Non-equilibrium electrolyte permeability in poly(vinyl alcohol) membranes

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Permeability of poly(vinyl alcohol) membranes was studied as a function of exposure time in 45% aqueous potassium hydroxide and quantity of residual water in film. The presence of non-equilibrium and equilibrium periods in electrolyte permeability of PVA films containing aqueous KOH solution or residual water were found and were explained from the viewpoint of change in the diffusion mechanism of permeability. The influence of cross-linking on permeability of PVA films was examined.

INTRODUCTION

Commercially available poly(vinyl alcohol) (PVA) films are used in alkaline batteries as a separator material. Separators in secondary batteries have two primary functions :(1) to keep positive and negative plates physically apart so electronic current will be constrained to flow outside the cell and (2) to allow ionic transport in the electrolyte between plates. PVA separators exhibit low electrical resistance (good ionic permeability) but poor long term stability in the electrolyte environment. Attempts to improve the chemical stability of PVA by cross-linking have led to increased brittleness and sometimes increased electrical resistance of the separator. Therefore, employing a cross-linking agent which can correct the chemical deficiencies without aggravating the mechanical and permeability properties of PVA films, will increase the cycle life of the battery.

PVA is a hydrophilic polymer and transport of electrolytes through hydrophilic films has been an extensively studied phenomenon. The theory that transport of electrolytes through the hydrophilic polymers is a process of diffusion permeability[1] has found general recognition. The process of permeability consists of three stages: sorption, diffusion and desorption. The main idea was that the electrolyte should be dissolved in the polymer in order for the process of permeability to occur. Transport of electrolytes can be described by the permeability coefficient P[2].

$$P = DK \tag{1}$$

Where: D = diffusion coefficient; K = distribution constant, which determines the concentration of electrolyte in the polymer.

Solubility of salts in hydrophilic polymers is related to presence of water in the polymer[3]. Therefore, concentration and distribution of water in polymer are very important for the permeation process[4,5]. Concentration of electrolyte in the polymer becomes equal to concentration of electrolyte in the external solution at a high concentration of water in the polymer[3]. The coefficient of electrolyte diffusion is also a function of concentration of water in the polymer. The theory of free (void) volume was the basis for deducing the following formula,[3,6] which correlates the coefficients of electrolyte diffusion in water (D_0) and in the polymer (D).

$$\log D = \log D_0 - K\left(\frac{1}{H} - 1\right) \tag{2}$$

Where K = constant which does not depend on the nature of the polymer; H = concentration of water in the polymer (v.p.).

According to equation (2) the diffusion coefficient should steadily increase with an increase in the quantity of water in the polymer film.

A study of the relationship between permeability of aqueous 45% potassium hydroxide solution and quantity of residual water in PVA film was undertaken in this work. Knowledge of such dependence is necessary for development of the separator material with the required properties.

EXPERIMENTAL PROCEDURE

Poly(vinyl alcohol) polymer with 99–100% hydrolysis was used in the powder form and dissolved in water or in a mixture of water and methanol (75:25 v.p.). Initial concentration of the solution was 10–11% by weight of PVA. The reagents were pure and not subjected to additional cleaning. Films with thicknesses of 1.5–2.5 mils* were formed by a doctor blade on a metal sheet in a drying oven. The temperature of formation in every experiment was constant to ±1°C. The time of film formation varied for each constant temperature. Concentration of the residual solvent was calculated by the equation:

$$C = \frac{P_w - P_d}{P_w} \cdot 100\% \tag{3}$$

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* 1 mil = 25 μm

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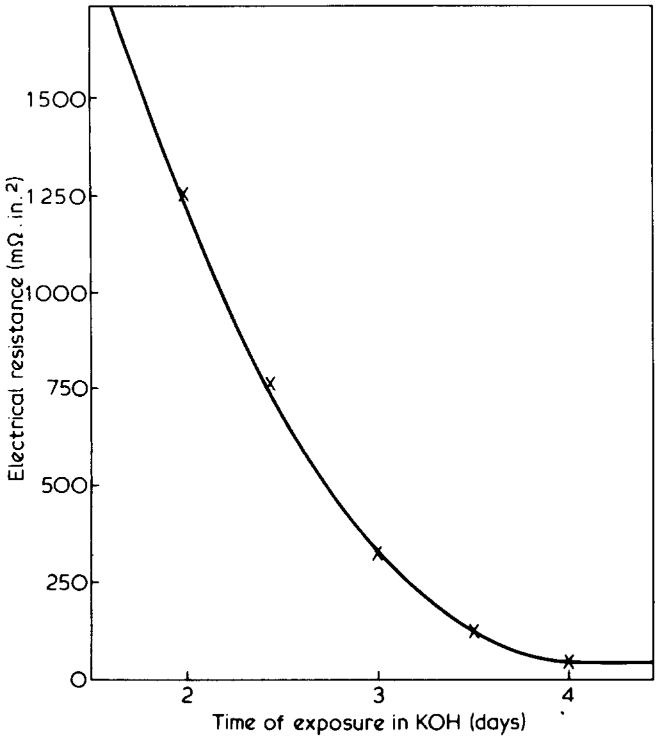

Figure 1 Dependence of electrical resistance on time of exposure in KOH for commercial PVA film

Where: C = concentration of residual solvent in film; P_w = wet weight of the film; P_d = dry weight of the film after drying to constant weight.

The specimens were weighed on an analytical balance. PVA was cross-linked by dimethylolurea (DMU). PVA films with 10 wt% DMU were produced at room temperature and after that were heat treated in a nitrogen atmosphere for 1.5 h at different temperatures to complete the cross-linking reaction.

Electrical resistance measurement

These measurements are carried out by measuring the voltage drop with d.c. current between two reference electrodes with and without the material in 45% KOH solution. The area of the sample being measured is usually 0.78 in.^{2}. Electrical resistance measurements are carried out over a period of six months, after initial values are obtained after 24 h.

Procedure

Separator samples are cut to $1\frac{1}{4}$ inch × $1\frac{1}{4}$ inch and soaked for 24 h in potassium hydroxide of the concentration to be used. The membrane is then placed in the resistivity cell so that it is approximately centred on the cross tube. The cell is closed and the wing nuts tightened with firm finger pressure. Electrolyte of the concentration to be used is then allowed to flow through the cell, through the pores, and fill the wells containing the reference electrodes up through the capillary tubes. A pinch clamp is used to close one of the filling tubes to prevent conduction around the cell. Care is taken to exclude air bubbles from the cross tube and the capillaries.

A current of 20 mA is passed through the cell between the working cadmium electrodes and the potential drop is determined using the potentiometer. Duplicate readings on the same sample may be obtained using the same procedure after draining the electrolyte from the cell and shifting the position of the membrane.

Before and after measuring the separator resistance, a run is made without the membrane. The membrane resistance (R'') is then calculated using equation (4).

$$R'' = \frac{E' - E}{I} A \tag{4}$$

Where: E' = voltage drop with membrane in place; E = voltage drop for the cell blank; I = current in amperes; A = area of the cross tube (in.^{2}).

The time necessary for soaking a membrane can be determined by starting with a dry membrane, filling the cell, and measuring resistance with time until a constant value is obtained.

RESULTS AND DISCUSSION

Variation in the electrical resistance (permeability) of PVA films as a function of exposure time in aqueous electrolyte was studied. Experimental data show a sharp decrease of electrical resistance during the first three to four days. A further four to five months in KOH does not essentially change the electrical resistance of PVA (see *Figure 1*). The results obtained indicate that electrolyte which had been absorbed for three to four days created conditions in PVA for equilibrium permeability. Several experiments were performed to verify this concept. PVA films were formed from aqueous solution under different conditions. Variation of the temperature or time of film drying results in a different quantity of residual solvent (water) which remains in the film after completing the formation process. The presence of a definite amount of water in the film creates certain conditions for electrolyte permeability. Therefore it was reasonable to assume that electrical resistance of PVA is a function of water content of the film. Experimental data (see *Table 1*) indicate that electrical resistance of PVA really depends on the quantity of water in the film. Electrical resistance was measured on the films not exposed to KOH solution before the test. The amount of water remaining in the film was related to the production process. An increase in quantity of water resulted in a sharp decrease in electrical resistance. This dependence is valid up to ≈6% of residual solvent. A further increase in water content of the film does not influence the electrical resistance (permeability) which reaches an equilibrium value for this film.

After these experiments, a combined influence of residual water and water absorbed during exposure of the films in KOH was studied. Dry film (with ~1 to 1.5% residual water) and wet film (with more than 6% residual

Table 1 Concentration of residual solvent and electrical resistance of PVA films

No.	Conditions of drying		Resistance mΩ in.^{2}	Residual solvent, %
	Temperature, °C	Time, min.		
1	70	180	too high	2.7
2	70	166	too high	3.1
3	70	130	1000	3.5
4	70	110	315	4.1
5	70	80	40	6.65
6	70	75	45	8.6
7	70	60	43	8.9

Table 2 Variation in electrical resistance of PVC films containing different initial quantity of residual solvent

No.	Conditions of drying		Dry thickness, mil	Resistance, mΩ in.^{2}	Time in KOH 23°C, days	Initial concentration of residual solvent, %
	Temperature, °C	Time, min.				
1	70	130	1.8	high 45 43	1 4 10	2.7
2	70	166	2.0	high 47 45	1 4 10	3.1
3	70	110	1.8	315 45 45	1 4 10	4.1
4	70	80	2.1	40 40 40	1 4 10	6.65
5	70	75	2.0	45 44 42	1 4 10	8.6
6	70	60	1.9	43 42 42	1 4 10	8.9

water) were tested for 10 days in KOH (see *Table 2*). Variation in the value of electrical resistance during the first ten days of ageing in KOH for the dry film has the same character as shown in *Figure 1*. Electrical resistance of wet film (>6% water) does not change during this period.

According to the data obtained, electrical resistance of PVA is a function of water content in the film and it is not affected by how this water gets into the film. The presence of non-equilibrium and equilibrium periods in electrolyte permeability of PVA films immersed in aqueous KOH solution is determined and attempts will be made to explain this phenomenon.

The permeability mechanism of aqueous electrolytes through the PVA membrane has solvent–polymer character. Therefore an analogy can be drawn with the process of solvent desorption which occurs during formation of the plastic films from solution. There are two periods of diffusion transfer in the process of film formation.

(1) Solvent bonded with the polymer takes part in the diffusion process. Transport of the solvent is realized by formation and breakdown of intermolecular bonds between the polymer and solvent. Activation energy of diffusion depends on solvent content of the polymer. While increasing the amount of solvent in the polymer (decreasing the effective activation energy of diffusion), the intermolecular interaction in the polymer weakens and the rate of diffusion increases. This process continues until the concentration of the solvent reaches the level where the intermolecular interaction is neutralized.

(2) Self-diffusion of the solvent which is not attached to the polymer occurs. The process of diffusion transport changes from diffusion of molecules bonded with a polymer to self-diffusion in the region of concentrations where intermolecular interaction in the polymer is localized by solvent molecules. Self-diffusion has low activation energy which does not depend essentially on the concentration of the solvent in the polymer.

Application of the diffusion mechanism described above to the permeability of aqueous electrolyte through the PVA membranes can explain the existence of non-equilibrium and equilibrium permeability and the relationship of the permeability rate to the amount of water in the film.

By analogy it is possible to assume that non-equilibrium permeability is controlled by diffusion of water bonded with the PVA. Therefore non-equilibrium permeability can be realized when the quantity of water is small and the activation energy of diffusion depends on PVA water content. Increase in water content results in decrease of the effective activation energy of diffusion and a substantial increase of permeability up to a certain level. This process continues until the local concentration of water reaches the level where the intermolecular interaction is substantially neutralized in certain amorphous regions and non-equilibrium permeability transforms into equilibrium permeability. The rates of diffusion and permeability are not dependent on the amount of absorbed or residual water if this quantity is higher than the quantity necessary to reach the equilibrium permeability (self-diffusion) level. Equilibrium permeability can be described by Fick's laws.

According to previous experimental data[7], approximately 20% of the solvent is required to change the mechanism of diffusion transport from activated diffusion of solvent bonded to the polymer to self-diffusion of the solvent. The amount of water which should be obtained in the polymer to achieve this self-diffusion level differs for the process of film formation and for electrolyte diffusion. Such a difference is related to the fact that aqueous electrolyte is not a solvent for PVA and, therefore, the diffusion process occurs through the channels in amorphous regions where the local concentration of water is higher than in the bulk film.

Applicability of the ideas concerning the mechanisms of film formation to a wide range of polymer–solvent systems[7] allows the supposition that permeability of any polymer membrane for any solution can be increased if the polymer membrane contains a certain quantity of solvent which is employed in solution.

Utilizing the data obtained regarding the influence of water in PVA film on ionic resistivity, it is thus possible to

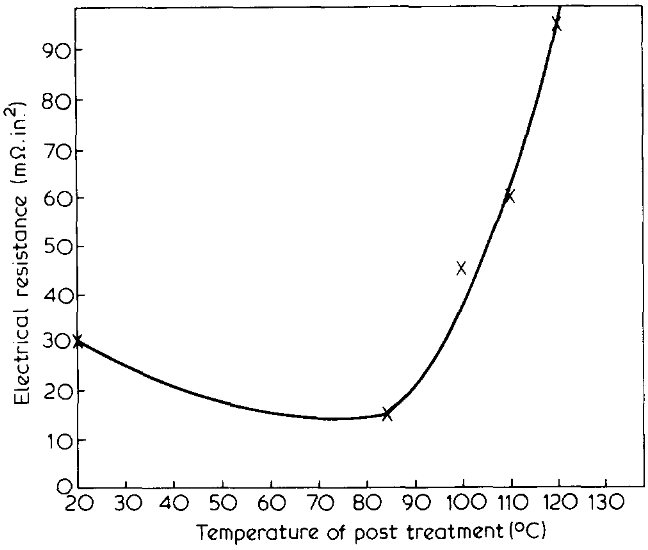

Figure 2 Dependence of electrical resistance on temperature of post treatment for PVA + 10% DMU film

formulate a relationship of the ionic resistivity to degree of cross-linking in PVA. The proposed idea is based on dependence of crystallinity and equilibrium level of water which can be kept in PVA on the degree of cross-linking. A slight increase of the cross-linking leads to a decrease in the degree of crystallinity but does not reduce the equilibrium quantity of water in film below the level of 6%. Therefore small degrees of cross-linking should result in a decrease of the ionic resistivity. Further increase in the degree of cross-linking reduces the equilibrium quantity of water in the film below 6%; this should result in an increase in the ionic resistivity of cross-linked PVA material. To conform to this viewpoint, the dependence of ionic resistivity on degree of cross-linking should have a minimum (see *Figure 2*).

However achievement of the minimum value of ionic resistivity is not the main goal of cross-linking of the PVA films for battery separators. From the viewpoint of increasing chemical stability, the degree of cross-linking should be increased to its maximum. Therefore consideration of all described requirements leads to the necessity of selecting the optimum degree of cross-linking; this allows production of PVA films with low ionic resistivity and high chemical stability.

These concepts were experimentally examined on PVA film cross-linked by dimethylolurea. Electrical resistance of the films with 10 wt% DMU and heat treatment at various temperatures was measured.

Data obtained indicates that the dependence of electrical resistance on the temperature of post-treatment has a minimum as shown in *Figure 2*.

It is possible to assume that degree of cross-linking is proportional to temperature of post-treatment according to the equation which is similar to the Arrhenius equation[8].

These results confirm that the theory regarding the influence of cross-linking on electrical resistance of PVA films discussed above was correct and can be a guide in selection of production technology for cross-linked PVA separator films.

CONCLUSIONS

Permeability of PVA films immersed in aqueous solutions of potassium hydroxide increase sharply during the first three to four days. Further immersion for four to five months in KOH does not essentially change the permeability properties of PVA films.

Permeability of PVA films containing more than 6 wt% residual water does not change during exposure in 45% KOH.

Presence of non-equilibrium and equilibrium periods in electrolyte permeability of PVA films containing aqueous KOH solution or residual water was explained from the viewpoint of changing the diffusion mechanism of permeability.

Diffusion of the electrolyte through the relatively dry polymer is realized by formation and breaking down of intermolecular bonds between the polymer and solvent. Activation energy of diffusion depends on quantity of residual or absorbed solvent in the film. Change in quantity of solvent in the film results in variation of permeability properties and causes a non-equilibrium period of permeability.

Diffusion of the electrolyte through the wet polymer is realized by the mechanism of solvent self-diffusion. Activation energy of self-diffusion is low and does not depend on quantity of solvent in the film. Therefore permeability through wet polymer has an equilibrium character.

Only 6% of the average weight concentration of water is enough to create conditions for equilibrium electrolyte permeability through PVA membranes.

Influence of cross-linking on electrical resistance (permeability) of PVA was examined based on the ideas discussed above and experimental confirmation of the ideas was obtained.

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