

Permselective membrane separators for organic electrolyte batteries

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The electrical resistances, transference numbers and $\text{Li}^+ \leftrightarrow \text{Cu}^{++}$ and $\text{Br}^- \leftrightarrow \text{ClO}_4^-$ interdiffusion rates through a variety of cation-exchange and neutral membranes were measured in propylene carbonate (PC) solutions at 25°C. Of the 19 commercial and specially prepared membranes which were studied, the only membranes with electrical resistances in 0.50 M LiClO_4/PC low enough to be of further interest as separators for organic electrolyte batteries were the AMF C-322, Amicon UM-05, Ionac MC-3470 and Corning No. 7930 porous glass (0.25 mm thick). The resistances of these membranes were 117, 2.3×10^2 , 3.4×10^2 and $75.0 \Omega \text{ cm}^2$, respectively.

In order to benefit from the reduced resistance of thin membranes without sacrificing mechanical strength, laminated phenolsulfonic acid-formaldehyde (PF) membranes consisting of a thin layer of cation exchange resin on an inert porous support were prepared. Interdiffusion measurements showed that the laminated PF membranes are a more effective diffusion barrier towards anions in PC solutions than a commercial ultrafiltration membrane, the Amicon UM-05. The anion interdiffusion fluxes for Br^- between 0.10 M LiBr/PC and 0.10 M LiClO_4/PC through the PF and UM-05 membranes were 6.17×10^{-11} and 1.5×10^{-10} mole $\text{s}^{-1} \text{ cm}^2$, respectively.

1. Introduction

Considerable efforts have been made during the last decade to develop a practical non-aqueous high energy density battery utilizing a lithium anode and a copper halide cathode [1, 2]. Although high energy densities have been achieved with CuF_2 and CuCl_2 cathodes, rapid self-discharge and copper dendrite formation on the lithium anode due to the reduction of soluble copper species remain as serious difficulties even after the completion of several studies directed towards the solution of these problems [1, 2, 3]. Self-discharge on open circuit occurs because both CuF_2 and CuCl_2 are slightly soluble in propylene carbonate (PC), and various ionic species of copper migrate from the copper halide cathode to the lithium anode where they are immediately reduced to copper metal. This investigation is concerned with permselective membranes which in principle can greatly reduce

the rate of self-discharge by retarding the diffusion of ionic species which harm the lithium anode while allowing sufficient Li^+ to pass to keep ohmic losses to a minimum. To evaluate the effectiveness of a variety of commercial and specially prepared membranes for this application, measurements were made of the electrical resistance, interdiffusion flux and transference numbers in anhydrous PC solutions. Although attention is focused on copper halide-propylene carbonate systems, it is apparent that the membrane phenomena observed are of general relevance to other organic electrolyte cells where self-discharge results from soluble cathode reactants.

The exact selective properties required for organic electrolyte battery membranes are not well-understood because the mechanism of self-discharge and the constitution of the ionic species in the electrolyte are unknown. For the $\text{Li}-\text{CuCl}_2/\text{PC}$ cell, it has been postulated [3, 4]

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that the copper species causing self-discharge are the chlorocuprate complexes CuCl_3^- and CuCl_2^- and to a much lesser extent Cu^{++} and Cu^+ . Solubilities of 4.9×10^{-3} , 2×10^{-4} and 4.6×10^{-3} mole l^{-1} have been reported [5, 6] for CuCl_2 , CuF_2 and CuCl respectively in PC at 25°C.

Due to uncertainties concerning the self-discharge mechanism in copper halide/PC batteries, it was necessary in the present work to make the assumption that the undesirable copper species are primarily anionic. Consequently, either cation-exchange membranes which should exclude anions and permit only cations to pass or, in a few cases, neutral membranes were selected for investigation. The more difficult problem of finding a membrane which can exclude Cu^+ and Cu^{++} yet allow a high Li^+ flux was set aside although some information relevant to this problem was obtained from the cation interdiffusion measurements.

Propylene carbonate solutions have much lower electrical conductances (e.g., $\kappa = 7.3 \times 10^{-3} \Omega^{-1} \text{cm}^{-1}$ for 1 M LiClO_4 at 25°C [7]) than aqueous solutions, consequently many commercial membranes optimized for use in aqueous systems have too excessive ohmic losses to be practical non-aqueous battery separators. In order to keep ohmic losses to a minimum, it has been estimated that a suitable battery membrane should have a resistance of less than $100 \Omega \text{cm}^2$ in 0.5 M LiClO_4/PC . The electrical resistance of a membrane which does not meet this criterion could be decreased either by making the membrane thinner or by increasing the degree of swelling. However, many of the factors which would decrease the resistance, such as increasing the radii of the 'micropores', would also reduce the permselectivity. Since there is an optimum balance between electrical resistance and permselectivity, electrical resistance results cannot be meaningfully evaluated unless information is available concerning the effectiveness of the membrane as a diffusion barrier. It was for this reason that interdiffusion and transference number experiments were undertaken in addition to the electrical resistance measurements.

Calculations, which will be presented later, have shown that a considerable decrease in membrane resistance is possible through reductions in membrane thickness before a membrane

resistance comparable to that of the diffusion layer is reached. Because of these considerations it was decided to concentrate our first efforts on laminated (sandwich-type) membranes consisting of a thin cation-exchange membrane on an inert porous support. Such membranes would combine the desirable properties of low resistance, selectivity and mechanical strength. Polymers of phenolsulfonic acid-formaldehyde were selected to prepare membranes for the present investigation because they are insoluble in PC and their degree of crosslinking and porosity can be easily adjusted [8, 9, 10].

2. Experimental

2.1. Materials

Propylene carbonate (Jefferson Chemical Company, Houston, Texas) was distilled with a Podbielniak* Semi-Cal (Series 3650) adiabatic vacuum fractional distillation apparatus after first being dried with molecular sieve pellets '5A' (Linde Division, Union Carbide Corp.). The distillation column (30 mm \times 122 cm) was filled with 'Heli-pak'* (nichrome) and the receiver system, in order to avoid contamination with stopcock grease, was designed with glass drip tops and Teflon needle valve stopcocks. To avoid decomposition the distillation was carried out under vacuum (1.0 ± 0.2 Torr) maintaining a column head temperature between 67 and 70°C. The reflux ratio was 80:1 and the first 10% and last 20% of the solvent were discarded. Gas chromatographic analysis [11, 12, 13] of the distilled PC showed a water content of approximately 6 p.p.m. and a propylene oxide concentration of 7 p.p.m. or less.

Reagent grade LiClO_4 , LiBr and $\text{Cu}(\text{ClO}_4)_2$ were vacuum dried ($< 30 \mu\text{m}$) at 150, 345 and 185°C, respectively [12, 13].

2.2. Membranes

Compatibility tests in propylene carbonate were completed for most of the membranes listed in Table 1 before characterization to determine if the membranes were sufficiently insoluble in PC

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to merit further investigation. Experimental procedures, results of the compatibility tests and suppliers of the membranes have been reported previously [13, 14]. The monomer solution used to make the phenolsulfonic acid-formaldehyde laminated membranes was prepared by mixing 50 parts by volume of a 65% solution of *p*-hydroxybenzene sulfonic acid (practical grade, J. T. Baker Chemical Co.) with 25 parts of an aqueous 35.4% formaldehyde solution (U.S.P.). After thorough mixing, the monomer solution was prepared in a sealed test tube in a constant temperature water bath ($\pm 0.05^\circ\text{C}$) at $45\text{--}70^\circ\text{C}$ for 120 min [14]. The viscous pre-cured solution was brushed onto a Gelman polypropylene filter* and the filter was clamped in place in a mounting assembly and cured for approximately 1 h at 100°C in a humidistat. Membranes in the series PF-1 to PF-6 were prepared with a humidistat water partial pressure of approximately 760 Torr whereas for the series PF-7 to PF-13, the humidistat was in equilibrium with a 5 M CaCl_2 solution with a water partial pressure of about 440 Torr.

2.3. Conductivity measurements

A cell suitable for the measurement of the electrical conductance of membranes in propylene carbonate must have a small volume in order not to use excessive amounts of the highly purified solvent, yet be sturdy enough to withstand the pressure required to properly seal the membranes. The cell used to measure the conductance of the membranes listed in Table 1 is shown in Fig. 1. A thick walled Pyrex cap 1 in. diameter, conical pipe, code 726253; Corning Glass Works) with a grooved glass flange was utilized as the electrode compartment. Each bright platinum electrode $\frac{3}{4}$ in diameter \times 0.003 in) was spot-welded to a platinum wire which was in turn spot-welded to a centerless ground tungsten wire (0.030 in). The membrane and a silicone rubber O-ring ($1\frac{1}{4}$ in i.d.) were held in place between the two halves of the cell with a cast-iron clamp fitted with neoprene sleeves. Solubility tests which were carried out for six types of rubber O-rings in PC [13] showed that silicone rubber and fluorosilicone rubber O-rings (R. W. Scott, Berkeley, California)

* 47 mm diameter, 10 μm mean pore size, 200 μm thick; Gelman Instrument Co., Ann Arbor, Michigan.

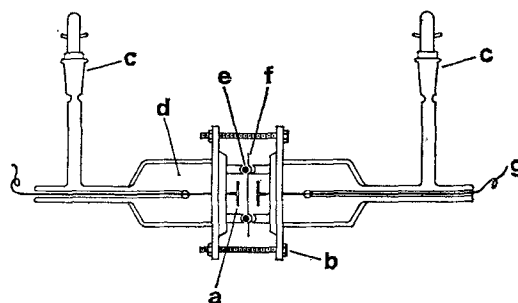


Fig. 1. Membrane conductance cell. a, platinum electrode; b, cast iron clamp; c, filling tube with 7/25 standard taper joint and cap; d, Pyrex glass to tungsten seal; e, $1\frac{1}{4}$ -inch silicone rubber O-ring; f, membrane; g, electrical leads to electrode.

were the most insoluble and resistant to swelling of the materials tested. When the conductance cell was assembled, the electrodes were spaced about 6 mm on either side of the membrane.

The membranes were successively transferred in a series of four 0.50 M LiClO_4/PC solutions, remaining in each solution at least 8 h prior to conductance measurements. This pretreatment procedure [13] was carried out in order to allow the membranes sufficient time to lose absorbed water and to achieve equilibrium with the solution.

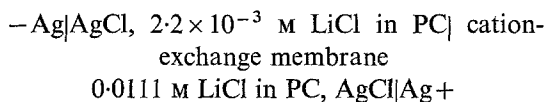
Although all the non-aqueous solutions used for the experiments described in this paper were prepared and stored in a dry box, the cells were assembled and filled outside the dry box. After filling and during the measurements the cells were either promptly stoppered or connected to drying tubes filled with anhydrous $\text{Mg}(\text{ClO}_4)_2$.

The electrical resistances at $25^\circ\text{C} \pm 1^\circ\text{C}$ of the majority of the membranes listed in Table 1 were measured with a Beckman (Model RC-16B2) a.c. bridge at 1000 Hz. The resistances of the other membranes were either measured with an electrometer (Model 601, Keithley Instrument Co., Cleveland, Ohio) for membranes with a resistance $> 5 \cdot 10^6 \Omega \text{ cm}^2$, or with an impedance comparator (Model 1654, General Radio Co., Concord, Mass.) at 1000 Hz for membranes with resistances $< 200 \Omega \text{ cm}^2$.

2.4. Transference number measurements

An attempt was made to measure the transference numbers of Li^+ and Cl^- through a

cation-exchange membrane (Ionac MC-3470-25-50) using a cell of the following composition:



where the concentrations given are those at the start of the experiment. To prepare the 0.0111 M LiCl/PC solution used in the transference experiment it was found [13] that it was necessary to add 1400 p.p.m. water to increase the solubility of LiCl in PC. Although a transference number of 0.64 ± 0.04 was obtained for Cl^- , the effect of the 1400 p.p.m. water is not well understood and it was decided to carry out measurements of the diffusion rates which would be less difficult experimentally and easier to interpret.

2.5. Diffusion measurements

The cell used for the interdiffusion measurements consisted of two 90° elbows (2.54 cm i.d. with grooved flanges) of thick walled Pyrex conical pipe between which were clamped the membrane and a silicone rubber O-ring. The membranes were pre-treated prior to the measurements using the same procedure described for the conductivity measurements but distilled PC was used instead of LiClO_4/PC . For measurements of the interdiffusion of anions through membranes in PC, one compartment of the cell was filled with 0.10 M LiBr/PC and the other compartment was filled with 0.10 M LiClO_4/PC whereas for the cation interdiffusion measurements, the respective compartments were filled with 0.10 M $\text{Cu}(\text{ClO}_4)_2/\text{PC}$ and 0.10 M LiClO_4/PC .

To begin an interdiffusion experiment the two compartments were filled simultaneously with 50.0 ml of the particular PC solutions required using two pipettes. Interdiffusion was allowed to take place between the two solutions at $25^\circ\text{C} \pm 1^\circ\text{C}$ for from 24 to 72 hours, during which time both compartments were stirred (approx. 160 rev/min). Both compartments of the cell were simultaneously emptied for analysis at the end of an experiment in order to prevent any pressure induced leakage between the compartments.

For an anion interdiffusion experiment the contents of each compartment were analyzed for bromine (to within $\pm 0.4\%$) by coulometric

titration with Ag^+ and amperometric indication of end point [14].

The contents of each of the compartments from a cation interdiffusion experiment were analysed for both Li^+ and Cu^{++} after vacuum distillation to remove the propylene carbonate. Copper was determined spectrophotometrically with dithiazone [14] to within 2% and lithium with Thoron [*o*-(2-hydroxy-3,6-disulfo-1-naphthalazo)-benzenearsonic acid] at $485\text{m}\mu$ [14, 15].

Salt diffusion measurements [14] were carried out using the same cell used for the interdiffusion experiments with the compartments filled with purified PC and 0.10 M $\text{Cu}(\text{ClO}_4)_2/\text{PC}$. The solutions used in the salt diffusion experiments for the Amicon UM-05 and the PF-2 membranes were unstirred in order to duplicate the natural convection of batteries.

Table 1. Electrical resistances of membranes in 0.50 M LiClO_4 Propylene carbonate solutions at 25°C

Membrane	Resistance* of unit area $R, \Omega \text{ cm}^2$	Thickness (mm)
PF-2	4.3×10^2	0.17
PF-9	2.64×10^3	0.25
PF-12	1.07×10^3	0.25
PF-13	4.1×10^2	0.27
AMF C-60	4.0×10^6	0.3
AMF C-103	5.6×10^7	0.22
AMF No. 11567	3.2×10^4	0.050
AMF C-322	117	0.225
7930 porous glass (Corning)	259.3	1.0
7930 porous glass (Corning)	75.0	0.25
Ionac MC-3470-25-50	3.4×10^2	0.4
Amicon UM-05	2.3×10^2	0.2
Asahi CK-1	1.2×10^5	0.23
Cation-exchange (Negev Inst.)	5.75×10^8	0.279
MEM-213 silicone-polycarbonate copolymer (General Electric)	1.04×10^5	0.025
Unbacked dimethyl silicone (General Electric)	3.6×10^7	0.025
Dimethyl silicone backed on one side with 5-mil polyester (General Electric)	1.26×10^5	0.15
SWRI 3-3566 (JPL)†	6.9×10^4	0.075
119GX (JPL)†	8.9×10^4	0.075

* The resistance of 0.3 mm of 0.50 M LiClO_4/PC is $5.4 \Omega \text{ cm}^2$ for comparison.

† Polyethylene backbone, radiation grafted with acrylic acid.

Table 2. Interdiffusion fluxes through membranes in propylene carbonate at 25°C

System	Membrane*	Experimental time (h)	Flux mole s ⁻¹ cm ⁻²
0.10 M LiClO ₄ /PC	Amicon*	72.00	Li ⁺ 3.45 × 10 ⁻¹⁰
0.10 M Cu(ClO ₄) ₂ /PC	UM-05		Cu ⁺⁺ 1.35 × 10 ⁻¹⁰
0.10 M LiBr/PC	Amicon	24.00	Br ⁻ 1.5 × 10 ⁻¹⁰
0.10 M LiClO ₄ /PC	UM-05		
0.10 M LiBr/PC	PF-13	24.00	Br ⁻ 6.2 × 10 ⁻¹¹
0.10 M LiClO ₄ /PC			

* The Amicon UM-05 membrane is a weakly cationic commercial hyperfiltration membrane.

3. Results

The electrical resistance values measured for 19 membranes in 0.500 M LiClO₄/PC at 25°C are listed in Table 1. The resistance values (\bar{R}) given in Table 1 were calculated using the relation:

$$\bar{R} = (R_t - R_0)A \quad (1)$$

where R_t is the resistance of the cell with the membrane (ohms), R_0 the resistance of the cell with only the electrolyte present (i.e. 51 Ω with 0.500 M LiClO₄/PC for a 12 mm electrode separation) and A the area of the membrane (i.e. 7.16 cm²).

The fluxes for cation and anion interdiffusion through the UM-05 and PF-13 membranes at 25°C in propylene carbonate are given in Table 2. The interdiffusion fluxes were calculated by simply dividing the total moles of ion diffused by both the experimental time in seconds and the area of the membrane (7.15 cm²). This simplifica-

tion is possible because the amount transported is small compared to the amount present on the high concentration side.

Table 3 lists the diffusion fluxes and coefficients obtained from the salt diffusion measurements with Cu(ClO₄)₂. The diffusion coefficients, D in Table 3, refer to solution concentrations. In other words, they were calculated on the assumption that Fick's first law of diffusion is valid in this case [8].

4. Discussion

The high electrical resistance of membranes in aprotic non-aqueous solvents is a significant factor which limits the practical application of many membranes. However, it is evident from Table 1 that some of the membranes tested have sufficiently low electrical resistances in 0.50 M LiClO₄/PC to merit consideration as organic electrolyte battery separators. Two of the membranes, the AMF C-322 and the Corning No. 7930 porous glass (0.25 mm thick), either meet or come reasonably close to meeting the requirement of a resistance ≤ 100 Ω cm² for a practical separator. All the polyethylene base membranes which have been tested, including the AMF C-60, C-103 and No. 11567, have a high electrical resistance, possibly as a direct result of the failure of these membranes to swell in PC (e.g. the AMF No. 11567 membrane swelled 9.7% more in water than in PC).

Corning No. 7930 porous glass, because of its low electrical resistance in PC, well-defined structure and hyperfiltration capabilities [16], is one of the most promising of the membranes

Table 3. Diffusion of copper (II) perchlorate through membranes in propylene carbonate*

Membrane	Time of experiment (h)	Diffusion flux J mole s ⁻¹ cm ⁻²	Diffusion coefficient D cm ² s ⁻¹
PF-2	19	8.4 × 10 ⁻¹⁰	1.5 × 10 ⁻⁷
Amicon UM-05	22	1.01 × 10 ⁻¹⁰	2.0 × 10 ⁻⁸
Polypropylene†	6	1.08 × 10 ⁻⁸	2.16 × 10 ⁻⁶

* Initial conditions: 0.1 M Cu(ClO₄)₂/PC in one half-cell, pure PC in the other.

† Gelman polypropylene filter.

investigated. It is obtained as an intermediate product in the production of 96% silica glass (Vycor), has an average pore diameter of $4 \times 10^{-3} \mu\text{m}$ (40Å) and 28% of volume void space.

Inspection of Table 1 shows that the electrical resistance of the 1 mm thick plate of Corning No. 7930 porous glass is 3.46 times the resistance of the 0.25 mm thick plate rather than four times the resistance of the thinner plate as would have been expected. The 13% discrepancy is probably due to slightly different alignments of the samples in the cell in addition to resistance variations in the membrane. Thus the almost linear dependence of the electrical resistance on thickness confirms that the low resistance of the 7930 porous glass is not an anomaly and suggests that further substantial reductions in the electrical resistance can be obtained by reductions in thickness (e.g. glass electrodes as thin as 0.001 mm have been prepared).

One disadvantage of Corning No. 7930 porous glass for separator applications is the neutral charge of the membrane and therefore the absence of ion-exchange properties. This problem could be overcome by using the porous glass as a support on which an ion-exchange membrane could be dynamically formed at high pressure [17] using a feed solution of a high molecular weight polyelectrolyte. In principle, the polyelectrolyte would become permanently entrapped in the pores of the glass support transforming the neutral porous glass into a permselective ion-exchange membrane.

Of the various membranes investigated, the AMF C-322 and the Corning No. 7930 porous glass appear to be the most promising for use as organic electrolyte battery separators. Gabano and co-workers [2] have tested the effectiveness of the AMF C-322 membrane as a separator in the Li/PC, LiAlCl_4 (1 M), CuCl_2 cell. When cells with a cathode capacity of 1Ah were stored for 15 h and then discharged through a 200 Ω resistor, the cathode discharge efficiencies using a polypropylene mesh and an AMF C-322 membrane were 17% and 44% respectively. Neither transference number nor interdiffusion measurements have been carried out for the Corning No. 7930 porous glass membrane in PC. Thus, it will be difficult to compare the relative merits

of the AMF C-322 and the Corning No. 7930 porous glass as battery separators and the possibilities for improving their performance by modification, until additional interdiffusion and self-discharge tests are undertaken.

It will be necessary to discuss the various factors affecting membrane resistance before proceeding further, since the electrical resistance of membranes in non-aqueous solutions is a subject which has only recently been of interest. Thus, the resistance problem has not previously been considered in a systematic manner. The three major factors which affect the electrical resistance of a membrane in an electrolyte solution are (1) the thickness, (2) the swelling, (3) the electrical resistance of the diffusion layer. The degree of swelling [8] is influenced by a variety of structural factors [18] and the extent of the interaction of the polymer matrix and the fixed ionic groups of the membrane with the electrolyte solution.

One method for reducing membrane resistance is to decrease the thickness of the membrane. Although the problem seems straightforward, the existence of a diffusion layer at the membrane-solution interface due to concentration polarization suggests that thickness reductions may eventually reach a point of 'limiting returns' when this layer becomes rate-controlling.

The resistance of the diffusion layer can be estimated using the Nernst-Planck equations, assuming conditions similar to those in a non-aqueous battery, in order to obtain some indication of the importance of concentration polarization. In the case of steady-state ion transport through the solution in the diffusion layer, the solution concentration profile in the diffusion layer becomes time-invariant and does not vary along the membrane. This simplified picture is shown schematically in Fig. 2 which depicts the diffusion layers at a cation-exchange membrane in a 1 M LiClO_4/PC solution. It should be noted that when positive current flows from left to right, the current density i is taken as positive. Electrical potential gradients are taken as potential on the right, minus potential on the left, divided by the distance. Therefore, in Fig. 2, the electric potential is positive.

The thickness of the diffusion layer, δ , which is required to calculate the diffusion layer resist-

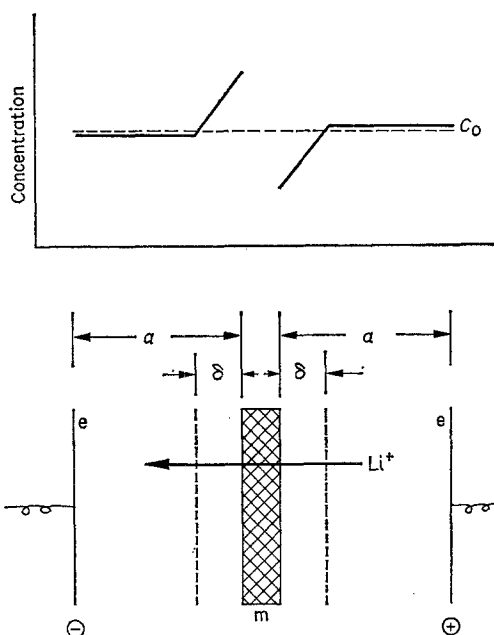


Fig. 2. Model used in calculation of diffusion layer resistance. a , membrane-electrode distance, 1 mm; δ , diffusion layer thickness; m , cation-exchange membrane; e , electrode; C_0 , concentration of LiClO_4 in the solution (i.e. 1 M LiClO_4/PC).

ance, was obtained from an expression reported by Tobias and co-workers [19], for the effect of natural convection on the diffusion layer thickness at an electrode

$$Sh_h = (h/\delta) = 0.68 (Sc \times Gr_h)^{\frac{1}{2}} \quad (2)$$

where Sh_h is the Sherwood number (Nusselt number for mass transport), Sc the Schmidt number, Gr_h the Grashof number, and h the characteristic length. The following parameters were used for the calculation of the Grashof number: characteristic length 10 cm (approximately the height of a battery membrane), density of the bulk solution, $\rho' = 1.254 \text{ g cm}^{-3}$, density of the depleted solution at the membrane surface, $\rho_m = 1.203 \text{ g cm}^{-3}$, the acceleration due to gravity, g , and the kinematic viscosity, $\nu = 5.65 \times 10^{-4} \text{ cm}^2 \text{ s}^{-1}$, calculated by dividing the viscosity of the 1 M LiClO_4/PC solution ($\eta' = 7.08$ centipoise) by ρ' (ρ' and η data from reference [20]).

$$Gr_h \equiv \frac{g(\rho' - \rho_m)h^3}{\rho_m \nu^2} = 13 \times 10^6$$

The value of the diffusion coefficient of

LiClO_4 , $D = 3.4 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ [20], was used in the calculation of the Schmidt number:

$$Sc \equiv \eta' / (\rho' D) = 16.6 \times 10^3$$

On substitution of these values in Equation (2), the diffusion layer thickness $\delta = 0.022 \text{ cm}$ is obtained.

The ohmic drop across the diffusion layer R_m , can now be calculated using Equation (3).

$$R = \frac{-\Delta E_b}{i} = -\left(\frac{B}{\lambda i}\right) \ln\left(1 - \frac{\delta i}{BC_0}\right) \quad (3)$$

where B is a constant defined in equation [4], λ , the equivalent conductance ($\Omega^{-1} \text{ cm}^{-2} \text{ Eq}^{-1}$) and, C_0 , the concentration of LiClO_4 in the bulk solution outside the diffusion layer (mole cm^{-3}). The development of Equation (3) from the Nernst-Planck equations is somewhat lengthy, and follows closely the earlier treatment of the diffusion layer resistance in reference [21]. The constant B in Equation (3) is defined by the expression

$$B = FD / (\bar{i}_+ - t_+) \quad (4)$$

where t_+ and \bar{i}_+ are the transference numbers of Li^+ in the solution and membrane respectively, F , Faraday's constant, and D the diffusion coefficient of the electrolyte (LiClO_4) in solution. The units used are identical or consistent with those reported earlier [22].

From the work of Dey [3] for Li^+ , using an AMF C-60 membrane in γ -butyrolactone, it is assumed that $\bar{i}_+ = 0.98$ (i.e. the membrane is highly permselective with respect to cations). The values used for t_+ and λ ($t_+ = 0.20$, $\lambda = 7.3 \text{ cm}^2 \Omega^{-1} \text{ eq}^{-1}$) were obtained from the measurements reported by Keller and co-workers [5] and Boden *et al.* [7] respectively for 1 M LiClO_4/PC . Substituting these values into Equation (3), the resistances of the diffusion layer, R , calculated were 3.10, 3.43 and 9.06 $\Omega \text{ cm}^2$ at current densities of 1, 4 and 18 mA cm^{-2} respectively. It can be shown from Equation (3) that the ohmic drop, $\Delta E_b''$, tends to infinity as a limiting current of 19.1 mA cm^{-2} is approached.

A limiting current of 19 mA cm^{-2} cannot presently be regarded as a problem restricting the application of permselective membranes as non-aqueous battery separators. However, the calculated limiting current is only an approximate

estimate and concentration polarization will not be precisely estimated until actual limiting current measurements are performed with suitable separators. From the calculated values of the diffusion layer resistance it can be concluded that even at current densities as high as 18 mA cm^{-2} , the resistance is sufficiently small ($<9.1 \Omega \text{ cm}^2$), that it is possible to achieve considerable reductions in membrane resistance by decreasing the membrane thickness before the resistance of the membrane approaches that of the diffusion layer. (At that point further reductions of thickness contribute little to the reduction of the overall resistance.)

On the basis of these considerations regarding the diffusion layer, it was decided to prepare the phenolsulfonic acid-formaldehyde membranes as laminated membranes consisting of a thin layer of the cation-exchange resin on an inert porous polypropylene support. Using this configuration it was possible to combine the desirable properties of low resistance, mechanical strength and selectivity.

The electrical resistance values given in Table 1 for the PF membranes are under $450 \Omega \text{ cm}^2$ for two of the membranes. Since the resin layer penetrated into the polypropylene support for all of these membranes to give a total resin thickness of about 0.15 mm , the goal of $100 \Omega \text{ cm}^2$ could be achieved if the thickness of the resin layer could be reduced to $<0.05 \text{ mm}$ as originally intended.

The diffusion layer calculations also indicate that the resistance variations of the Corning 7930 glass membranes are more significant than they might first appear. For example, the reduction in membrane resistance with thickness that was observed is probably typical of the substantial reductions that can be expected if the thickness is reduced further. The electrical resistance of a membrane can sometimes be decreased by decreasing the amount of crosslinking of the polymer matrix of the membrane, causing increased swelling of the membrane (i.e. increasing its porosity). However, this reduces the permselectivity. Hence, an optimum balance between conductivity and permselectivity must be found for each membrane-solvent system. For this reason, membrane electrical resistance results alone can not be evaluated unless informa-

tion is available concerning the effectiveness of the membrane as a diffusion barrier. Therefore, the interdiffusion and salt diffusion experiments were undertaken.

Although transference number experiments were carried out, it was decided [13, 14], partially on the basis of the low solubility of LiCl in PC, that diffusion measurements are best suited for exploratory studies of a large number of membranes. Transference numbers as a measurement of permselectivity for very selective membranes (\bar{t}_+ between 0.98 and 1.0) are restricted by the 0.1% accuracy limitation of most analytical techniques whereas diffusion measurements can be made more sensitive merely by increasing the length of the experiment to several days or, if necessary, weeks.

When the salt diffusion fluxes presented in Table 3 are compared, it can be concluded that the Amicon UM-05 membrane is superior to membrane PF-2 in having not only a lower electrical resistance, but also eight times the effectiveness as a diffusion barrier. Extending the comparison to the interdiffusion results in Table 2 for Br^- interdiffusion, it appears that the PF-13 membrane functions as a more effective diffusion barrier than either the PF-2 or UM-05 membranes, but only at the expense of a higher electrical resistance when compared to the UM-05.

Further examination of Table 2 reveals that the Amicon UM-05 membrane has only weak cation-exchange properties in PC since the interdiffusion flux of Br^- is a significant fraction of the Li^+ flux. The UM-05 ultrafiltration membrane possesses a net negative charge on its polymeric backbone and although its composition is a commercial secret, it is probably similar to the membranes previously described by Michaels [23].

It is particularly interesting to compare the cation and anion interdiffusion fluxes found for the UM-05 membrane with the interdiffusion fluxes reported by Gabano and co-workers [2] for the AMF C-322 in PC solutions. For cation interdiffusion between $0.1 \text{ M LiClO}_4/\text{PC}$ and $0.1 \text{ M AgClO}_4/\text{PC}$ through an AMF C-322 membrane, Gabano found a Li^+ flux of $3.6 \times 10^{-10} \text{ Eq cm}^{-2} \text{ s}^{-1}$. Although the two membranes have almost identical Li^+ interdiffusion

fluxes, the AMF C-322 has a much lower electrical resistance (cf. Table 1). The AMF C-322 has superior permselective properties because it achieves low electrical resistance without any accompanying loss in selectivity.

From Table 2 it can be seen that the rate of Li^+ interdiffusion through the UM-05 membrane is 2.55 times greater than the rate of Cu^{++} interdiffusion. If it assumed that both LiClO_4 and $\text{Cu}(\text{ClO}_4)_2$ are fully dissociated, and if no perchlorate diffusion occurs, then to conserve electric neutrality it would be expected that the rate of Li^+ diffusion should be exactly twice the rate of Cu^{++} diffusion occurring in the opposite direction. Since the $\text{Li}^+/\text{Cu}^{++}$ flux ratio is greater than 2.0, it can be concluded that Cu^{++} and Li^+ ions are not the only migrating species.

Of the membranes that were prepared, the PF-13 membrane clearly functioned as the most effective diffusion barrier, but only at the expense of an increase in electrical resistance. In principle, the electrical resistance could be lowered considerably if the thickness of the resin layer of the membrane were reduced. Improving the selectivity and effectiveness of the PF membranes as a diffusion barrier is a more complex problem. The improved selectivity of the PF laminated membranes cured at low partial pressures of water (e.g. 440 Torr for PF-13) gives support to the thermodynamically based hypothesis [14] that lowering the water vapor pressure in the humidistat during curing decreases the average 'pore radius'. If the water vapor pressure during the curing of PF membranes is in fact a key variable controlling the permeability of these membranes, then a considerable improvement should result when this factor is optimized.

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