable) resistivity and a lower zincate diffusion rate. Films cross-linked by the one-step method dried smooth and wrinkle free. However, they also exhibited some unacceptable swelling when placed in 45 percent KOH.

The use of fillers in cross-linked PVA films was explored in some depth since earlier tests indicated that in addition to improved resistivity, cycle life was also improved.

The two filler combinations shown in Table X both contain an electrolyte reactive filler, fine particle silica, which would tend to reduce resistivity, but enhance zincate diffusion. Evaluation of filler combinations containing no soluble or electrolyte reactive filler over the range from 5 to 20 weight percent of PVA showed that some enhancement of zincate diffusion and hydroxyl ion diffusion could be attained with these non-reactive filler combinations while not adversely affecting the resistivity. The 5 percent and 10 percent weight range produced films of acceptable flexibility, films with 20 percent fillers were brittle.

Several pilot plant production batches were run to demonstrate feasibility of producing cross-linked PVA film separators on PVA film casting machinery. These acid catalyzed one-step cross-linked materials were produced with and without fillers. The 10 percent weight level of two non-reactive filler combinations was selected for pilot plant production. The results of comparison tests on one step cross-linked films are shown in Table XI. Results on two commercially available separators, Celgard 3401 and Cellophane, are included for reference. These results show that inclusion of 10 w/o fillers does improve zincate diffusion and in one case (2xTi) increases hydroxyl diffusion by 50-60 percent when compared to PVA with no fillers. Some increase in resistivity is evident. When compared to the commercially available films, the PVA films with 10 percent fillers show 1/10 the zincate diffusion rate, lower resistivity, and in the case of 2xTi, a 50 percent to 60 percent increase in hydroxyl diffusion rate. The inclusion of inert fillers would appear to enhance separator properties.

Figure 4 provides a comparison of cycle life results of cross-linked PVA films without fillers and with 10 percent fillers with Celgard 3401 (2 layers). The average cycle life of cells with PVA films without fillers was 116 ± 8 cycles. The average cycle life of cells with PVA with 10 percent K168 fillers was 112 ± 10 cycles. The average cycle life of cells with PVA separators with 10 percent 2xTi fillers was 153 ± 15 cycles. Cells containing two wraps of Celgard 3401 produced 80 cycles. The use of the 2xTi filler combination at 10 weight percent improved cycle life by approximately 30 percent. The use of fillers in the acid catalyzed one-step method appears to compensate somewhat for the loss in cycle life resulting from the non-periodate cross-linking method. Based on the results of performance characterization and cycle life tests in small Ni/Zn cells, the one-step method of cross-linking provides essentially the same results as the two-step acid cross-linking method for pilot plant production films. Hence it appears that cross-linked PVA films made on commercial production equipment have acceptable properties and perform as well as the commercially available separators to which they were compared.

The third cross-linking method studied was radiation cross-linking. The method could be adapted to manufacturing procedures since only casting, irradiation and a drying step were needed to cross-link the films. Films cross-linked using this procedure resulted in lower resistivity but swelling of the films was difficult to control. Studies proved that the PVA cross-linking mechanism was self-quenching which resulted in a low degree of cross-linking. The lower the degree of cross-linking the higher the swelling of the membranes. Since

diffusion rate while the DAF had the highest resistivity. Table XV compares results of a cross-linked PVA blended with PAA to the cross-linked copolymer. The resistivity and zincate penetration rates are both higher for the copolymer.

A comparison among different cross-linking methods and cross-linker amounts on 6VA-1AA copolymer is presented in Table XVI. From it we can see that the higher the amount of cross-linking the higher the resistivity and penetration rate. Electrolyte retention is good in all of them but better when a two-step cross-linking method is used. The hydroxyl diffusion rate is almost constant in the different methods. The one-step cross-linking method seems to be the alternative to develop if a commercial production is desired since the resistivity is very low while keeping the other properties in a good range. It also prevents wrinkling and handling problems of the final product.

The high electrolyte retention, low resistivity and the fact that different functional groups could be incorporated in it make the copolymer a good candidate for further study in different electrochemical systems. The electrochemical fluorination of copolymers is being attempted since it will improve greatly the oxidation resistance of the films. These films are expected to keep some functional groups, therefore providing a high conductivity to the membranes which will be studied in different systems such as fuel cells. The copolymer is a prime candidate for fluorination since the presence of the carboxylic acid group should yield membranes with low resistivities.

Concluding Remarks

Our study of the cross-linked PVA film concept applied to alkaline batteries as separators had led to some general conclusions:

- 1) The quality of PVA films used as alkaline battery separators is improved by cross-linking. Incorporation of various hydrophilic functional groups within the cross-linking agent permits flexibility in the design of separators for specific applications.
- 2) Chemically cross-linked PVA films exhibit better separator properties and better cell performance than uncross-linked PVA.
- 3) It is important to use acid periodate in-situ cross-linking techniques to eliminate the weak structural 1,2-diol units. This improves cell cycle life in both silver-zinc and nickel-zinc cells when compared with acid cross-linking techniques.
- 4) The introduction of carboxylate functional groups to the cross-linked films reduces resistivity. When used in smaller amounts (less than 35 percent of theoretical reaction amount) other film properties are not altered significantly.
- 5) It was demonstrated that cross-linked PVA films can be processed on commercial film casting equipment. However, production is limited to films with sufficient strength to be machine processed. As a result commercially produced membranes were restricted to those that could

be processed in one-step, thus eliminating the need for handling materials wet with the acid cross-linking solutions.

- 6) The incorporation of fillers into cross-linked PVA films tends to improve film properties and yields increased cell cycle life. Films with fillers have been produced on commercial equipment and cross-linked in one step.
- 7) Copolymerization of PVA and PAA can be used to incorporate carboxylic acid functionality into the films. Crosslinked copolymers have acceptable properties as alkaline battery separators. The high electrolyte retention values and low resistivities make copolymer films attractive for several electrochemical systems.

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TABLE I. - POLYVINYL ALCOHOL

PVA DESIGNATED	VISCOSITY (cP) 4% AQUEOUS	SOURCE
LV	4 - 6	POLYSCIENCES, INC.
MV	28 - 32	POLYSCIENCES, INC.
HV	55 - 65	POLYSCIENCES, INC.
LV	13 - 15	DU PONT-ELVANOL
		90 - 50
MV	28 - 32	DU PONT-ELVANOL
		71 - 30

TABLE II. - ALDEHYDES USED FOR CROSS-LINKING PVA

ALDEHYDES	REPRESENTATIVES	SOURCE
ALIPHATIC DIALDEHYDES	GLUTARALDEHYDE (GDA)	FISHER SCIENTIFIC
FURAN DIALDEHYDES	FURAN-2,5-DIALDEHYDE (DAF)	QUAKER OATS
ARYL DIALDEHYDES	P-PHTHALIC ALDEHYDE (TPA)	FISHER SCIENTIFIC
OLIGOALDEHYDES	SUCROSE (PRECURSOR)	CANE SUGAR
POLYALDEHYDES	POLYACROLEIN	PREPARED IN LAB
POLYHYDROXY ALDEHYDES	DIALDEHYDE STARCH	FISHER CHEMICAL, HEXEL NATIONAL STARCH
POLYCARBOXYL ALDEHYDES	ALGINIC ACID (PRECURSOR)	KELCO
MISCELLANEOUS	GLYOXYLIC ACID (GOA)	FISHER SCIENTIFIC

TABLE III. - FILLER COMBINATIONS USED IN PVA FILMS

IDENTIFICATION	VOLUME, percent	FILLER	SOURCE
143	7.9	SiO ₂ (CAB-O-Sil)	CABOT CORP.
	92.1	200 MESH WHITE PINE WOOD FLOUR	WOOD FLOUR, INC
144	7.8	SiO ₂ (CAB-O-Sil M)	CABOT CORP.
	92.2	CALCIUM ZIRCONIUM SILICATE	TAM PRODUCTS
168	36.3	TiO ₂ (UNITANE 0-110)	AMERICAN CYANAMID
	7.7	LEAD ZIRCONATE TITANATE	TAM PRODUCTS
	16.1	TiO ₂ (P-25)	DEGUSSA
	39.8	KAOLINITE	GEORGIA KAOLIN
2xTi	81.8	TiO ₂ (UNITANE 0-110)	AMERICAN CYANAMID
	18.2	TiO ₂ (P-25)	DEGUSSA

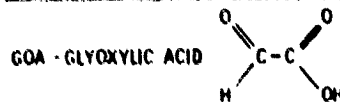
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TABLE VII. - EFFECT OF AMOUNT OF ALGINIC ACID CROSS-LINKING AGENT ON RESISTIVITY OF PERIODATE CROSS-LINKED LVPVA-ALDEHYDE MEMBRANES

PVA - ALDEHYDE	DRY FILM THICKNESS,		VOLUME RESISTIVITY,
	(cm)	(mils)	(ohm-cm)
PVA ONLY	2.7×10^{-3}	1.1	100.7
PVA - 2% ALGINIC ACID	3.9×10^{-3}	1.4	50.6
PVA - 10% ALGINIC ACID	3.9×10^{-3}	1.4	21.3

TABLE VIII. - EFFECT OF GOA IN MVPVA ON RESISTIVITY AND ZINCATE DIFFUSIVITY (ACID CROSSLINKED)

% GOA IN FILM	VOLUME RESISTIVITY, Ω -cm	ZINCATE DIFFUSIVITY, $\text{moles/cm}^2 \cdot \text{min}$
10	24	3.5×10^{-7}
25	21	3.9×10^{-7}
50	13	6.2×10^{-7}
100	4	2.0×10^{-6}



*WET FILM THICKNESS RANGED FROM 0.013 TO 0.017 cm.

TABLE IX. - 2 PERCENT SUCROSE IN MVPVA WITH VARYING AMOUNTS OF GOA, PERIODATE CROSSLINK; WET FILM THICKNESS 0.014 TO 0.028 CM

% GOA	VOLUME RESISTIVITY, Ω -cm	ZINCATE DIFFUSIVITY, $\text{moles/cm}^2 \cdot \text{min}$	ZINC DENDRITE PENETRATION RATE, cm/min
0	122	2.9×10^{-8}	4×10^{-5}
10	28	3.1×10^{-7}	6×10^{-5}
35	14	5.5×10^{-7}	9×10^{-5}
70	12	3.9×10^{-6}	2×10^{-4}

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TABLE X. - COMPARISON OF PROPERTIES OF FILMS MADE USING THE TWO-STEP CROSS-LINKING METHOD WITH FILMS CROSS-LINKED BY THE ONE-STEP METHOD

CROSS-LINKER, ^a percent	VOLUME RESISTIVITY, ohm-cm		ZINCATE DIFFUSIVITY, moles/cm ² min	
	TWO-STEP METHOD	ONE-STEP METHOD	TWO-STEP METHOD	ONE-STEP METHOD
2 DAF	21	40	6.8×10^{-7}	3.1×10^{-7}
2 TPA	21	20	1.2×10^{-6}	4.7×10^{-7}
2 DAF + 5 wt % FILLERS (143)	5	17	1.6×10^{-6}	3.0×10^{-7}
2 DAF + 5 wt % FILLERS (144)	7	23	3.8×10^{-6}	6.9×10^{-7}

^aPERCENTAGE OF THEORETICAL AMOUNT REQUIRED TO REACT WITH ALL HYDROXYL GROUPS PRESENT IN PVA

TABLE XI. - COMPARISON OF ONE-STEP CROSS-LINKED PVA FILMS WITH FILLERS WITH FILMS CONTAINING NO FILLERS

COMPOSITION MVPVA-2% DAF-10% GOA

WT % FILLERS	VOLUME RESISTIVITY (Ω cm)	ZINCATE DIFFUSIVITY (moles/cm ² /min)	OH- DIFFUSIVITY (moles/cm ² /min)
0	8.6	7.1×10^{-7}	2.6×10^{-4}
10% 168	15.9	2.1×10^{-7}	2.2×10^{-4}
10% 2xT ₁	15.8	2.4×10^{-7}	4.3×10^{-4}
CELGARD 3401	31.2	2.9×10^{-6}	2.4×10^{-4}
CELLOPHANE	20.0	2.3×10^{-6}	2.3×10^{-4}

TABLE XII. - RADIATION CROSS-LINKED SEPARATORS;
PVA-PAA BLENDS

MEMBRANE	VOLUME RESISTIVITY (Ω cm)	PENETRATION RATE (cm/min)	ZINCATE DIFFUSIVITY (moles/cm ² min)
PVA	13.1	1.3×10^{-4}	6.6×10^{-7}
10 PVA - 1 PAA	17.4	2.2×10^{-4}	8.5×10^{-6}
7 PVA - 1 PAA	7.0	2.9×10^{-4}	3.2×10^{-6}
3.5 PVA - 1 PAA	2.7	2.7×10^{-4}	1.3×10^{-6}
1 PVA - 10 PAA	1.9	1.1×10^{-3}	5.0×10^{-5}

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TABLE XIII. - VINYL ACETATE-ACRYLIC ACID COPOLYMERS-
10 PERCENT GLUTERALDEHYDE; ACID CROSS-LINKED

MATERIAL	AREA RESISTIVITY (Ωcm^2)	VOLUME RESISTIVITY (Ωcm)	PENETRATION RATE (cm/min)	ZINCATE DIFFUSIVITY (mole/cm ² min)
MVPVA	1.91	100.6	3.3×10^{-5}	6.8×10^{-5}
7VA-1AA	.06	5.3	2.9×10^{-3}	1.9×10^{-6}
6VA-1AA	.15	6.1	2.3×10^{-4}	2.5×10^{-6}
5VA-1AA	.10	3.7	4.9×10^{-4}	2.9×10^{-6}
4VA-1AA	.11	8.6	6.4×10^{-4}	1.3×10^{-6}
3VA-1AA	.06	2.6	1.6×10^{-3}	

WHERE XVA-YAA IS THE MOLECULAR UNITS RATIO

7VA-1AA-7 VINYLACETATE MOLES PER ONE ACRYLIC ACID

TABLE XIV. - 6VA-1AA COPOLYMER: VARIOUS CROSS-LINKING
AGENTS; ACID CROSS-LINKED

CROSSLINKER	AREA RESISTIVITY (Ωcm^2)	VOLUME RESISTIVITY (Ωcm)	PENETRATION RATE (cm/min)	ZINCATE DIFFUSIVITY (moles/cm ² min)
10% GDA	.15	6.1	2.3×10^{-4}	2.6×10^{-6}
10% TPA	.03	2.8	4.4×10^{-4}	9.5×10^{-7}
10% DAF	.12	14.3	2.9×10^{-4}	7.0×10^{-7}

TABLE XV. - PVA - PAA BLEND VS COPOLYMER CHARACTERISTICS

	AREA RESISTIVITY (Ωcm^2)	VOLUME RESISTIVITY (Ωcm)	PENETRATION RATE (cm/min)
4VA-1AA (BLEND) 10% GDA	.04	3.7	1.3×10^{-4}
4VA-1AA COPO 10% GDA	.11	8.6	6.5×10^{-4}

TABLE XVI. - THE EFFECT OF CROSS-LINKING METHODS AND CROSS-LINKING AMOUNTS ON 6 VA-1AA
COPOLYMER FILM PROPERTIES.

6 VA-1AA COPOLYMER						
MEMBRANE	AREA RESISTIVITY (Ωcm^2)	VOLUME RESISTIVITY (Ωcm)	PENETRATION RATE (cm/min)	ZINCATE DIFFUSION (moles cm ² min)	HYDROXYL DIFFUSION (moles cm ² min)	ELECTROLYTE RETENTION (%)
10% DAF AIRDRIED (ONE STEP CROSSLINKED)	.12	18.2	4.6×10^{-4}	6.0×10^{-7}	3.0×10^{-4}	102
10% DAF OVENDRIED (ONE STEP CROSSLINKED)	.05	6.9	---	1.7×10^{-6}	4.5×10^{-4}	237
10% DAF (TWO STEP ACID CROSSLINKED)	.12	14.2	2.8×10^{-4}	8.0×10^{-7}	4.0×10^{-4}	366
20% DAF (TWO-STEP ACID CROSSLINKED)	.14	22.8	6.1×10^{-4}	---	3.3×10^{-4}	363

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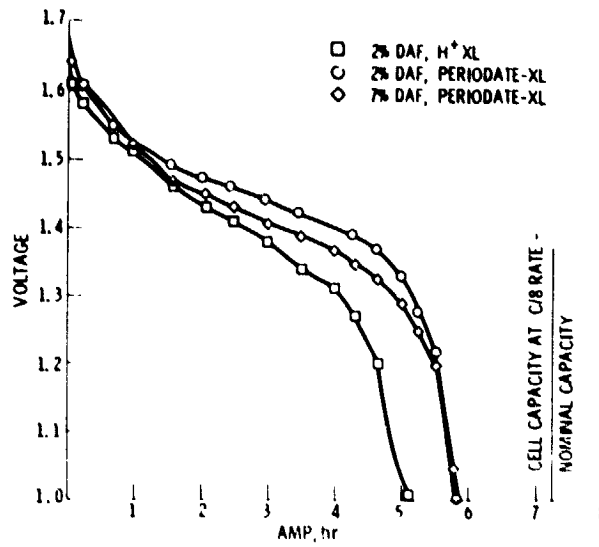


Figure 1 - Voltage versus Amp-hr; C rate discharge in 7.2 Amp-hr Ni/Zn cells.

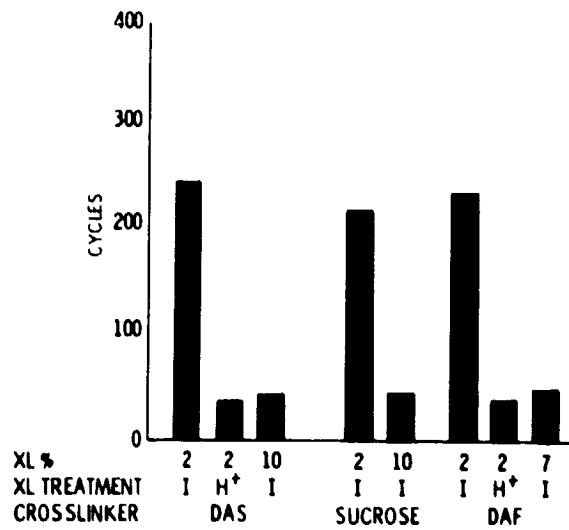


Figure 2 - Cycle life of LVPVA-dialdehyde cross-linked films in 7.2 Amp-hr Ni/Zn cells-50% DOD; 3 cycles/day.

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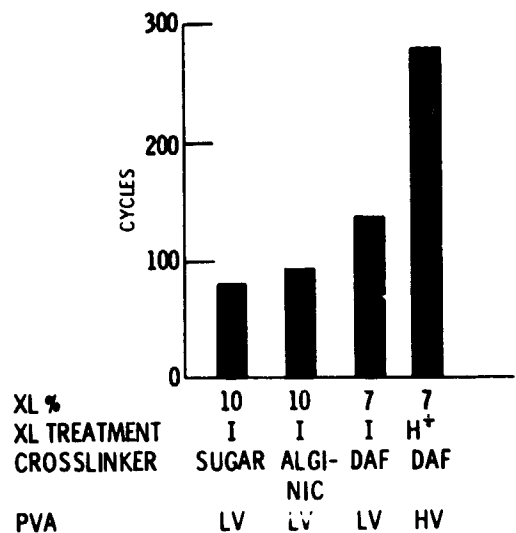


Figure 3. - Cycle life of PVA-dialdehyde cross-linked film in 8 Amp-hr Ag/Zn cells-50% DOD; 3 cycles/day.

PVA COMPOSITION: ELVANOL 71-30 + 2% DAF + 10% GOA + FILLER

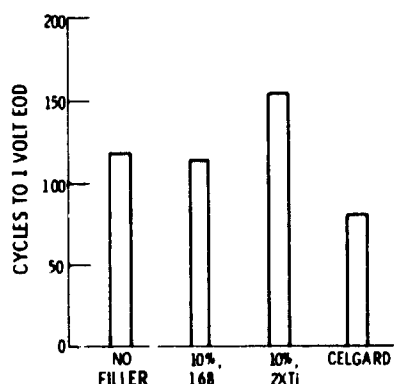


Figure 4. - Comparison of cycle life of one-step cross-linked PVA films with Celgard.