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NASA Technical Memorandum 82619

(NASA-TM-82619) INEXPENSIVE CROSS-LINKED
POLYMERIC SEPARATORS MADE FROM WATER SOLUBLE
POLYMERS (NASA) 16 p HC A02/MF A01 CSCL 07D

N81-23205

Unclas
G3/25 42343

Inexpensive Cross-Linked Polymeric Separators Made From Water Soluble Polymers

Li-Chen Hsu and Dean W. Sheibley
Lewis Research Center
Cleveland, Ohio

Prepared for the
Annual Meeting of the Electrochemical Society, Inc.
Los Angeles, California, October 14-19, 1979



INEXPENSIVE CROSS-LINKED POLYMERIC SEPARATORS
MADE FROM WATER SOLUBLE POLYMERS

Li-Chen Hsu* and Dean W. Sheibley*

National Aeronautics and Space Administration

Lewis Research Center

Cleveland, Ohio 44135

ABSTRACT

Polyvinyl alcohol (PVA) crosslinked chemically with aldehyde reagents produces membranes which demonstrate oxidation resistance, dimensional stability, low ionic resistivity ($<0.8 \text{ ohm-cm}^2$), low zincate diffusivity ($<1 \times 10^{-7}$ moles/cm²-min), and low zinc dendrite penetration rate (>350 min) which make them suitable for use as alkaline battery separators. They are intrinsically low in cost and environmental health and safety problems associated with commercial production appear minimal. Preparation, property measurements and cell test results in Ni/Zn and Ag/Zn cells are described and discussed.

INTRODUCTION

Polyvinyl alcohol (PVA) was selected for development of a polymeric separator because it is low in cost, water soluble, may be readily crosslinked, and has minimal environmental health and safety problems associated with commercial production. Commercial production equipment and methods for fabri-

*Electrochemical Society Active Member.

cation of PVA films are well established in U.S. industry. Commercially available PVA films have been used as battery separators. However, they are prone to oxidative degradation similar to films made from cellulosic materials. This is attributed to the content of small amounts of 1,2-diol units present in the essentially 1,3-diol structure of industrial grade PVA. The 1,2-diol units are susceptible to cleavage in an oxidative environment thereby breaking the polymer backbone causing disintegration of the film.

Polyvinyl alcohol films have been made water insoluble by acetalization with aldehydes, such as formaldehyde (Ref. 1). This is usually accomplished by immersing the film in a hot aqueous solution of the aldehyde containing a small amount of mineral acid and a salting out reagent, such as sodium sulfate, to decrease solubility of the film during the acetalization reaction. The extent of acetalization by this method is difficult to control, usually proceeding too far, and produces inhomogeneous films with poor ionic conductivity in alkaline electrolytes. We have attempted to solve the problems of degradation and control of acetalization by expanding upon our previously reported in-situ self crosslinking technique (Ref. 2). This development led to better oxidation resistant PVA films suitable for use in secondary alkaline nickel-zinc and silver zinc cells.

In the work described here, two methods for the in situ crosslinking of water soluble PVA films were used:

- (1) treatment of a PVA film containing a specified amount of a dialdehyde (for example, glutaraldehyde) with a dilute acid solution. This treatment catalyzes acetalization crosslinking.

- (2) treatment of a PVA film containing a specified amount of dialdehyde (or an aldehyde precursor) with acid periodate. This cleaves the 1,2-diol units present in the PVA (and the aldehyde precursor). This results in the

formation of aldehyde groups which produce crosslinking via acetalization of the 1,3-diol groups (Ref. 2).

The first method affords best control over the extent of crosslinking. The second, the treatment with acid periodate solution, provides the greatest oxidation resistance to the crosslinked film because the easily oxidized 1,2-diol units are eliminated. A more detailed discussion of the crosslinking methods is found in Reference 4.

Standard tests which measure separator properties for alkaline zinc batteries were used (ref. 3). It was desired to measure differences resulting from the crosslinking methods and the composition and amount of aldehyde crosslinking reagent used. Crosslinked PVA films were evaluated in Ni/Zn and Ag/Zn cells. The results of the cell characterization and cycle tests are described.

Experimental

Materials. - The sources and grades of commercially available PVA used in this study are shown in Table 1. 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.

Categories of aldehydes evaluated are shown in Table 2. The oligoaldehydes and polycarboxylaldehydes as represented by sucrose and alginic acid are considered aldehyde precursors, since the aldehyde functional groups are generated in situ in the PVA film upon treatment with acid periodate solution. Dialdehyde starches were obtained from Fisher Chemical, Hexcel Corp., and National Starch Company.

The furan 2,5-dialdehyde was supplied by the Quaker Oats Chemical Co. Tetraaldehyde sugar, and a water soluble polyacrolein were prepared in the laboratory using a proprietary process. Alginic acid was obtained from KELCO.

General Procedure for the Preparation of Aldehyde Crosslinked PVA Membrane Separators

To an aqueous solution of 10-20 percent by weight PVA, a specified quantity of an aldehyde or a precursor such as saccharide was added. The well mixed viscous solution was cast on a smooth clean glass plate with the aid of a Gardner knife and air-dried at room temperature. The air-dried film of desired thickness was cut into pieces of 3-1/2"x8" size. Envelope bags (3"x4") were made from the film by heat sealing. The separator bag was treated in sodium sulfate saturated dilute sulphuric acid solution at 70-90°C for several hours until the PVA film was crosslinked to the degree that it no longer dissolved in boiling water.

The saccharides used as crosslinkers required treatment with acid periodate solution to achieve crosslinking. Both dialdehyde and saccharides were used in an amount to produce from 3 percent to 10 percent crosslinking of the PVA.

The crosslinked PVA separator bag was washed with water, neutralized with dilute sodium bicarbonate solution and again washed with water. The separator bag was then soaked in concentrated KOH solution prior to characterization testing and evaluation.

Screening Tests of the Crosslinked PVA Membrane Separators

The crosslinked PVA membranes were screened by determining their ion resistivity, zinc dendrite penetration rate, and zincate ion diffusivity according to the methods described by Cooper and Fleisher (Ref. 3).

Cell Test Evaluation of the Crosslinked PVA Membrane Separators

Cell test evaluation of the crosslinked PVA membrane separators was performed in Ni/Zn and Ag/Zn cells of ~8 Amp-hr capacity. The zinc electrodes were enclosed in a PVA separator bag. A U-fold of a 7 mil electrical grade

asbestos (M-111, Manning Paper Company, Troy, N.Y.) was placed on the electrode within the separator bag. The positive electrodes of both cell types were covered with a bag made of the electrical grade asbestos. 45 percent KOH was used as the electrolyte in the Ag/Zn cells; 35 percent in the Ni/Zn cells. Ampere-hour efficiencies reached 95 percent after 3 formation cycles. Overcharge was limited to 10 percent in the Ni/Zn cells, while a 2.00 volt cut-off was used for the Ag/Zn cells. The Ni/Zn cell electrode configuration was Ni/Zn/2Ni/Zn/Ni while the Ag/Zn cell was Zn/Ag/Zn. Electrode sizes were 7.3 cm x 9.4 cm with thickness ranging from .075 cm for the positive electrodes to 0.225 cm for the zinc oxide electrodes.

Performance was characterized at the discharge rates of C/8 (the 8 hour rate), C/4, C/2, C, and 2C. Midpoint voltage was recorded as was the ampere-hour capacity above 1 volt.

Cycle testing consisted of 8 hour cycles (6 hours of charge) (C/12 rate) and 2 hours discharge (C/4 rate). The discharge current density was about 15 ma/cm². The testing was continuous; 3 cycles/day, 7 days/week. Depth of discharge was 50 percent based on nominal ampere-hour capacity.

Cell failure was determined to occur when the cell would no longer deliver 50 percent of nominal capacity above 1V for 3 consecutive cycles.

RESULTS AND DISCUSSION

Effect of Aldehyde Concentration on Ionic Resistivity and Zincate Diffusivity

To select a candidate aldehyde for incorporation into PVA, it was necessary to determine the effect of the aldehyde concentration on several parameters which effect acceptance for use as a separator for cells containing a zinc electrode. We selected a relatively inexpensive commercially available dialdehyde starch (polyhydroxyaldehyde) for this study. The data in Table 3

were obtained from films made from medium viscosity (MV) PVA and "Sumstar-190" from Hexcel Corp. The films were crosslinked in an acid solution saturated with sodium sulfate. The resistivity results obtained from ~3 mil dry films show that as the amount of the aldehyde increased, the resistivity decreased and the zincate diffusivity increased.

Our previous experimental results on the glutaraldehyde crosslinked PVA films (Ref. 4), showed that as the amount of crosslinking agent increased, there was a corresponding increase in resistivity of the films. This was logical since the crosslinking reaction consumes two hydrophilic OH groups for each acetal ring structure formed.

The results with dialdehyde starch led us to conclude that Hexcel's water soluble dialdehyde starch may not be pure polyhydroxydialdehyde, but contains a considerable amount of carboxylic acid groups which in this case do not function as a crosslinking agent, but can provide the PVA film with better ionic conductivity.

Effect of Crosslinking Agent and Method on Ionic Resistivity

The method of crosslinking in an acid solution with or without a periodate was evaluated to determine the effect on ionic resistivity. The data in Table 4 compare these results. The 2 percent polyhydroxyaldehyde (dialdehyde starch from National Starch) was blended with a low viscosity PVA (DuPont Elvanol 90-50) to better observe the effect of the periodate since the low viscosity grade PVA contains more 1,2-diol than the higher molecular weight grades.

With the acid crosslinking method, the resistivity was measured at 0.17 ohm-cm^2 . However, the use of acid periodate crosslinking solution produced a film of higher resistivity, 0.88 ohm-cm^2 , presumably due to loss of more hydroxyl groups caused by 1,2-diol cleavage and a greater extent of crosslinking. The results with two levels of polycarboxyaldehydes (alginic acid), show

the effect on resistance of a dialdehyde precursor crosslinking agent which contains carboxylic acid functionality. These films must be treated with acid periodate to cleave the adjacent OH groups in the saccharide rings which then form aldehydes used to crosslink the PVA. The data shows that with a periodate crosslinking treatment, the carboxylic acid group significantly reduces resistivity when compared to dialdehyde starch at 2 percent (Table-3). When the alginic acid content is increased from 2 percent to 10 percent by weight, a greater drop in resistivity results. This is expected since the carboxylate ion is formed in the alkaline electrolyte and is more hydrophilic than hydroxyl groups. Table 4 also shows a resistivity value of 0.29 ohm-cm^2 for periodate crosslinked medium viscosity PVA compared with 0.19 ohm-cm^2 for uncrosslinked PVA. Comparison with the alginic acid crosslinker points out the effect of the carboxylic acid on resistivity. Comparison with the starch in low viscosity PVA treated with acid periodate would indicate a preference for medium viscosity PVA which contains fewer 1,2-diol units. The use of medium viscosity PVA with a dialdehyde crosslinking reagent would provide better control of crosslink density in the film.

Table 5 provides a comparison of resistivity and zincate diffusivity results for a variety of crosslinking agents.

The compositions represent approximately 10 percent of the crosslinker except for the furan-2,5-dialdehyde which is 7 percent due to its limited solubility in water. The sucrose, corn starch, and alginic acid are preceded by a (1) to indicate acid periodate crosslinking treatment. Others were catalyzed with acid only. Although Table 5 represents a diversity of crosslinkers and treatments, it does illustrate the level of resistivity and zincate ion diffusivity obtained in these laboratory prepared samples (5-mils dry film thickness). The alginic acid crosslinked film had high ion conductivity and

at the same time had low zincate diffusion which implies a degree of selectivity.

The zincate ion diffusivity of several commercial alkaline battery separator materials is shown in Table 6. For comparison, diffusivity data are shown for commercial unplasticized uncrosslinked PVA, periodate crosslinked low viscosity (LV) and medium viscosity (MV) PVA's, and pilot plant versions of 2 percent alginic acid and 2 percent dialdehyde starch (National Starch) in MVPVA. These data show that the crosslinked MVPVA and MVPVA-- dialdehyde films exhibited lower zincate diffusion characteristics than the commercial products, cellophane, sausage casing, and SAC EAHT-2016.

Testing of PVA Films in Ni/Zn and Ag/Zn Cells

The PVA films used in cell tests for performance characterization and cycle life testing were made 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 crosslinking treatment (periodate or acid) and concentration of crosslinker. Films containing 2 and 7 percent DAF, 2 and 10 percent DAS, and 2 and 10 percent sugar were evaluated in Ni/Zn cells. The results of performance characterization showed that higher concentrations of crosslinker resulted in lower ampere-hour (10-15 percent) capacity and midpoint voltages (5 to 10 percent) at the 2C and C discharge rates.

The most notable result was that the 10 percent DAS showed a 60 percent drop in capacity and a 30 percent drop in midpoint voltage compared to the other crosslinkers. At the 2 percent crosslinker concentration, the differences between crosslinking method (acid vs periodate) were small (<5 percent) for all three crosslinkers. Typical C rate (1 Hr) discharge curves for voltage or 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. Cycle life tests were terminated when the end of discharge voltage dropped below 1.0V. This was the principal mode of failure. In all tests with these membranes, the periodate treated films with 2 percent crosslinker exhibited the greater cycle life. One can conclude that the effect of the method of crosslinking is significant as well as is the concentration of crosslinker in Ni/Zn cells.

Ag/Zn Cell Tests

The Ag/Zn test cells were of nominal 8-ampere-hour capacity. They were constructed, formed, and performance characterized in the same manner as the Ni/Zn cells. The results of mid-point voltage and ampere-hour capacity comparisons were different from the Ni/Zn cells. For all PVA-dialdehyde blends tested; LVPVA-DAF, LVPVA-alginic acid, LVPVA-sucrose, the 10 percent concentrations were superior to the 2 percent concentrations of cross-linker regardless of cross-linking method in that higher mid-point voltages and ampere-hour capacity output resulted.

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. Cycle life data comparisons for 10 percent sucrose, 10 percent alginic acid, 7 percent DAF are shown in Figure 3. Figure 3 also shows results of a film made from high viscosity PVA with 7 percent DAF which was cross-linked by acid treatment. This also exhibited good cycle life presumably due to the lower, 1,2-diol content of the HVPVA.

FAILURE ANALYSIS RESULTS

Examination of the films taken from failed Ag/Zn and Ni/Zn cells produced the following results:

- (1) There appears to be no significant film degradation as a result of continuous cycling from 50 to 300 cycles.
- (2) Resistivity values showed a slight, but general decrease in Ni/Zn cells and were generally unchanged in Ag/Zn cells.
- (3) Zincate diffusivity increased by a factor of 2 to 10 in Ni/Zn cells, and remained constant or decreased slightly in Ag/Zn cells.
- (4) Zinc dendrite penetration rates showed an increase as a result of cycling in both cell types: the maximum increase was a factor of 10. _____
- (5) Ag/Zn cells failed by dendritic shorting. There was very little shape change or loss of active material from Zn electrode.
- (6) Loss of capacity led to the "failure" of the Ni/Zn cells. Very few dendritic shorts were found. Some Zn electrode shape change occurred. However, the zinc electrodes were in good condition.

CONCLUDING REMARKS

Our study of the crosslinked PVA film concept applied to alkaline batteries as separators leads to some general conclusions:

1. The quality of PVA films used as alkaline battery separators is improved by crosslinking. Incorporation of various hydrophilic functional groups within the crosslinking agent permits considerable flexibility in the design of separators for specific applications.
2. In general, the periodate crosslinking technique used on low viscosity PVA improves cell performance when compared with acid crosslinking techniques.
3. In alkaline electrolyte, ionic conductivity is improved (lower resistivity) when the crosslinking agent contains a carboxylate functional group.

4. It seems important to apply the in-situ self-crosslinking technique (periodate) to eliminate the weak structural 1,2-diol units, thereby improving cycle life.
5. The in-situ oxidation by periodate allows the use of saccharides as cross linking agents as shown by results from sucrose and alginic acid.
6. The in-situ crosslinking technique not only allows selection of the crosslinking agent, but variation in amount.
7. Based on performance characterization and cycle life tests in Ag/Zn and Ni/Zn cells, the crosslinked PVA films represent a practical, low cost potential improvement in alkaline separator technology.

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3. J. E. Cooper and A. Fleischer, eds., "Characteristics of Separators for Alkaline Silver Oxide Zinc Secondary Batteries; Screening Methods." Air Force Systems Command, Wright-Patterson AFB, OH, (1964).
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TABLE 1. - POLYVINYL ALCOHOL

PVA designated	Viscosity (cP)		Source
	4 percent aqueous		
LV	4 - 6		Polysciences, Inc.
MY	28 - 32		Polysciences, Inc.
HY	55 - 55		Polysciences, Inc.
LV	13 - 15		Du Pont-Livanol
			90 - 50
MY	28 - 32		Du Pont-Livanol
			71 - 30

TABLE 2. - ALDEHYDES USED FOR CROSSLINKING PVA

Aldehydes	Representatives
Aliphatic dialdehydes	Glutaraldehyde
Furan dialdehydes	Furan-2,5-dialdehyde
Aryl dialdehydes	P-Phthalic aldehyde
Oligoaldehydes	Sucrose (precursor)
Polyaldehyde	Polyacrolein
Polyhydroxy aldehydes	Dialdehyde starch
Polycarboxyl aldehydes	Alginate acid (precursor)
Miscellaneous	Glyoxylic acid

TABLE 3. - EFFECT OF POLYHYDROXYALDEHYDES* ON IONIC RESISTIVITY AND ZINCATE DIFFUSIVITY OF MEDIUM VISCOSITY PVA-ALDEHYDE BLEND MEMBRANE**

Weight percent of aldehyde	Areal resistivity ohm-cm^2	Zincate ion diffusivity, $\text{mole/cm}^2\text{-min}$
2	0.91	2.2×10^{-7}
4	.82	-----
6	.68	2.2×10^{-7}
8	.5	5.4×10^{-7}
16	.56	5.4×10^{-7}

*Hescl Incorporation's dialdehyde starch.

**Dry film thickness, 3 mils.

TABLE 4. EFFECT OF CROSS-LINKING AGENT AND METHOD ON RESISTIVITY OF PVA-ALDEHYDE BLEND MEMBRANES

PVA-aldehyde	Dry film thickness, mil	XL method	Areaal resistivity, ohm-cm ²
7 percent polyhydroxy-aldehydes*	1.8	acid	0.17
2 percent polyhydroxy-aldehydes*	1.8	Periodate	.88
2 percent polycarboxy-aldehydes**	1.4	Periodate	.18
10 percent polycarboxy-aldehydes**	1.3	Periodate	.076
PVA only	1.1	Periodate	.29
PVA only	1.1	None	.19

*National starch's dialdehyde starch.

**Alginate acid, Keltan.

TABLE 5. - PVA FILMS CROSSLINKED WITH VARIOUS ALDEHYDES*

Aldehyde	Areaal resistivity, ohm-cm ²	Zincate diffusivity, mole/cm ² -min ⁵
Glutaraldehyde	1.15	6.88x10 ⁻⁸
Tetraaldehyde-sugar	1.06	
(1) Sucrose	1.17	1.83x10 ⁻⁷
Dialdehyde starch (Fisher)	1.75	5.80x10 ⁻⁸
Dialdehyde starch (Hessell)	1.67	5.50x10 ⁻⁸
Dialdehyde starch (DAF)	1.85	periodate
(National starch)		
(1) Corn starch	1.05	4.64x10 ⁻⁷
(1) Alginate acid	1.67	1.30x10 ⁻⁹
Form-2,5-dialdehyde (DAF)	1.21	1.23x10 ⁻⁸
1-Phthalic aldehyde	.93	1.50x10 ⁻⁷
Polyacrolein	1.89	
Glyoxylic acid	1.71	2.3x10 ⁻⁷

*Dry film thickness = 5 mils.

TABLE 6. - COMPARISON OF ZINCATE DIFFUSIVITY IN VARIOUS MEMBRANES WITH STANDARD* SEPARATOR MATERIALS

Membrane	Crosslink method	net thickness, mil	Diffusivity, mole/cm ² -min
PURCO Cellophane*	None	1.36	3.0x10 ⁻⁶
Sausage casing*	↓	2.4	1.4x10 ⁻⁷
SAC EAH1-2016		2.5	1.3x10 ⁻⁶
PVA (Commercial - not cross-linked, non-plasticized)		1.6	4.0x10 ⁻⁸
PVA (MV)	Periodate	1.1	1.7x10 ⁻⁸
PVA (LV)	Periodate	1.6	3.5x10 ⁻⁷
**2 Percent Alginate acid in PVA (MV)	Periodate	3.5	5.2x10 ⁻⁸
**1 Percent starch in PVA (LV)	acid	1.3	1.2x10 ⁻⁷
**2 Percent starch in PVA (LV)	Periodate	1.6	2.1x10 ⁻⁷

*Standard separator materials.

**Dry film thickness = 5 mils.

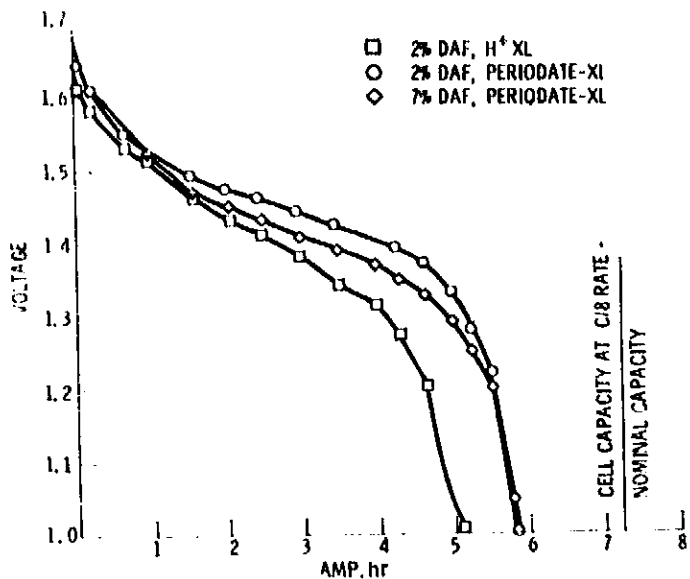


Figure 1. - Voltage versus amperes-hours - C rate discharge in 7.2 amp-hour Ni/Zn cells.

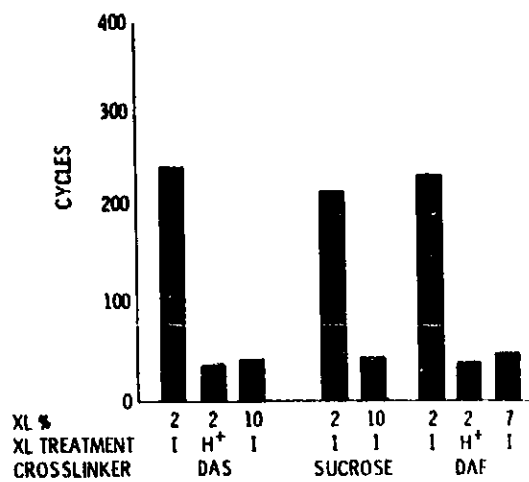


Figure 2. - Cycle life of LVPVA-dialdehyde crosslinked films in 7.2 amp-hour Ni/Zn cells - 50% DOD; 3 cycles/day.

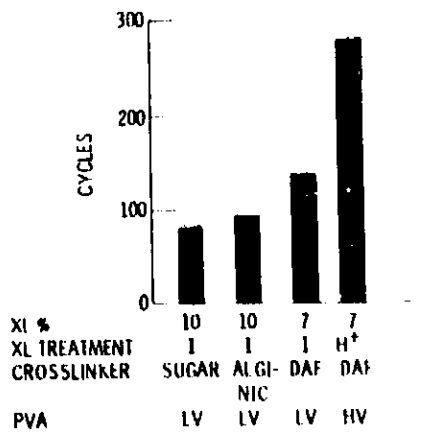


Figure 3. - Cycle life of PVA-dialdehyde cross-linked film in 8 amp-hour Ag/Zn cells - 50% DOD; 3 cycles/day.