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Diffusion Measurements on a New Battery Separator Membrane (Polyphenylquinoxaline-Cellulose Acetate)

A Comparison with Standard Separator Materials

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INTRODUCTION

The function of a separator in a battery is to prevent mass mixing of the anolyte and catholyte and to prevent direct contact (shorting) of the electrodes. An efficient separator should allow the passage of conducting ions to insure a low specific resistance and should also exhibit thermal and oxidative stability in the battery environment. One of the problems associated with conventional alkaline batteries is that standard separator materials, such as cellophane, undergoes oxidative degradation during long-term storage and operation.[1]

Polymeric membranes are currently being developed that have excellent high temperature stability to oxidation and have shown promise for use as separator materials in alkaline zinc batteries.[2] This note reports on the most promising membrane material, a mixture of 60% polyphenylquinoxaline (PPQ) and 40% cellulose acetate (CA).

The rate of diffusion of zincate ion through the separator is of paramount importance. This zincate flux is thought to be an integral part of the mechanism of zinc dendrite growth,[3] which is often attributed to be a cause of cell shorting.

The diffusive characteristics of a PPQ-CA membrane have been compared with standard separator materials.

EXPERIMENTAL

Preparation of the PPQ polymer[4] and the procedure for casting the membrane films[5] have been reported. The PPQ-CA membrane was prepared by adding CA (40% acetyl content) to a 10% PPQ solution in *m*-cresol. Add 100 ml of chloroform until a 60% PPQ: 40% CA homogeneous solution forms. Cast a film and allow the solvent to evaporate slowly for 2 to 3 minutes. Immerse in a 1 : 1 methanol-water solution for ten minutes, remove, wash with water and air dry.

Diffusion of OH^- ions through the membranes were studied by following pH changes across the separator by the method of Harris.[6]

Zincate diffusion was studied by differential pulse polarography (DPP) using a PAR 174A instrument and a modified diffusion cell described by Harris.[6] The zinc-rich compartment contained 250 ml of 1 M ZnO in 42% KOH and the zinc-poor side contained 250 ml of 42% KOH. At intervals, the zincate-deficient solution was stirred and a 2 ml aliquot was removed and placed in a polarographic cell containing 25 ml of distilled water. The cell employed a working dropping mercury electrode, a platinum wire counter electrode and a Hg/HgO reference electrode. After purging with water saturated argon, the DPP curves were recorded and the peak heights were compared to a DPP calibration curve. Approximately 2 ml of the zincate-rich solution was simultaneously removed to prevent osmotic pressure errors.

DISCUSSION OF RESULTS

The rates of diffusion of zincate across several membranes are illustrated in Figure 1. All measurements were made on a single piece of film cut into sections. The standard deviation of the PPQ-CA membrane was comparable to those of the standard materials. This indicates, that for a given film, the casting, gelation and drying technique produced a homogeneous membrane. The standard deviation increases to approximately 0.3, if PPQ-CA films from different castings are compared with one another, which verifys the homogeneity of the membrane.

In order to compare the membranes on an equivalent basis, it was necessary to normalize each membrane to a constant thickness of one mil. The zincate flux values, reported as moles zincate/min. in^2 for a 1.0 mil. wet thickness, are tabulated in Table I.

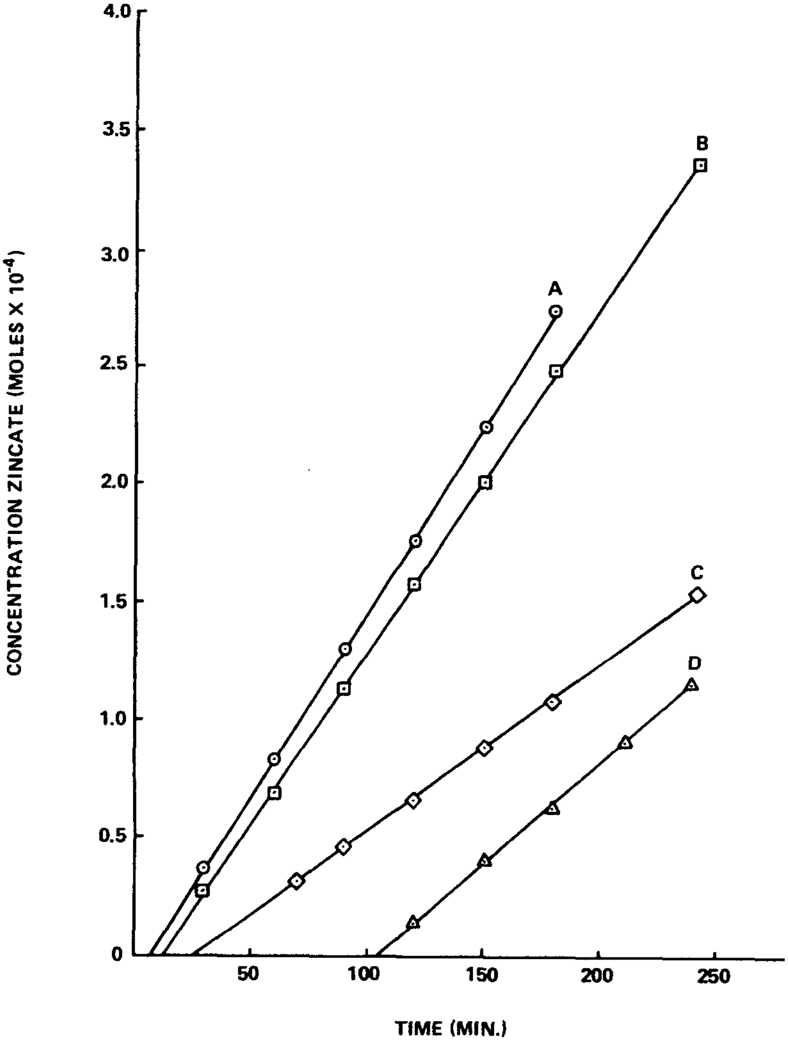

FIGURE 1 Comparison of the rates of zincate diffusion through various membrane materials. Curve A—cellophane; Curve B—silver cellophane; Curve C—Sausage Casing; Curve D—60% PPQ-40% CA.

Figure 1 illustrates the relative rates of "wetting," that is, the time for diffusion to be appreciable. The cellophane materials and the sausage casing are hydrophilic and have the ability to absorb KOH electrolyte which allows diffusion to occur somewhat faster. The slower wetting time of the PPQ-CA is the result of the nonpolar and hydrophobic nature of the PPQ polymer. It is the CA portion that provides the wettability.

TABLE I

Comparison of zincate diffusion in PPQ-CA membranes with standard separator materials for a 42% KOH solution

Membrane material	Wet thickness (mil)	Average Zincate flux (moles/min in^2)	Standard deviation	Zincate diffusion coefficient (cm^2/sec)
pudo cellophane	3.36	6.7×10^{-6}	0.34	1.9×10^{-7}
sausage casing	7.24	6.6×10^{-6}	0.15	4.0×10^{-7}
silver cellophane	3.06	5.7×10^{-6}	0.50	1.5×10^{-7}
60% PPQ–40% CA	0.88	8.8×10^{-7}	0.21	6.5×10^{-9}

Despite the somewhat slower rates of electrolyte absorption, the PPQ-CA membrane offers the advantage of slower diffusion of zincate. This may reduce the mechanism of cell failure by electrical short-circuiting, generally initiated by a supply of zincate feeding the growth of conducting metallic zinc dendrites. Table I shows the PPQ-CA has almost an order of magnitude slower zincate flux than the standard separator materials.

In order to determine if there was also an appreciable decrease in the permeation of the KOH electrolyte in the PPQ-CA separator, the diffusion of KOH through a PPQ-CA membrane was compared with that of cellophane. The flux for the cellophane membrane, normalized to 1 mil. thickness was 2.9×10^{-3} moles OH$^-$/min. in^2 whereas the PPQ-CA membrane was found to have a value of 3.4×10^{-4} moles OH$^-$/min. in.^{2} The upper current density of the PPQ-CA separator can be calculated from Faradays Law to be 0.55 amp/in.^{2}

The diffusion coefficient for the zincate ion at 24°C has been reported to be 9.9×10^{-7} cm^2/sec in 45% KOH.[7] The diffusion coefficients for the zincate ion in the various membranes have been calculated and are listed in Table I. Comparison of the diffusion coefficients indicates that the PPQ-CA membrane has either a greater tortuosity or a smaller selective pore size than the standard separator materials. Studies on this membane are in progress.

Acknowledgment

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