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RESEARCH ON SEPARATORS FOR ALKALINE ZINC BATTERIES
Final Report

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October 1984

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LBL-18574

RESEARCH ON SEPARATORS FOR ALKALINE ZINC BATTERIES

Final Report

October 1984

by

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for

Technology Base Research Project
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This work was supported by the Assistant Secretary for Conservation and Renewable Energy, Office of Energy Systems Research, Energy Storage Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098, subcontract no. 4522210 with the Lawrence Berkeley Laboratory.

SUMMARY

This project is concerned with the research and development of a hybrid separator as an improved battery separator in alkaline zinc secondary batteries. Particular emphasis has been directed toward mitigating the failure of zinc electrodes by controlling the permselectivity of the separator.

Hybrid separators were synthesized and fabricated by Dr. J. Lee (RAI Research Corporation). These separators consist of a microporous film, radiation-grafted with a monomer containing ion-exchange groups. The new separator incorporates the favorable aspects of both ion-exchange membranes and microporous separators. Such a hybrid separator should ideally be highly specific for fast transport of electrolyte while inhibiting zincate diffusion.

Hybrid separators with a wide range of percent graft (0 to 60%) were made by varying the monomer concentration and radiation time. The grafting of these ionic groups imparts the ion selectivity of the separators. The ion-exchange capacity of these hybrid separators increases with increasing percent graft. The fixed-ion concentration is as high as 8 mole/litre, while the zincate ion concentration in the hybrid separators is less than 0.1 mole/litre. This implies the ion selectivity of the hybrid separators is as effective as the ion-exchange membranes.

The electrolyte uptake of hybrid separators is ca. 60 wt%. The higher the percent graft of the separator, the higher the water uptake and the lower the KOH uptake that are observed. The high electrolyte uptake suggests that hybrid separators can provide low cell internal resistance and high cell capacity. The electrolytic resistance of the hybrid separators ranges from 26 $m\Omega\text{-}cm^2$ to 6.5 $\Omega\text{-}cm^2$ depending on percent graft, the prehistory of the film, electrolyte concentration, and temperature. The permeability of hydroxyl ion in the hybrid separators is 1~3 x 10^{-6} mole/cm^2/sec, in good agreement with the electrolytic resistance value predicted by the Nernst-Einstein relation.

The permeabilities of zincate ions were measured for a series of hybrid separators. The initial concentration of zincate solution was 0.7M in 40% KOH. The zincate permeability for hybrid separator 229-3C was 9.6 x 10^{-11} mole/cm^2/sec, while the permeability for ion-exchange membrane P2291 40/20 and microporous separator Celgard 3401 were 5.4 x 10^{-9} and

2.5×10^{-8} mole/cm^2/sec, respectively. It was also found that the diffusion coefficient of zincate ion in these separators can be described by the free volume theory. As expected, the tortuosity of the ion-exchange membranes is higher than that of the hybrid separators.

The hydraulic permeability of electrolyte in the hybrid separators varies from 1.74×10^{-7} to 6.66×10^{-7} ml.cm/sec.cm^2.atm. For comparison, the hydraulic permeability of Celgard 3401 and P2291 40/20 is 4.74×10^{-7} and 1.16×10^{-9} ml.cm/sec.cm^2 atm, respectively. The effective pore size of the hybrid separators is 45 to 63 Å while that of ion-exchange membranes is 4 to 15 Å, as estimated from the hydraulic permeability data.

Results strongly suggest that the hybrid separators exhibit excellent selectivity against zincate ions, while the hydroxide ions and water transport behaviors through these hybrid separators are not altered by the presence of the ion-exchange groups. These new separators show promise as potentially useful separators for alkaline zinc batteries.

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1. BACKGROUND

The alkaline zinc batteries have some unique properties. These batteries possess higher practical volumetric and gravimetric energy density, as well as being able to deliver higher specific power than other near term batteries. However, the useful cell cycle life of present alkaline zinc batteries is relatively short. This is mainly due to the failure of the zinc electrodes (1). It has been generally agreed that one of the major factors for this failure is the cell separator (2,3). In this project, an attempt was made to mitigate the failure of the zinc electrode by controlling the permselectivity of the cell separator.

On the basis of membrane transport theories (4,5), we believe that a microporous separator with "optimum" ion selectivity against zincate ions and high solvent transport rate is the ideal separator for this application. The separator will embrace the advantages of both the microporous separator and the ion-exchange membrane. A thin, microporous ion-exchange separator is new and unique in concept, and can be tailor made to meet the specific requirements for application in alkaline zinc batteries.

2. TECHNICAL ACCOMPLISHMENTS

2.1 Synthesis and Fabrication of Separators

A series of hybrid separators have been made by radiation grafting technique (6,7). A microporous sheet was soaked in the desired monomer solution. A chain transfer agent was then added to the solution, and the film was exposedto γ-radiation of a specific dose rate for a preset time. The "SC" process was employed because it is of lower cost, and it gives products with relatively short chain graft compared to the conventional "Permion" process. Short grafted chains offer less steric hinderance than long chains. The conversion of SC grafts can proceed more readily and this gives lower electrolytic resistance. It also gives much higher graft uniformity. The film produced by SC process can generally be heat-sealed and has excellent mechanical strength.

The high energy γ-radiation causes the cleavage of carbon-hydrogen bonds of the polymer and yields a highly reactive free radical, as illustrated in Figure 1. In the presence of olefinic monomers, the grafting process occurs preferentially. During the grafting reaction, little crosslinking or scission takes place since the amount of radiation used is small. Crosslinking produces a three dimensional

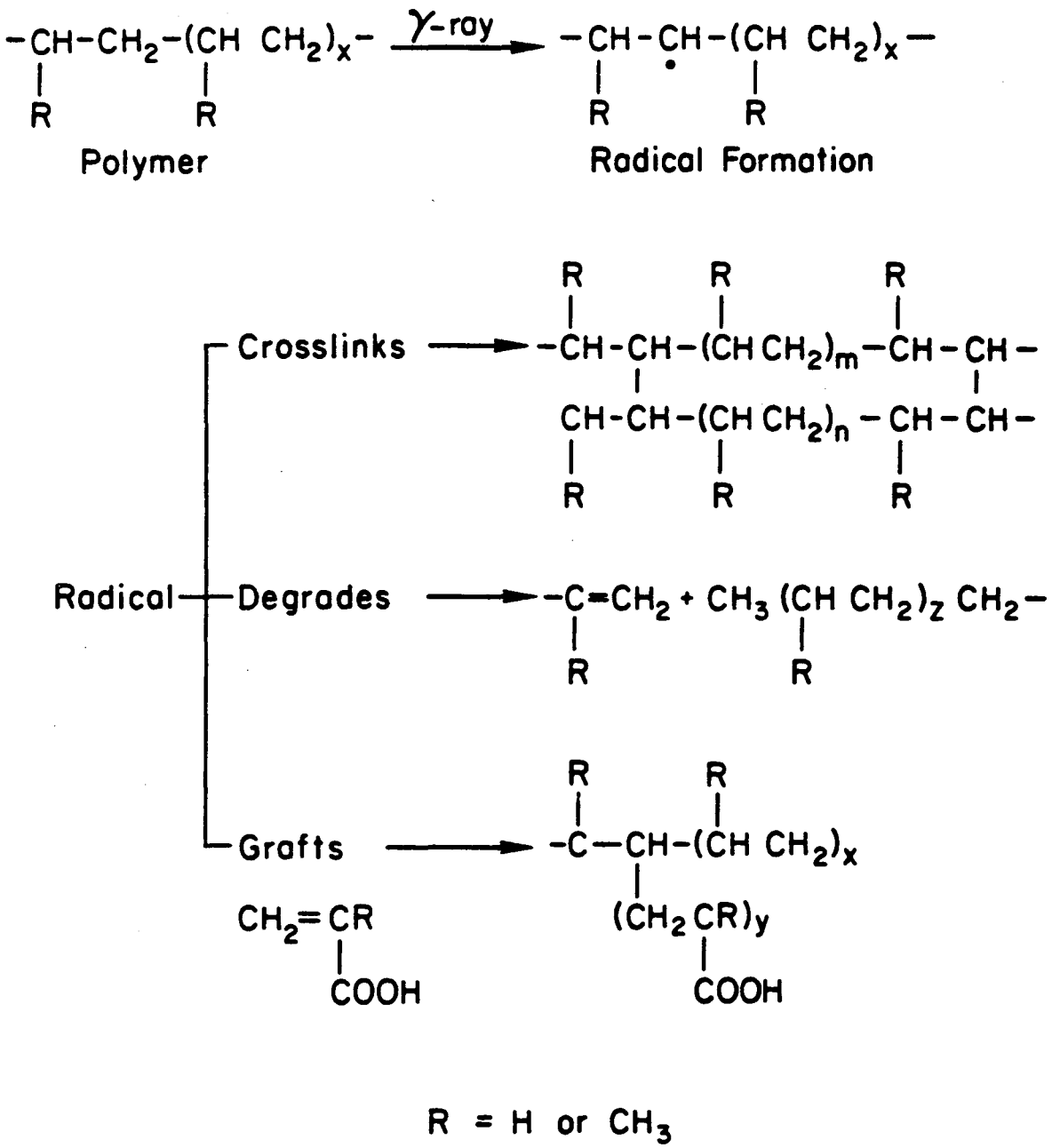

Figure 1. Radiation Reactions

structure while scission leads to molecular cleavage and polymer degradation. The mechanism and kinetics of radiation grafting are essentially the same as those of a standard polymerization reaction (8).

Hybrid separators with a wide range of percent graft were made by varying the monomer concentration and radiation time. The grafting of these carboxylic acid groups imparts the ion selectivity of the separators. Figure 2 shows a plot of ion exchange capacity versus percent graft for hybrid separators and ion-exchange membranes. The ion-exchange capacity of the separators increases with increasing percent graft.

2.2 Separator Stability

The ionic groups of the hybrid separators are chemically bonded onto the polymer backbone. These active groups will not be leached out by the electrolyte and will not be mechanically disintegrated during the separator wetting and dewetting processes. It is well known that polyolefin and fluoropolymer films are stable in strongly alkaline solutions. These polymers are also inert toward the electrochemical reactions of nickel and zinc electrodes. However, certain modifications of the polyolefin films are required for their use in batteries with strong oxidants, such as silver-zinc and zinc-ferricyanide cells (7).

The incorporation of ionic groups in the polymer chains has a drastic effect on the physical properties of hybrid separators. The thermal stability and tensile strength of the separator increase markedly (9). Figure 3 shows the thermal drying curves of the hybrid separators. It can be seen that the separators are thermally stable up to 92°C.

2.3 Electrolyte Uptake

The permselectivity properties of separators and the operating characteristics of an alkaline zinc battery are strongly related to the electrolyte uptake of the separator. A maximum amount of absorbed electrolyte is desirable to achieve minimum cell internal resistance and to maximize capacity. However, the ion selectivity of the separator may be markedly reduced if the electrolyte uptake is too high.

The uptake of various components of the electrolyte by a separator can be given by:

Electrolyte Uptake, $Q_e = (W_e - W_o)/W_o$ [1]

Water Uptake, $Q_{water} = (W_e - W_1)/W_o$ [2]

Salt Uptake, $Q_s = Q_e - Q_{water}$ [3]

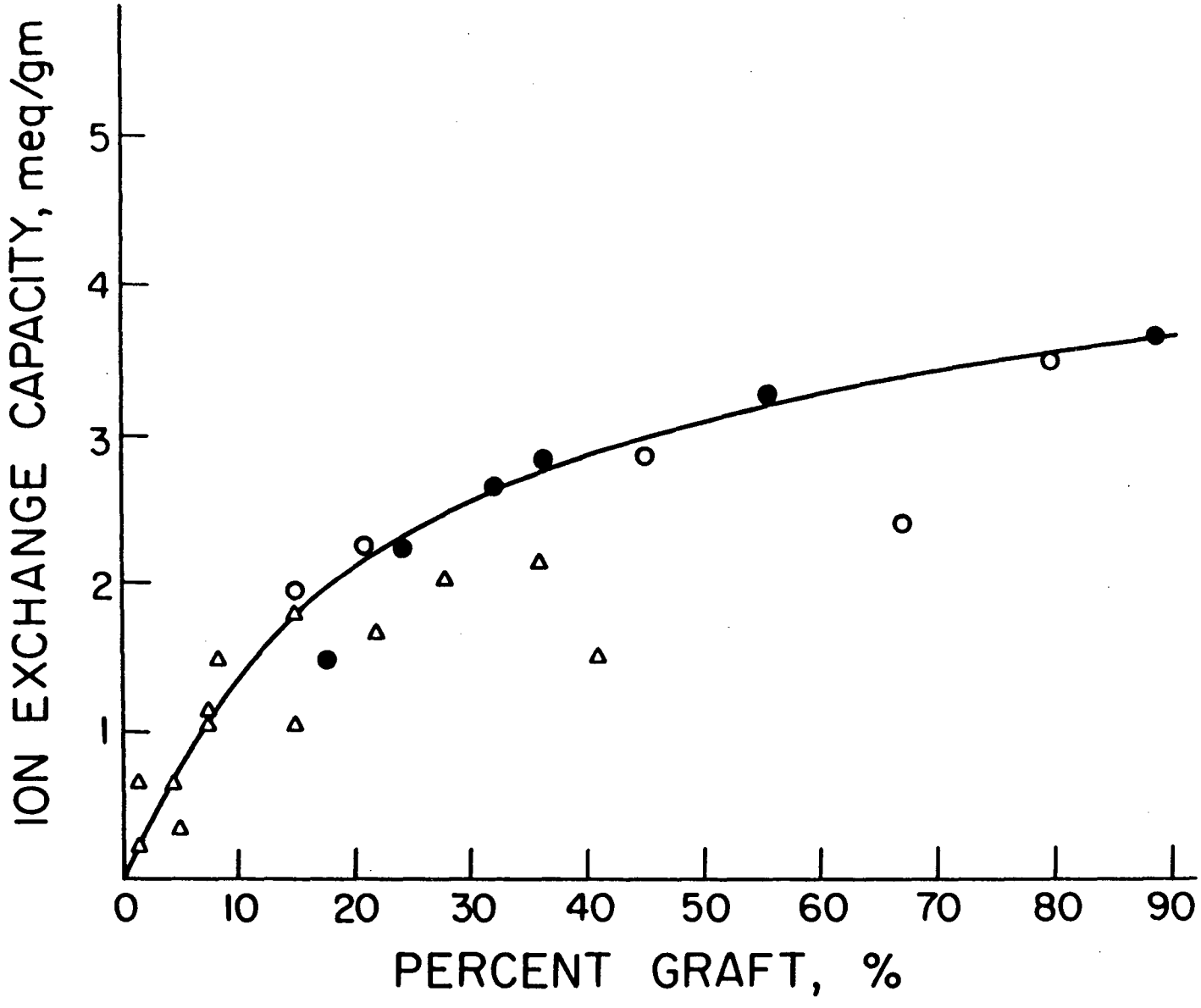

Figure 2. Ion exchange capacity for hybrid separators (Δ) and ion exchange membranes (o). Close symbols: RAI data; open symbols: PRI data.

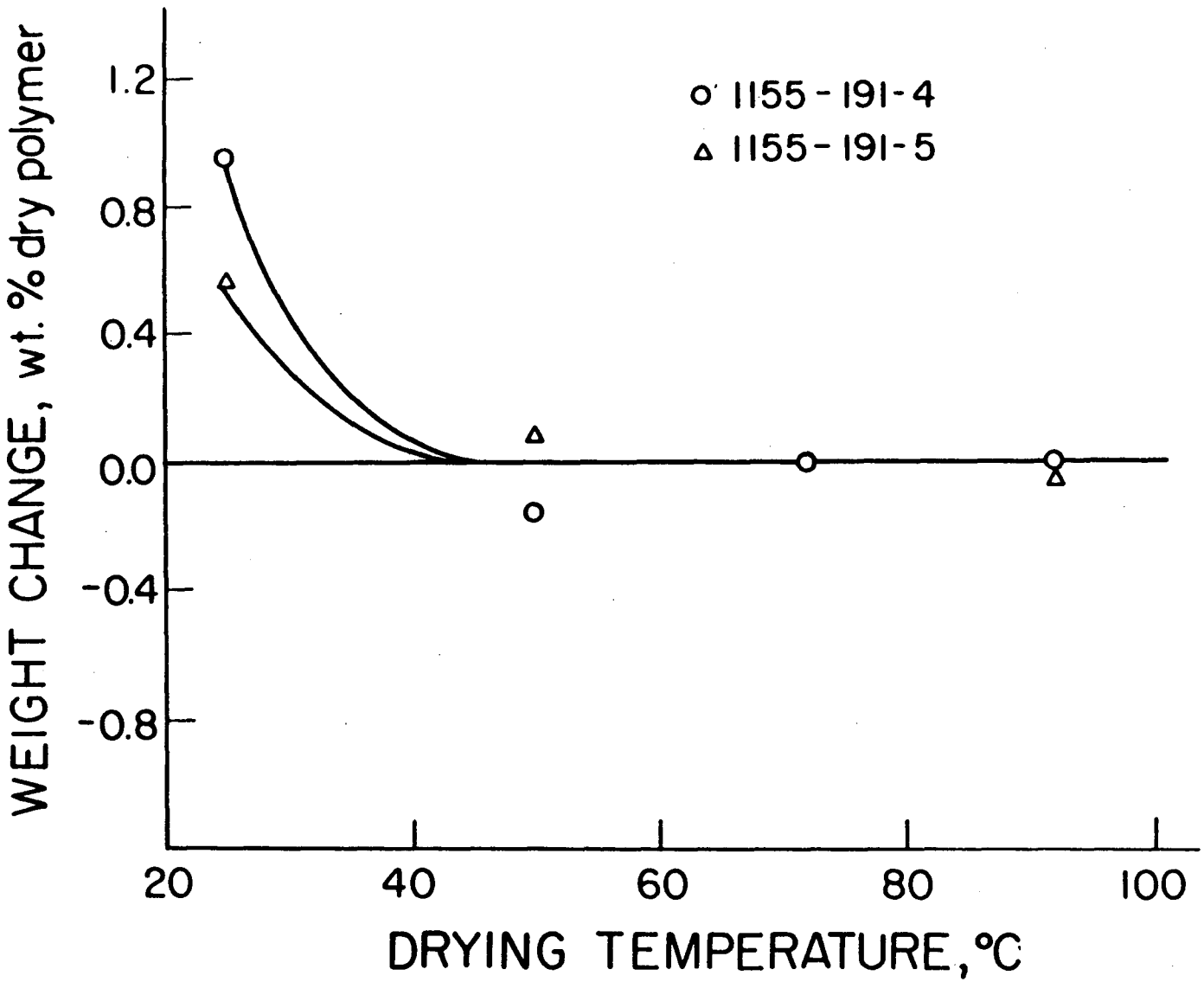

Figure 3. Thermal drying curves of hybrid separators

where W_e is the total weight of the separator with the electrolyte; W_o and W_1 are the dry weights of the separator before and after soaking in the electrolyte, respectively.

Figure 4 shows the water uptake and salt uptake of the hybrid separators and ion-exchange membrane P2291 in 40% KOH solution. The water uptake increases with increasing percent graft because the degree of swelling is related to the ion-exchange capacity of the separator. The salt uptake of the hybrid separator decreases with increasing percent graft as dictated by the Donnan-exclusion principle (4). The maximum salt uptake at ca. 40% grafted for the ion-exchange membranes is likely due to a decrease in membrane swelling at low percent graft and an increase in membrane ion-exchange capacity at high percent graft.

2.4 Sorption of Co-ions in Separators

Ions of charge similar to that of the charges bound to the ion-exchange polymer network are called co-ions. They are mostly, though not completely, excluded from the separator by electrostatic effect, often referred to as the Donnan-effect. When an ion-exchange separator is in equilibrium with an electrolyte solution, the following relationships are established:

$$Z_g \bar{m}_g + Z_n \bar{m}_n + \omega \bar{m}_R = 0 \qquad [4]$$

$$a_n^{|Z_g|} \cdot a_g^{|Z_n|} = \bar{a}_n^{|Z_g|} \cdot \bar{a}_g^{|Z_n|} \qquad [5]$$

where $\bar{m}_R$ and ω are the molality and valency of the fixed charges of the separator, respectively. For a cation exchanger with univalent fixed charges, i.e., $\omega = -1$, a_g and a_n are the activities of the cation and anion in the electrolyte, respectively, whereas $\bar{a}_g$ and $\bar{a}_n$ are the activities in the separator phase. $\bar{m}_g$ and $\bar{m}_n$ are the molalities in the separator phase. The valencies Z_g and Z_n have signs, positive for cations and negative for anions. Eq. [4] and [5] give information on the concentrations of co-ions (e.g. zincate ion) which are taken up by the ion-exchange separator from the surrounding solution.

The fixed-ion concentration of the separator can be calculated from the ion-exchange capacity and water uptake (10). The concentration of zincate ion in the separator in

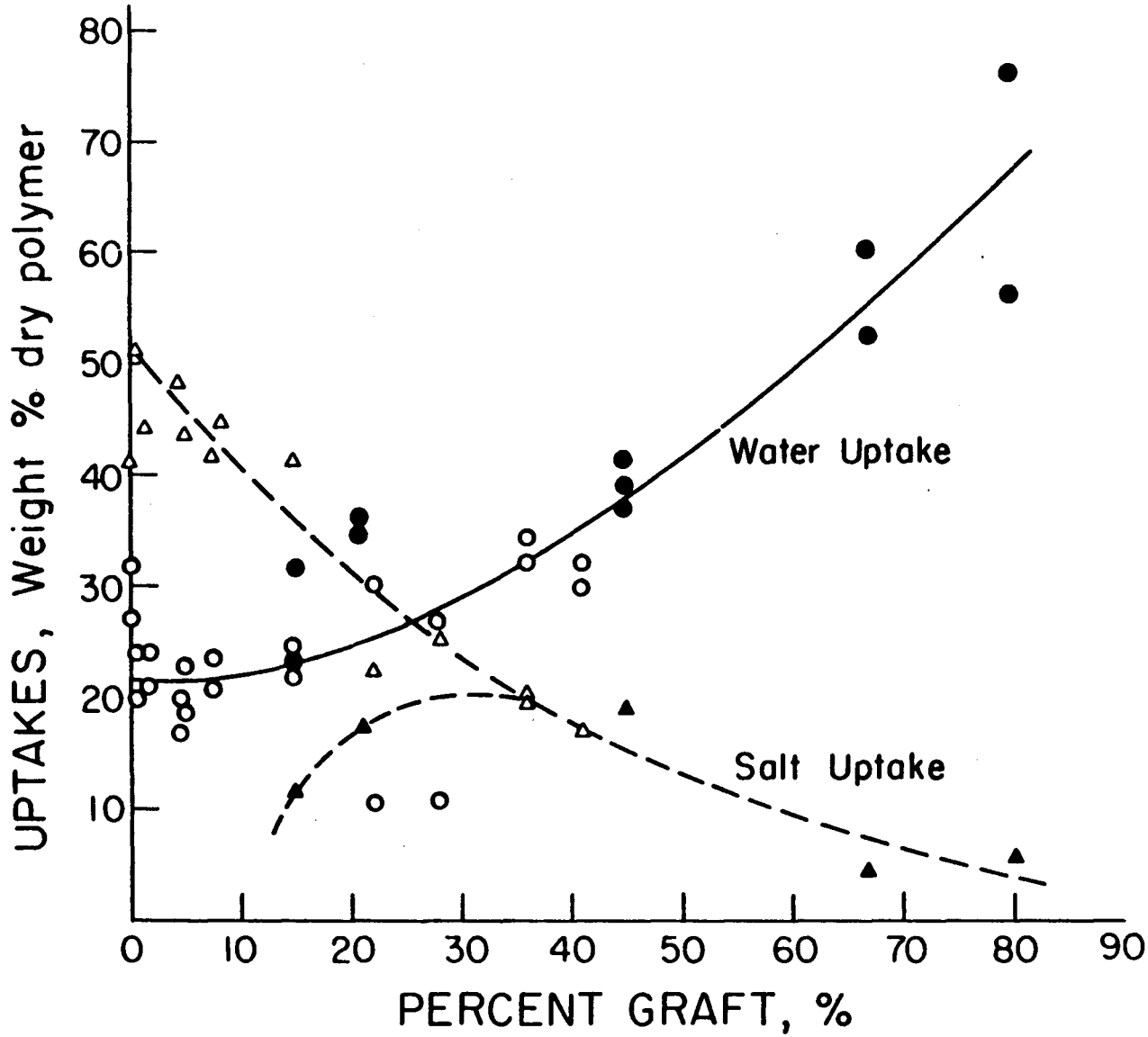

Figure 4. Water Uptake (o,●) and salt uptake (△,▲) as a function of percent graft for hybrid separators (open symbols) and ion exchange membranes (close symbols).

equilibrium with a 0.7 M zincate solution can be estimated from equations [4] and [5]. Table 1 summarizes the fixed-ion concentration and co-ion (zincate ion) concentration of the hybrid separators and ion-exchange membranes.

TABLE 1

CONCENTRATIONS OF FIXED-ION AND CO-ION IN BATTERY SEPARATORS

Sample	Fixed-Ion Concentration (mole/litre)	Co-Ion Concentration (mole/litre)
Hybrid Separators		
196-3	6.26	0.078
196-4	4.15	0.116
229-3C	7.31	0.067
229-4C	8.01	0.061
Ion-Exchange Membranes		
40/16	6.19	0.079
40/20	4.51	0.107
40/30	7.31	0.067
40/60	6.41	0.076

2.5 Electric Resistivity

The electric resistivity of hybrid separators has been studied. Figure 5 shows a plot of the resistivity in 40% KOH of the hybrid separators with varying degrees of graft. The dashed line is for the case of ion exchange membranes. A decrease in resistivity was observed with increasing degrees of graft, and, in turn, with increasing ion-exchange capacity. For samples with low percent graft, the separator resistivity also changes drastically depending on the prehistory of the film. Table 2 shows the influence of pretreatments on the separator resistivity.

The separator resistivity in various KOH concentrations and at various temperatures has been measured. It was found that the maximum conductivity of the hybrid separators occurs at 20% KOH, as shown in Table 3. The maximum in the conductivity is probably due to a decrease in hydroxyl ion concentration at low alkaline concentrations and a decrease in separator swelling with increasing alkaline concentrations. As expected, the separator conductivity increases at elevated temperature, as shown in Table 4. It is attributed to both the increase of electrolyte conductivity and the increase in separator swelling.

TABLE 2.
EFFECT OF PRETREATMENT ON RESISTANCE OF HYBRID SEPARATORS
ELECTROLYTE: 40% KOH: TEMPERATURE: 25°C

Sample	As Received (Ω-cm^2)	Leached in Acid (Ω-cm^2)	Leached and then boiled in dil. KOH (Ω-cm^2)
191-1	0.097	163.7	2.50
191-2	0.097	233.5	7.46
191-3	0.097	224.2	2.95
191-4	0.097	3.7	3.60

TABLE 3

CONCENTRATION DEPENDENCE OF SEPARATOR CONDUCTIVITY AT 25°C

Sample	10% KOH ($m\Omega$-cm^2)	20% KOH ($m\Omega$-cm^2)	30% KOH ($m\Omega$-cm^2)	40% KOH ($m\Omega$-cm^2)
229-3C	90.3	71.0	83.9	367.8
229-4C	167.8	154.8	296.8	283.9
196-3	90.3	58.1	64.5	96.8
196-4	219.4	193.6	258.1	96.8
Celgard-3400	96.8	64.5	64.5	77.4
P2291-40/20	129.0	103.2	109.7	141.9

TABLE 4

TEMPERATURE DEPENDENCE OF SEPARATOR CONDUCTIVITY
ELECTROLYTE: 30% KOH

Sample	10°C ($m\Omega$-cm^2)	25°C ($m\Omega$-cm^2)	35°C ($m\Omega$-cm^2)	45°C ($m\Omega$-cm^2)	65°C ($m\Omega$-cm^2)
229-3C	103.2	83.9	71.0	64.5	51.5
229-4C	458.1	296.8	200.0	135.5	83.9
196-3	96.8	64.5	51.6	45.2	32.3
196-4	348.4	258.1	200.0	154.8	109.7
Celgard-3400	90.3	64.5	51.6	45.2	32.3
P2291-40/20	135.5	109.7	83.9	58.1	38.7

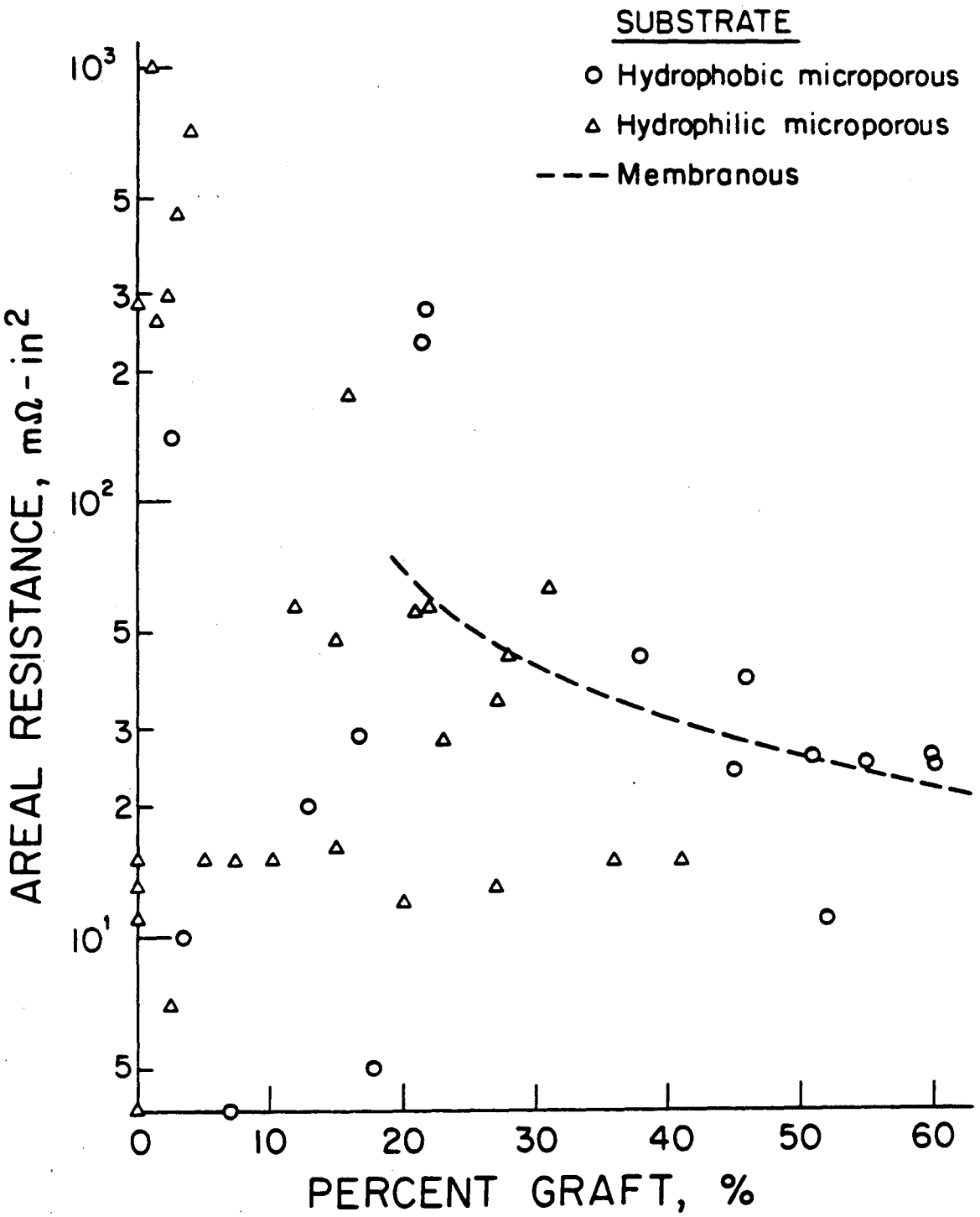

Figure 5. Areal resistance of separators with varying percent graft.

2.6 Ion Selectivity

Permeability of the membrane to electrolyte constituents is an important factor of separator performance. The permeability reflects the diffusivity of ionic species through the membrane matrix and any interaction between permeant and membrane. In conjunction with measurements such as electrical conductivity and electrolyte uptake, the effective ionic diffusivity can ultimately be used to correlate membrane microstructure and battery performance.

2.6.1 Zincate Permeability

The selectivity of the hybrid separators to zincate ion was investigated. The measurement was performed in a two-compartment cell which is divided by a separator. Separators were presoaked in 40% KOH solution for 24 hours prior to use. Rapid stirring on the dilute side was used and the permeation of zincate into the dilute compartment was monitored by analysis of discrete samples removed at regular intervals. At the start of a typical run, a step change of zinc concentration (0.7M ZnO in 40% KOH) was introduced into the concentrated compartment. The same volume of 40% KOH was replaced for each sample removed from the dilute compartment to maintain a constant chamber volume. The zincate concentration was determined both by ICP analysis and by titration with 0.1M EDTA using Erichrome Black T as an indicator.

The permeability is related to the diffusion coefficient by the following equation (11):

$$P = D\,C / \ell \qquad [6]$$

where ℓ is the separator thickness, C is the concentration in the separator, and D is the diffusion coefficient. Table 5 shows the permeability and diffusion coefficient of zincate ions in the hybrid separators. Results for the ion-exchange membranes are also included for comparison. It is noted that hybrid separators exhibit excellent zincate selectivity, as good as that for ion-exchange membranes.

The function $V_p/(1-V_p)$, where V_p is the volume fraction of polymer in a water swollen material, is plotted against log $\bar{D}$ in Figure 6. The denominator of this term is therefore the volume fraction of water in the separator, calculated from sorption results. This function was developed by Yasuda and co-workers to treat diffusion in various hydrophilic polymers (12). Their equation:

$$\bar{D} = D^{\circ} \exp\,[-b\,V_p/(1-V_p)] \qquad [7]$$

TABLE 5

ZINCATE ION PERMEABILITY AND DIFFUSION COEFFICIENT IN HYBRID SEPARATORS AND ION EXCHANGE MEMBRANES

	Zincate Permeability (mole/cm^2/sec)	Zincate Diffusion Coefficient (cm^2/sec)
Hybrid Separators		
196-3	4.45×10^{-9}	1.4×10^{-7}
196-4	1.02×10^{-8}	2.2×10^{-7}
229-3C	9.6×10^{-11}	3.6×10^{-9}
229-4C	1.36×10^{-10}	5.7×10^{-9}
Ion-Exchange Membranes		
40/16	5.22×10^{-9}	1.67×10^{-7}
40/20	5.36×10^{-9}	1.27×10^{-7}
40/30	7.78×10^{-10}	2.94×10^{-8}
40/60	1.09×10^{-9}	3.63×10^{-8}

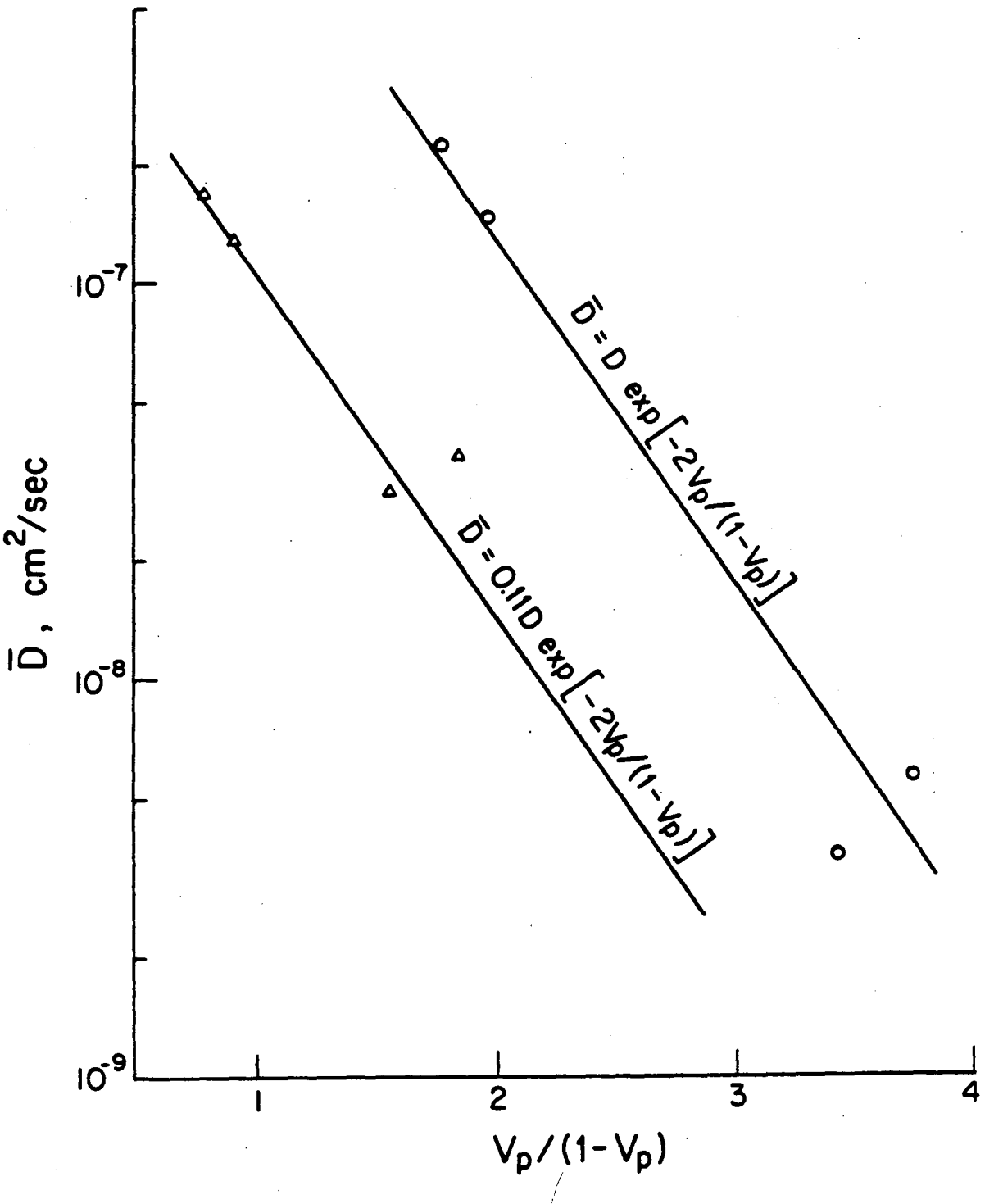

Figure 6. Plot of log $\bar{D}$ versus volume fraction function for hybrid separators (o) and ion exchange membranes (Δ).

describes the relationship between the aqueous and the polymer diffusion coefficients of a species, D° and D, respectively. The equation is related to that derived by Cohen and Turnbull for the diffusion coefficient of a molecule in a simple liquid

$$D = A \exp(-\gamma v^*/v_f) \qquad [8]$$

where v^* is a characteristic volume for diffusion of the species, v_f is the "free volume" per solvent molecule, and γ and A are constants (13). The constant b in Eq [7] is related to the exponent in Eq [8], where v_f now represents the free volume of water. The pre-exponential term in Eq [7] was found to depend on the electrostatic attraction of the counterion to fixed charge sites, in addition to D° for these ion exchange polymers.

As seen in Figure 6, the diffusion coefficients for hybrid separators and ion-exchange membranes are very different. Zincate ions have a much lower diffusion coefficient in ion-exchange membranes for a given water content. A pre-exponential factor of 0.11 D is observed. Tortuosity would thus be reduced in hybrid separators, compared to ion-exchange membranes, which have a more random distribution of ionic groups.

2.6.2 Hydroxyl Ion Permeability

The hydroxyl-ion permeability of a separator reflects the effect of the separator microstructure on the ionic migration, in perhaps the same manner as the separator affects the electrical resistance properties. It provides an additional means of characterizing separators. If one considers that the ionic mobility for diffusion is the same as that for conductance, then the ionic diffusivity can be related to the conductivity by the Nernst-Einstein equation (11,14):

$$D_i = \frac{RT}{F^2} \frac{\lambda_i}{|Z_i|} \qquad [9]$$

and

$$\lambda_i = t_i \Lambda \qquad [10]$$

where λ_i and Λ are the equivalent conductance of the ion and total equivalent conductance, respectively. $|Z_i|$ is the valence of the ion, t_i is the transport number of the ion, and R, T, F have their usual meanings. Table 6 lists the permeability of hydroxyl ion of various separators. However, the transport number that is calculated from the Nernst-Einstein relation can only be considered as an

approximate value because the solution within the separator may not be the same as in the bulk solution.

TABLE 6

HYDROXYL ION PERMEABILITY IN BATTERY SEPARATORS

Sample	Hydroxyl Ion Permeability ($mole/cm^2/sec$)
Hybrid Separators	
229-3C	1.78×10^{-6}
229-4C	1.71×10^{-6}
196-3	3.16×10^{-6}
196-4	2.97×10^{-6}
191-4	1.20×10^{-6}
191-8	1.23×10^{-6}
Ion Exchange Membranes	
P2291 40/16	3.43×10^{-6}
P2291 40/20	1.83×10^{-6}
P2291 40/30	2.35×10^{-6}
P2291 40/60	1.82×10^{-6}
Microporous Separator	
Celgard 3400	2.31×10^{-6}

2.6.3 Zinc Penetration

When zinc is plated out of alkaline solution, the product is dendritic and spongy. In an alkaline cell, the spongy deposit would rapidly grow across to the positive electrode and short out the cell if it were not for the separator. A principal function of the separator, therefore, is to retard the growth of the zinc sponge between the negative and the positive electrodes.

The main purpose of the zinc penetration test is to provide an accelerated test of the rate at which zinc dendrites penetrate the separator under controlled conditions. The approach is to determine the time for zinc dendrites to penetrate the separator and form a short circuit in the test cell. This method is commonly referred to as the Hull Test (15). The test equipment consists of a cell assembly which holds the separator sample between two zinc electrodes. Zincate-saturated 40% KOH solution was used as the electrolyte. One of the zinc electrodes serves as the anode and the other as the cathode. The zinc anode provides replenishment of the zincate as plating proceeds. Current is passed between the electrodes at a controlled current density until a zinc dendrite penetrates the separator. The test results for various separators are given in Table 7. The zinc penetration time for hybrid separators is generally the same as ion-exchange membranes, and is somewhat longer than that for microporous separators.

2.7 Transport of Solvent

The incentive for obtaining a better understanding of the electrochemical pumping effect in these separators is to determine the relationship between the structure and the solvent transport rate. With this in mind, the hydraulic permeability of electrolyte through various separators was measured. These measurements can be used to estimate the average size of the structural feature controlling transport, or the effective pore diameter, D_p. The hydraulic permeability was analyzed according to the expression (16):

$$D_p = (128\ \ell\ \eta\ L_p d^2/\pi)^{1/4} \qquad [11]$$

where ℓ is the thickness of the separator, η is the viscosity of the electrolyte, and L_p is the hydraulic permeability coefficient. Table 8 lists the hydraulic permeability and effective pore diameter for various separators. It is clear that the effective pore diameter for hybrid seprators is ca. 60Å. The dimension for Celgard 3400 is 20Å x 200Å. This pore size is equivalent to a circular pore with a diameter of 70Å.

TABLE 7

ZINC PENETRATION TIME OF BATTERY SEPARATORS

Sample	Hull Test Time (min.)
Hybrid Separators	
191-1	40
191-4	30
191-5	30
191-8	40
196-3	30
196-4	30
229-3C	45
229-4C	20
Celgard 3400	10
P2291 40/16	20
P2291 40/20	30

TABLE 8

HYDRAULIC PERMEABILITY AND EFFECTIVE PORE SIZE OF BATTERY SEPARATORS

Sample	Hydraulic Permeability ml.cm/sec.cm^2.atm x 10^9	Effective Pore Size (Å)	Reference
Hybrid Separators	174 - 666 (#)	45 - 63	This work
Celgard 3400	474 (#)	57	"
Ion-Exchange Membranes			
P 2291	1.16 - 1.25 (#)	4	"
Nafion-120 (E-form)	19 (*)	19	17
Nafion-117 (N-form)	6 (†)	14	18
Nafion-120 (N-form)	3.7 (*)	13	19
Nafion-125 (N-form)	8.1 (*)	15	20
Nafion-117 (N-form)	4.6 (*)	13	20

Electrolyte - (#) 40 wt% KOH; (*) H_2O; (†) 1.0N NaCl.

3. TECHNICAL FEASIBILITY

An ideal separator for alkaline zinc battery should have excellent selectivity against zincate ion while allowing fast hydroxyl ion transport. The ratio of hydroxyl ion permeability over zincate permeability is plotted against percent graft for hybrid separators and ion-exchange membranes in Figure 7. It is obvious that the permeability ratio for hybrid separators can be as high as four orders of magnitude.

Figure 8 depicts the zincate permeability and hydraulic permeability for hybrid separators, microporous separators, and ion-exchange membranes. An ideal separator should have low zincate permeability, high hydraulic permeability, and low electric resistivity (or high hydroxyl-ion permeability). The zincate permeability for microporous separators is higher than that of both the hybrid separators and ion-exchange membranes. On the other hand, the hydraulic permeability for the ion-exchange membrane is two orders of magnitude lower than the microporous separator and hybrid separator.

Table 9 summarizes all the advantages of hybrid separators. It is clearly shown that hybrid separators possess all the desirable properties for use in secondary alkaline zinc batteries.

4. PUBLICATION

R.S. Yeo and J. Lee, "Novel Hybrid Separators for Alkaline Zinc Batteries", in Advances on Battery Materials and Processes, Edited by J. McBreen, R.S. Yeo, D-T. Chin and A.C.C. Tseung, The Electrochemical Soc. Softbound Proceedings Series, Pennington, N.J., (1984) pg. 206.

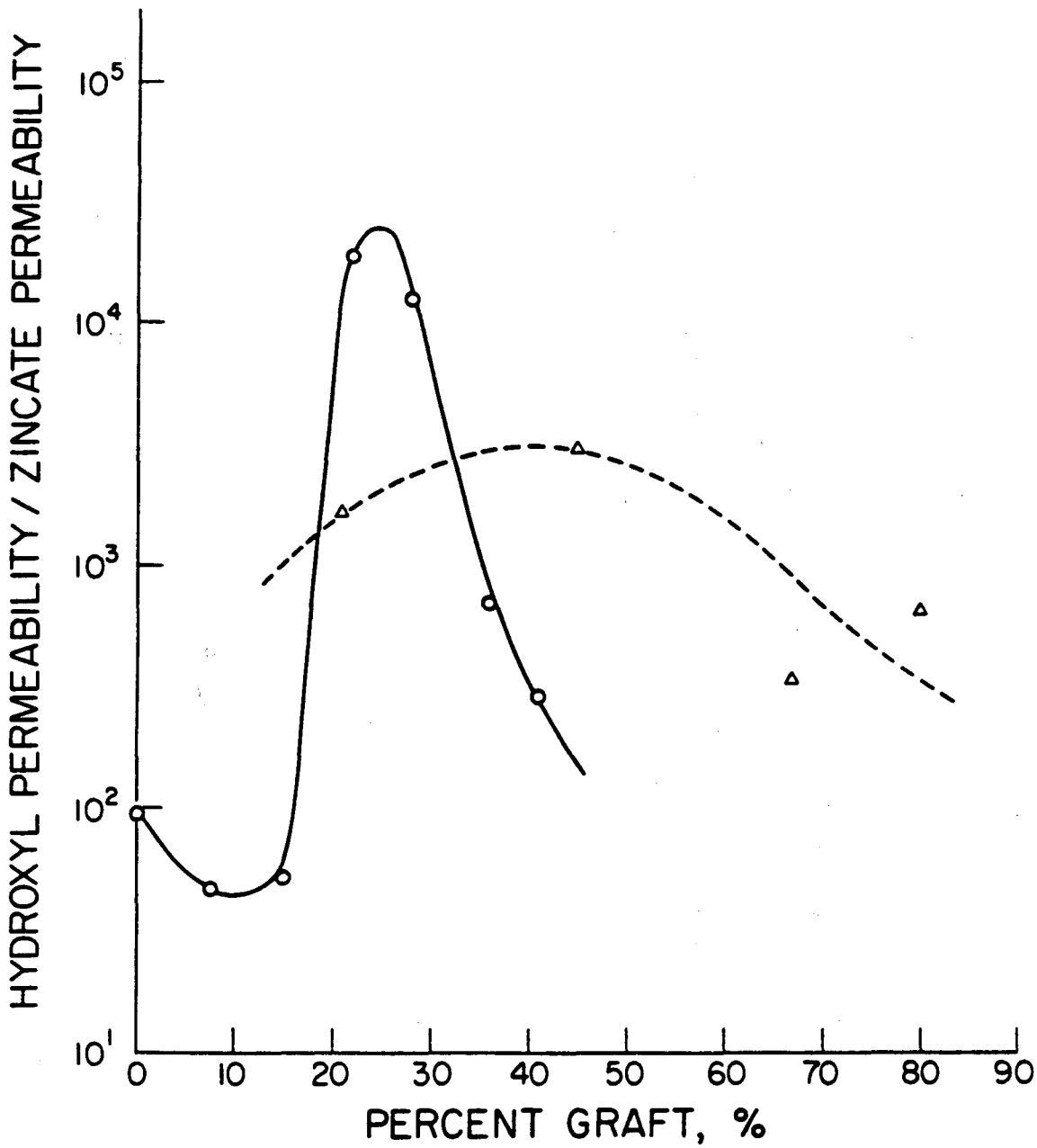

Figure 7. Plot of permeability ratio of hydroxyl ion over zincate ion as a function of percent graft for hybrid separators (o) and ion exchange membranes (Δ).

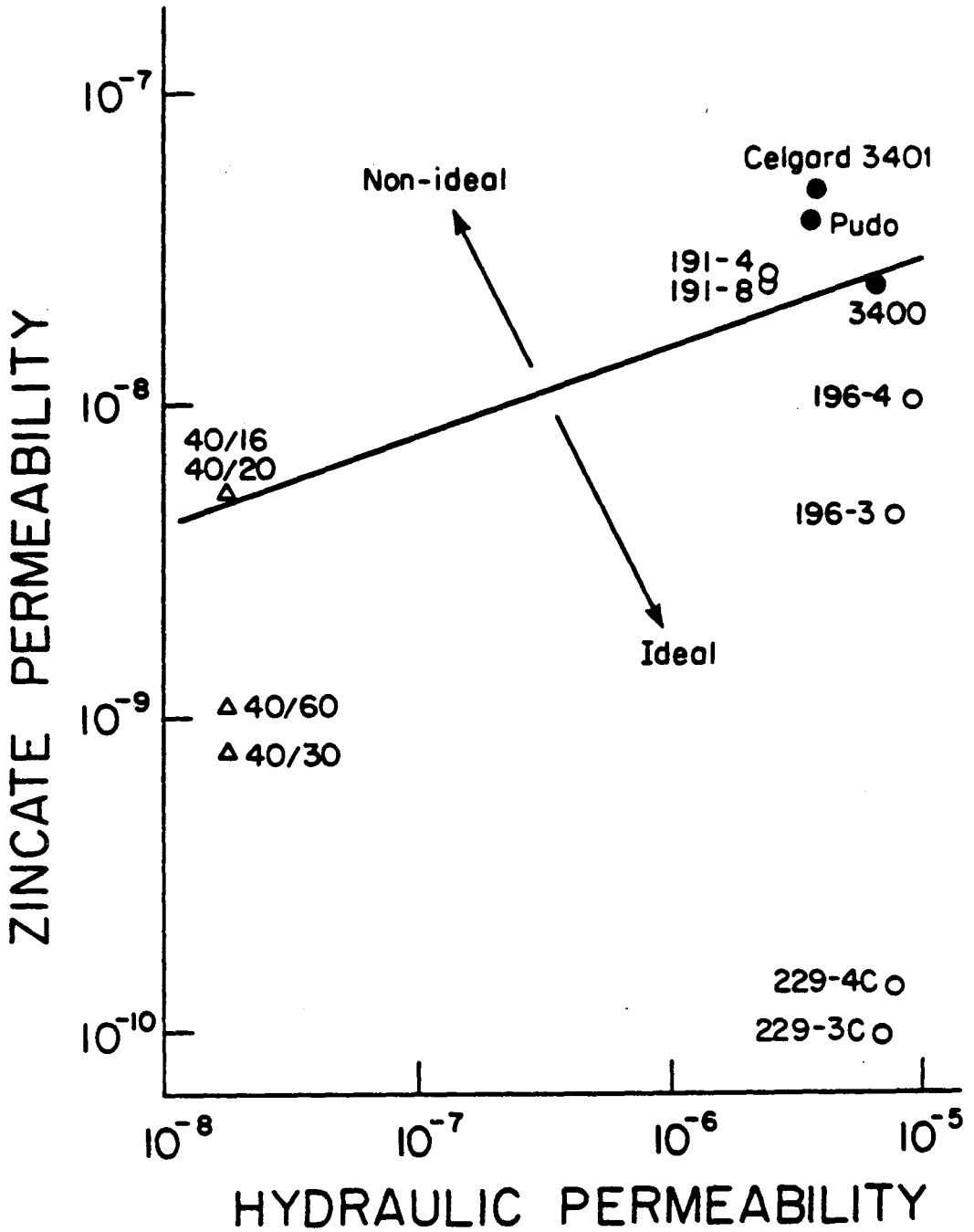

Figure 8. Plot of zincate permeability versus hydraulic permeability for hybrid separators (o), ion exchange membranes (Δ), and microporous separators (●).

TABLE 9

ADVANTAGES OF HYBRID SEPARATORS

A. Hybrid separator combines the advantages of both the microporous and the ion-exchange membraneous separators:

1. Cationic selectivity slows down the tendency for dendrite shorting.

2. Microporous properties allow easier electrolyte flow, reducing shape change problems.

3. Permanent water/electrolyte wettability.

4. Excellent chemical stability.

B. Best separator can be achieved by optimizing separator properties, such as electrolytic resistivity, ionic selectivity, pore size, crosslinking and fixed charge density.

C. Material cost and manufacturing cost are low ($<\$1/ft^2$).

D. Fabrication and handling techniques are easy.

5. ACKNOWLEDGEMENT

This work was supported by the Assistant Secretary for Conservation and Renewable Energy, Office of Energy System Research, Energy Storage Division, of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098, Subcontract No. 4522210 with Lawrence Berkeley Laboratory. Part of this work was performed by the subsubcontractor, RAI Research Company.

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This report was done with support from the Department of Energy. Any conclusions or opinions expressed in this report represent solely those of the author(s) and not necessarily those of The Regents of the University of California, the Lawrence Berkeley Laboratory or the Department of Energy.

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