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STUDY TO INVESTIGATE AND IMPROVE THE ZINC ELECTRODE FOR SPACECRAFT ELECTROCHEMICAL CELLS

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ABSTRACT

This program involves an investigation of the absorption and transport of zincate in separator membranes. The growth of dendritic zinc through separators is correlated with the deposition of zinc in free electrolyte and the absorption and transport of zincate through the membranes.

Radiation Applications, Inc. (2.2 XH) gives similar absorption effects for zincate as do the other membranes tested during this program. The addition of the surfactant, Emulphogene BC-610, does not affect the absorption of zincate in cellophane.

The diffusivity of zincate through six membranes was measured. The diffusion coefficient for zincate in the separators tested was approximately directly proportional to the conductivities of the membranes.

Zinc penetration tests on various separators indicate that the overvoltage at which zinc penetration of the membrane occurs has an inverse relationship to the diffusivity of zincate in the membrane.

The cycling of cells on a scanner, using -150 mV (w.r.t. to a zinc reference) as a cut-off on the zinc electrode resulted in penetration of cell membranes after 14 cycles.

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1. INTRODUCTION

Work to date indicates that zinc deposition occurs in a separator whenever the rate of diffusion of zincate to the metal substrate from the ambient electrolyte of the negative plate falls below the rate of zincate diffusion in the separator. Once the overpotential is sufficiently high for zinc deposition to occur in the membrane, the rate of zinc growth in the membrane will be determined by the concentration and diffusivity of zincate in the membrane. During the present report period, the diffusivity of zincate in various separators was determined. The separators investigated were C-19 (YEC), PUDO-300 (DuPont), 2.2 XH Series Z (R.A.I.), PVA (Monosol polyvinylalcohol) C-3 and 9107/5 (Borden Chemical Co.). The membranes were screened for zinc penetration by a potentiostatic method.

2. TECHNICAL DISCUSSION

2.1 Absorption Isotherms of Zincate in Separators

The zincate absorption studies were extended to include Radiation Applications, Inc. 2.2XH (Series 2) membranes in 44% KOH and Du Pont PUDO 300 in 44% KOH saturated with BC-610 Emulphogene (General Aniline & Film Co.). The experimental procedures are described elsewhere.(1)

Figure 1 shows a plot of the concentration of absorbed zincate per liter of absorbed KOH, versus the concentration of zincate in the ambient electrolyte for both separators.

It can be seen that addition of Emulphogene BC-610 to the electrolyte does not affect the concentration of absorbed zincate in PUDO-300. The 2.2XH material displays absorption characteristics for zincate which are similar to the other membranes tested in this program (e.g. Cellophane). The separation coefficient for zincate is 0.63, as determined by the slope of the plot in Figure 1.

2.2 Zincate Diffusion in Separators

Since the rate of diffusion of zincate to a growing dendrite in a separator will determine the rate of growth through the separator, it is important to know the zincate diffusivity in the separator. The diffusivity of zincate was determined for the following separators: Du Pont PUDO-300, Yardney Electric Corp. Ag treated PUDO-300 (C-19), Borden Chemical Co. C-3 and 9107-5, unplasticized polyvinylalcohol (Monosol PVA, General Film Corp.) and Radiation Applications, Inc. grafted polyethylene (2.2XH Series 2).

The above separators were cut into pieces 3" x 3" and soaked for three days in 44% KOH solution containing 1.0 M zincate. The separators were then dried by toweling and mounted in a two-compartment diffusion cell (see Figure 2). One compartment of the diffusion cell was filled with 17 cc 44% KOH + 1.0 M ZnO, while the other compartment was filled with 17 cc of 44% KOH. Arrangements were made for stirring the solution on the zincate dilute side of the membrane by bubbling purified nitrogen through a capillary. Samples of the solution (0.2 cc) were removed from the zincate-dilute compartment periodically. The samples were dissolved in a solution containing 1N NH_4 OH + 1N NH_4Cl (50 cc). The ammoniacal zinc solution was then analyzed polarographically. The amount of zincate that had penetrated the sample was determined. Corrections were made to take into account the volume of the samples removed.

Diffusivity measurements were also made for PUDO-300 and C-19 in 31% KOH. In this case, the membranes were soaked in 31% KOH + 0.6 M ZnO. In the diffusion cell the ambient on the zinc rich side of the membrane was 31% KOH + 0.6 M ZnO, while the electrolyte on the zinc dilute side of the membrane was 31% KOH.

The reason for presoaking the membranes in zincate solutions instead of pure KOH was to eliminate any zincate absorption effects in the membranes during measurements. The possibility exists that such effects could interfere with the measurement of the zincate diffusivity in the membrane.

Figure 3 shows a schematic representation of the concentration profile for zincate that is encountered in these measurements. The permeation process consists of the following steps:

1. Transfer of zincate from the electrolyte at x=0 to the membrane at x=0.
2. Diffusion of zincate through the separator from x=0 to x=L.
3. Transfer of zincate from the membrane at x=L to the electrolyte at x+L.

   Our previous work(1) shows that the concentration of zincate inside the membrane at x=0 (C_o^M) is not equal to the concentration of zincate in the ambient electrolyte at x=0 (C_o^E). The relationship between these two parameters is

$$C_o^M = kC_o^E \qquad \underline{\text{Equation 1}}$$

Other work in this laboratory shows that the rate of permeation of zincate through cellulosic membranes is inversely proportional to the thickness of the membranes. Thus, it can be concluded that the diffusion process is the rate determining step in the permeation process. If Q is the quantity of zincate that has penetrated a membrane, then the flux of zincate (J) is:

$$J = \frac{Q}{At} \qquad \underline{\text{Equation 2}}$$

where A is the area through which the penetration takes place and t is the time for the quantity (Q) to penetrate. Also,

$$J = \frac{P}{L}\,(C_o^E - C_L^E) \qquad \underline{\text{Equation 3}}$$

where C_L^E is the concentration of zincate in the electrolyte at x=L, L, the membrane thickness, and P, the permeation constant for the membrane. For the experimental conditions chosen $C_L^E \ll C_o^E$ then

$$J = \frac{PC_o^E}{L} \qquad \underline{\text{Equation 4}}$$

Also

$$J = \frac{DC_o^M}{L} \qquad \underline{\text{Equation 5}}$$

$$= \frac{DkC_o^E}{L} \qquad \underline{\text{Equation 6}}$$

Combining Equation 2 and Equation 6 gives

$$D = \frac{QL}{AtC_o^E k} \qquad \underline{\text{Equation 7}}$$

Figures 4-7 give plots of Q versus t for the various membranes. Table 1 gives values of J, P, k and D for the various membranes.

TABLE 1

	SEPARATOR	J moles/cm^2/sec	L cm x 10^3	P cm^2/sec	k	D cm^2/sec
44% KOH	C-19(YEC)	1.04×10^{-8}	7.61	7.92×10^{-8}	0.65	1.2×10^{-7}
	PUDO-300(DuPont)	1.04×10^{-8}	7.61	7.92×10^{-8}	0.695	1.13×10^{-7}
	PVA(Monsanto)	5.15×10^{-9}	5.59	2.88×10^{-8}	0.845	3.41×10^{-8}
	C-3(Borden)	1.97×10^{-9}	5.08	7.78×10^{-10}	0.0925	8.4×10^{-9}
	9107/5(Borden)	1.53×10^{-10}	5.08	1.34×10^{-8}	-	-
	2.2XH(R.A.I.)	1.79×10^{-9}	3.81	7.5×10^{-9}	0.285	2.63×10^{-8}
31% KOH	C-19	1.53×10^{-8}	7.61	1.95×10^{-7}	0.72	2.71×10^{-7}
	PUDO-(300)	1.53×10^{-8}	7.61	1.95×10^{-7}	0.72	2.71×10^{-7}

D and k values are not given for the Borden Co. material #9107/5. This membrane is a triple laminate and k values are not known for the various components of the laminate.

The zincate diffusivities in the membranes are one to three orders of magnitude lower than the diffusivity in free electrolyte. Figure 8 gives a plot of the diffusivity of zincate in the various membranes versus the membrane conductivities in the electrolyte. It can be seen that the relationship between zincate diffusivity and membrane conductivity is roughly linear. Both parameters are related to the pore size in the membranes; hence, the direct relationship. In the case of zincate diffusion in free electrolyte, the ratio of the zincate diffusivity in 31% KOH to that in 44% KOH was 4.65. In the case of cellulosic membranes (PUDO-300 and C-19) the ratio is 2.26. This result demonstrates the importance of the membrane properties in determining the zincate diffusivity.

2.3 Zinc Penetration of Separators Under Potentiostatic Conditions

During this reporting period, the penetration of separators was investigated under potentiostatic conditions. Figure 9 shows an exploded view of the zinc penetration test cell. The electrical circuit is shown in Figure 10.

The test procedure is as follows:

The separator under test and a sheet of Viskon paper are soaked for at least 24 hours in 44% KOH containing 81 grams of ZnO per liter. The cell is assembled as shown in Figure 9. Electrolyte (44% KOH + 1 M ZnO) is added and the zinc electrode is potentiostatted at the desired potential. The voltage between the platinum screen prior to penetration of the membrane is 1.3 V to 1.5 V. At penetration, the voltage drops by 0.1 V to 0.5 V. The separators tested by this method were as follows: PUDO-300 (Du Pont), silver treated PUDO-300 (YEC C-19), C-3 and 9107-5 (Borden Chemical Co.), and 2.2XH Series 2 (Radiation Applications, Inc.).

All of these separators were tested at -200 mV and -150 mV with respect to the reversible zinc potential. In all cases, zinc penetration through the separator occurred in less than 60 minutes. The time to zinc penetration varied considerably and was very irreproducible. At these potentials, we have considerable hydrogen evolution on the zinc. Apparently, the stirring caused by the hydrogen gassing varied the availability of zincate at the zinc electrode and thus, led to variations in the to zinc penetration. The important fact, however, was that in all cases the deposit was dendritic and that penetration occurred. The deposits were checked under the microscope. The deposits outside the membranes consisted of heavy nodular zinc dendrites, while the deposits in the membranes consisted of fine fern-like deposits. The differences in the deposits were due to the differences in the mass transport parameters for zincate in the free electrolyte and in the separators. Tests were conducted on C-19 separator at -100 mV and -75 mV. At -100 mV the zinc deposit was a mixture of mossy zinc and dendritic zinc. Zinc penetration of the separator occurred after 14 hours. At -75 mV, copious quantities of zinc were deposited, but no penetration of the separator occurred after a period of 36 hours. The deposit in this case was mossy zinc. No dendrites were found. The zinc deposit forced the membrane against the platinum screen. The imprint of the platinum screen could be seen on the separator. However, no penetration occurred.

Since no dendrites were found, it is evident that the deposition occurred under activation-controlled conditions. The fact that no dendrites were found in the deposit confirms this. At a potential where we have activation control of zinc deposition, the rate of zinc deposition will depend on the activity of zincate in the ambient electrolyte and the energy of activation for the zinc deposition process. The absorption tests indicate that the activity of zinc in the membranes is lower than that in the free electrolyte. Furthermore, there is a possibility that the initial state of the zincate ion in the membrane differs from that in the free electrolyte. In such a case, the activation energy for the deposition process would be different in the separator than in the free electrolyte. These two factors would explain the absence of zinc penetration in C-19 under activation-controlled conditions.

In the case of C-3 at -100 mV, no penetration occurred over a period of 54 hours. Here we had diffusion-controlled conditions for zinc deposition. However, the flux of zincate from the C-3 is very small, as indicated by the diffusivity measurements. The small, steady state current obtained for C-3, as compared with that for C-19, bears this out. This small flux of zincate was inadequate to initiate the growth of a dendrite in the C-3.

These tests will be continued and the potential below which no penetration occurs will be determined for the various separators.

2.4 Controlled Potential Cut-Off for Silver-Zinc Cells

The fact that it appears that there is a critical potential below which no zinc penetration through the separator will occur, offers interesting possibilities for the charge control of silver-zinc cells. During the last reporting period we procured a scanner which will cut off cells on charge, either when the cell voltage reaches a particular value or when the zinc overvoltage reaches a certain preset value.

A total of 36 10 AH silver-zinc cells was constructed for test on this program. The cells consisted of four positives and five negatives. The positives were enclosed in a bag of non-woven nylon, wrapped with five turns of separator and incorporated in the cell packs with the negatives in a normal "U" wrap. The cell pack was contained in a plastic case. A separate "U" (a reference electrode "U"), consisting of three turns of separator, was also incorporated in the case. A silver electrode was inserted in one arm of this "U" and a dry charged zinc electrode was inserted in the other arm of the "U". The completed cell case had four terminals: a positive, a negative, a zinc reference terminal, and a terminal for the silver electrode in the reference electrode "U". This silver electrode was incorporated to charge up the reference electrode if it self-discharged. This cell group consisted of six groups of six cells each. All factors in each cell were constant except the separator. The separators incorporated in these cells were PUDO-300 (Du Pont), C-19 (YEC), PVA (Monsanto

"Monocell"), C-3 and 9107/5 (Borden Chemical Co.), and 2.2XH grafted polyethylene (Radiation Applications, Inc.).

Preliminary tests were made with this scanner on 12 cells (two from each group). The cells were cut off at -150 mV with respect to the zinc reference. The cells were charged at the C/10 rate to this cut-off and discharged at the C/2 rate for one hour. After 14 cycles, penetration of the separator had occurred in all cells. When the cells were cycled on this regime the cell voltage always exceeded 2.1 volts before the zinc reached -150 mV. Gassing occurred on both positives and negatives before the cut-off was reached. Tests have been initiated on a second batch of 12 cells (two from each group), using -75 mV as the cut-off on the zinc electrode. In the first cycle the cell voltage exceeded 2.1 V before the cut-off was reached on the zinc electrode. However, on subsequent cycles the zinc cut-off was reached before the cells reached 2.05 V. The cells have now been cycled for six cycles. No gassing was observed on either the positives or negatives after cycle #1.

In using the zinc overvoltage as a cut-off, we charge up all the available zinc oxide on the first charge. When a low zinc cut-off is used (e.g. -75 mV) deposition of zinc does not occur in the separator and the cut-off is reached when the concentration of zinc in the vicinity of the negative plate falls below a certain value. In the case of the -150 mV cut-off, zinc deposition occurs in the separator. The cut-off will not be reached until the flux of zincate through the separator from the positive compartment is reduced below a critical value. Furthermore, above -100 mV the efficiency for zinc deposition is reduced as is indicated by the gassing on the negative plate. This inefficiency for zinc deposition above -100 mV, together with the fact that deposition occurs in the membranes, permits the silver electrode to come up to the oxygen evolution potential on every charge. However, when a cut-off of -75 mV is used, the plating inefficiency is at a minimum and no deposition of zinc occurs in the separator. The result is that after the first charge the silver electrode will not reach the gassing potential on charge. This result demonstrates the inherent danger of using the cell voltage alone as the cut-off for silver-zinc cells. Inter-electrode imbalance occurs in silver-zinc cells with cycling. This imbalance results in a buildup of zinc on the negative plate which will eventually cause the zinc electrode to come up on charge before the usual cut-off voltage for the silver-zinc cell is reached. Also, Oshe et al have found that if a silver-zinc cell is left on discharged stand for a period of time, the zinc electrode will polarize on subsequent charges before the cut-off voltage for the cell is reached.

3. SUMMARY AND CONCLUSIONS

The absorption of zincate has been determined for Radiation Applications, Inc. 2.2XH (Series 2) separator. The absorption effects are similar to those of other membranes tested in this program. The addition of Emulphogene does not affect the absorption of zincate in cellophane.

The diffusivity of zincate in the various membranes has been determined. The diffusion coefficient for the various membranes is approximately directly proportional to the conductivities of the membranes in the alkaline electrolyte. Both parameters are apparently related to the pore sizes of the membranes.

The penetration of zinc through membranes has been investigated, using a potentiostatic method. At this stage, it appears that membranes having a low diffusivity for zincate require a higher overvoltage for penetration to occur. In the case of cellulosic materials, an overvoltage in excess of 75 mV is required for penetration to occur.

The cycling of cells on a scanner, using -150 mV as a cut-off on the zinc electrode, resulted in penetration of all membranes after 14 cycles. Tests are now being conducted, using -75 mV as a cut-off for the zinc electrode. These tests will be continued until the end of the program.

REFERENCE

1 Study to Investigate and Improve the Zinc Electrode for Spacecraft Electrochemical Cells, Contract #NAS5-10231, Yardney Electric Corporation, First Quarterly Report.

2 Improved Separators for Silver Oxide-Zinc and Silver Oxide-Cadmium Cells for Spacecraft Application, Borden Chemical Co., Contract #NAS 5-9107.

3 Oshe, A.I. et al. Zhurnal Prikladnoi Khimii. 34 2254 (1961).

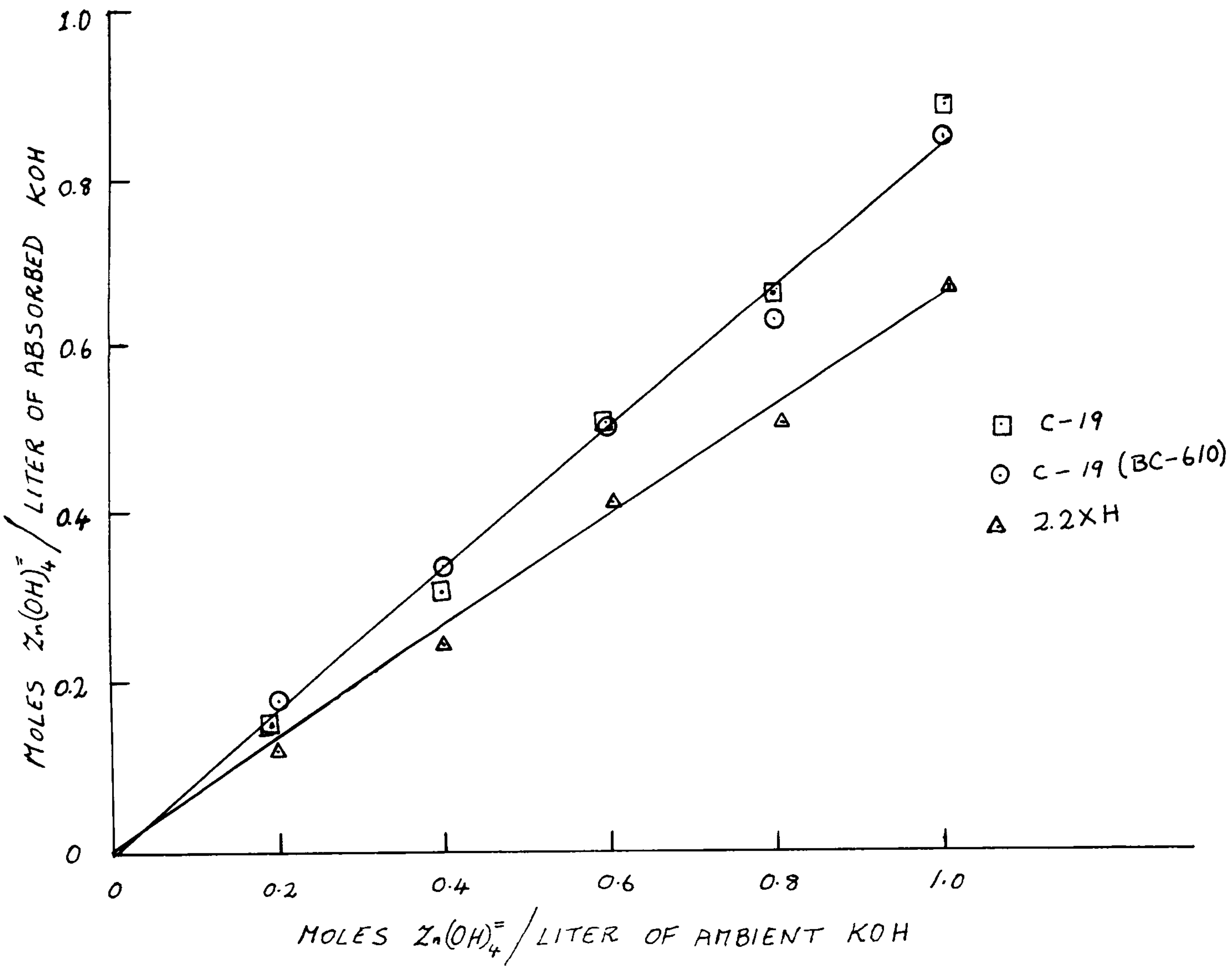

Figure 1. Absorption Isotherms for Zincate in 2.2XH (RAI) and C-19 (YEC)

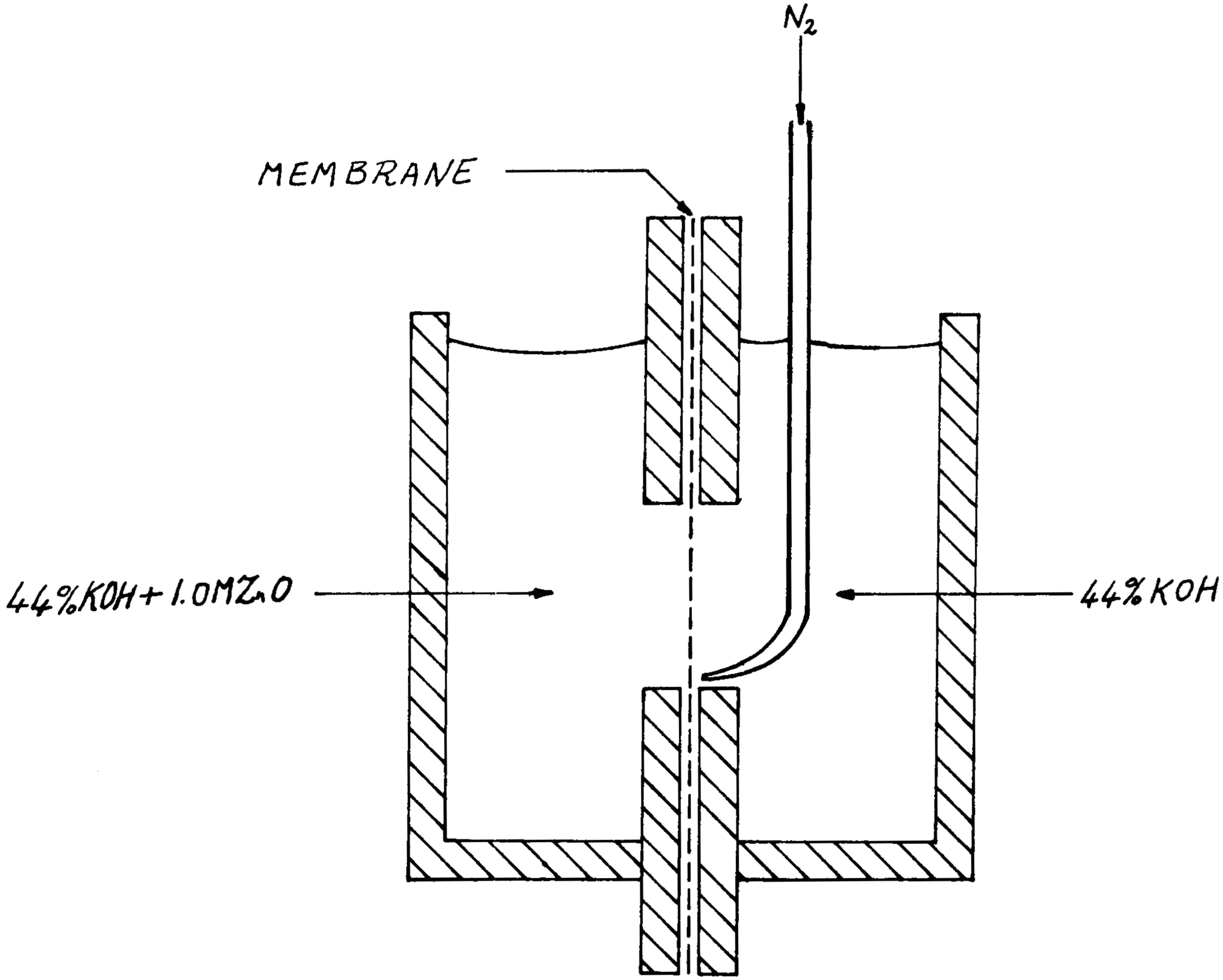

Figure 2. Apparatus for Zinc Diffusion Measurements

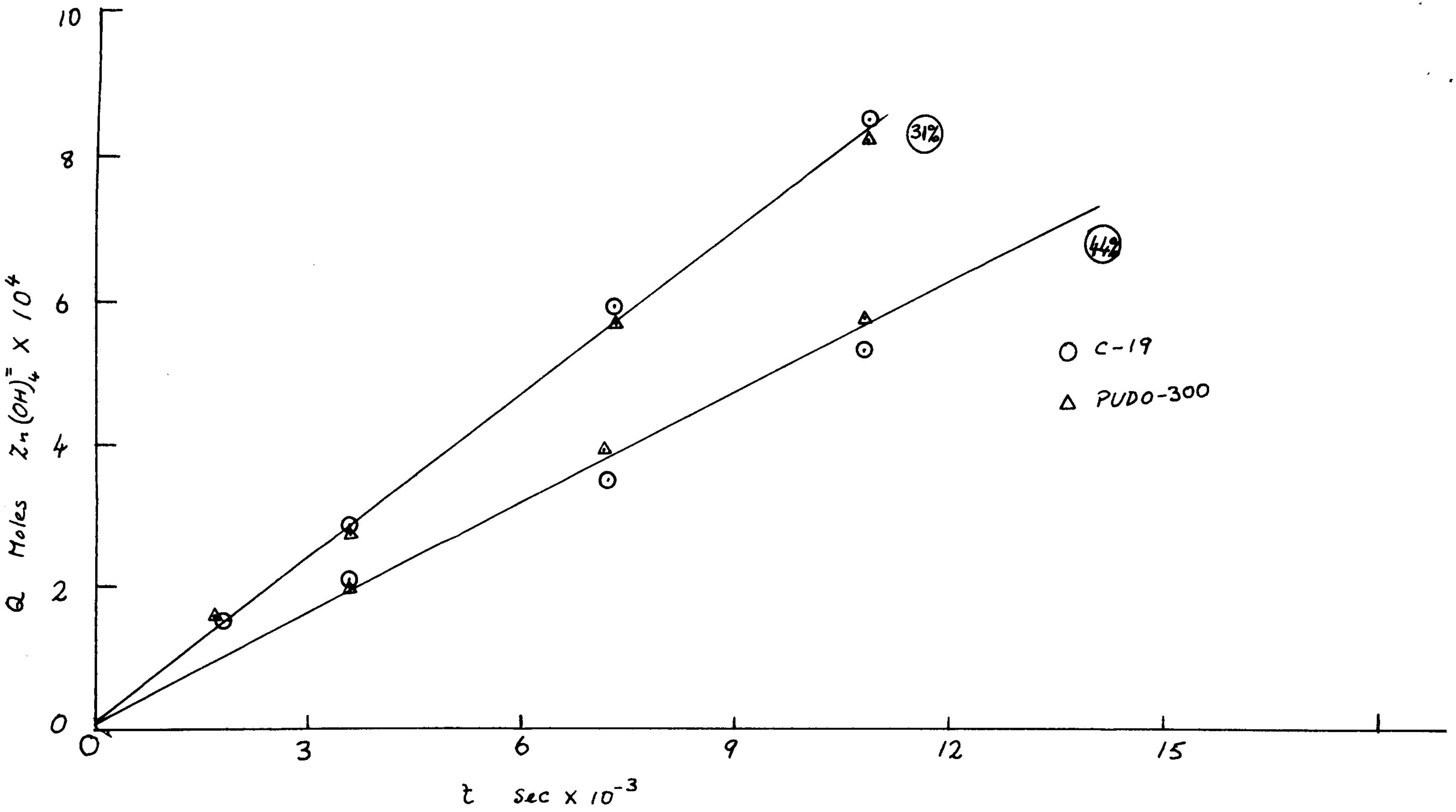

Figure 4. Permeation of Zinc Through PUDO-300 (Du Pont) and C-19 (YEC)

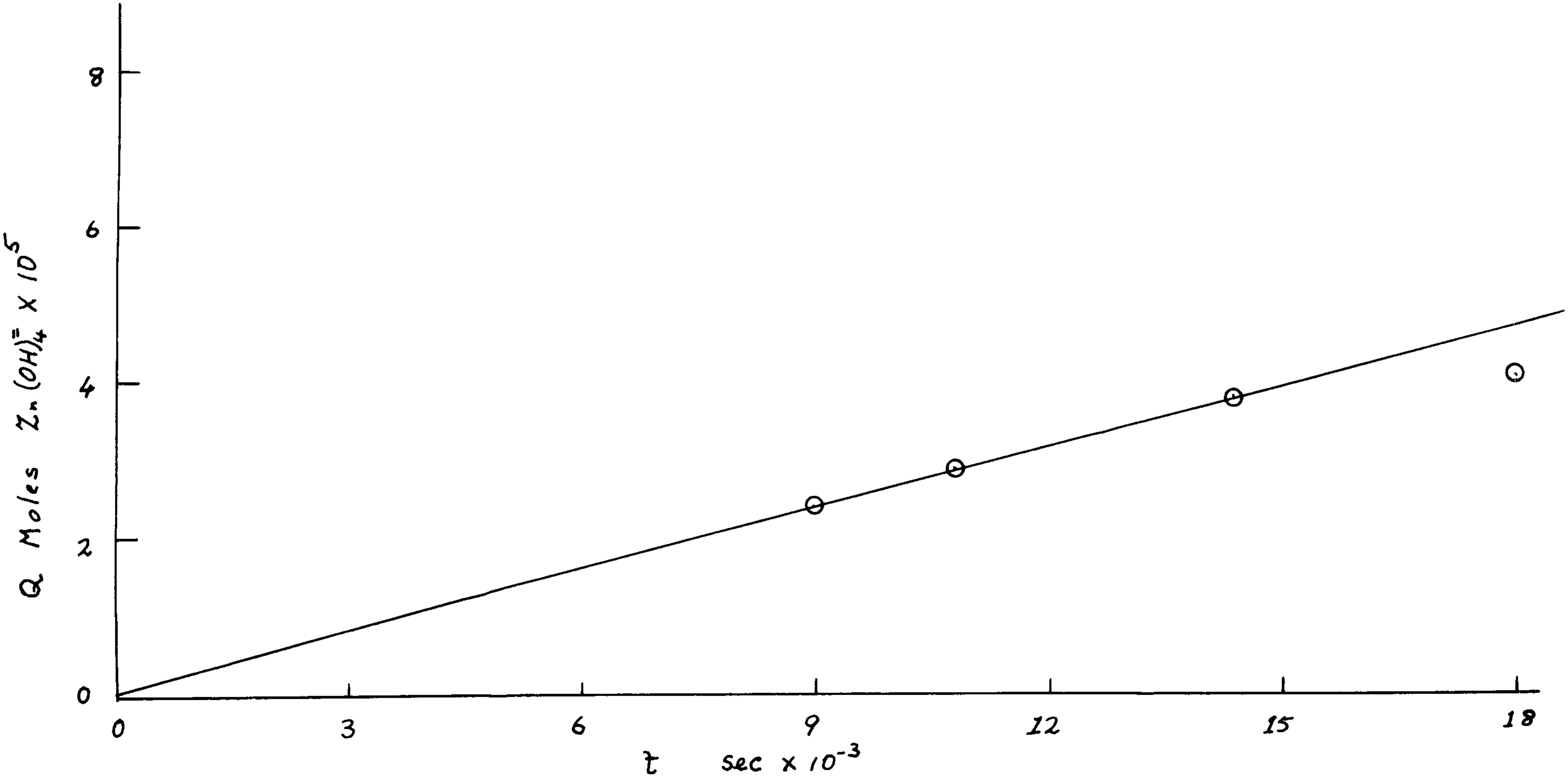

Figure 5. Permeation of Zinc Through PVA (Monsanto "Monocell")

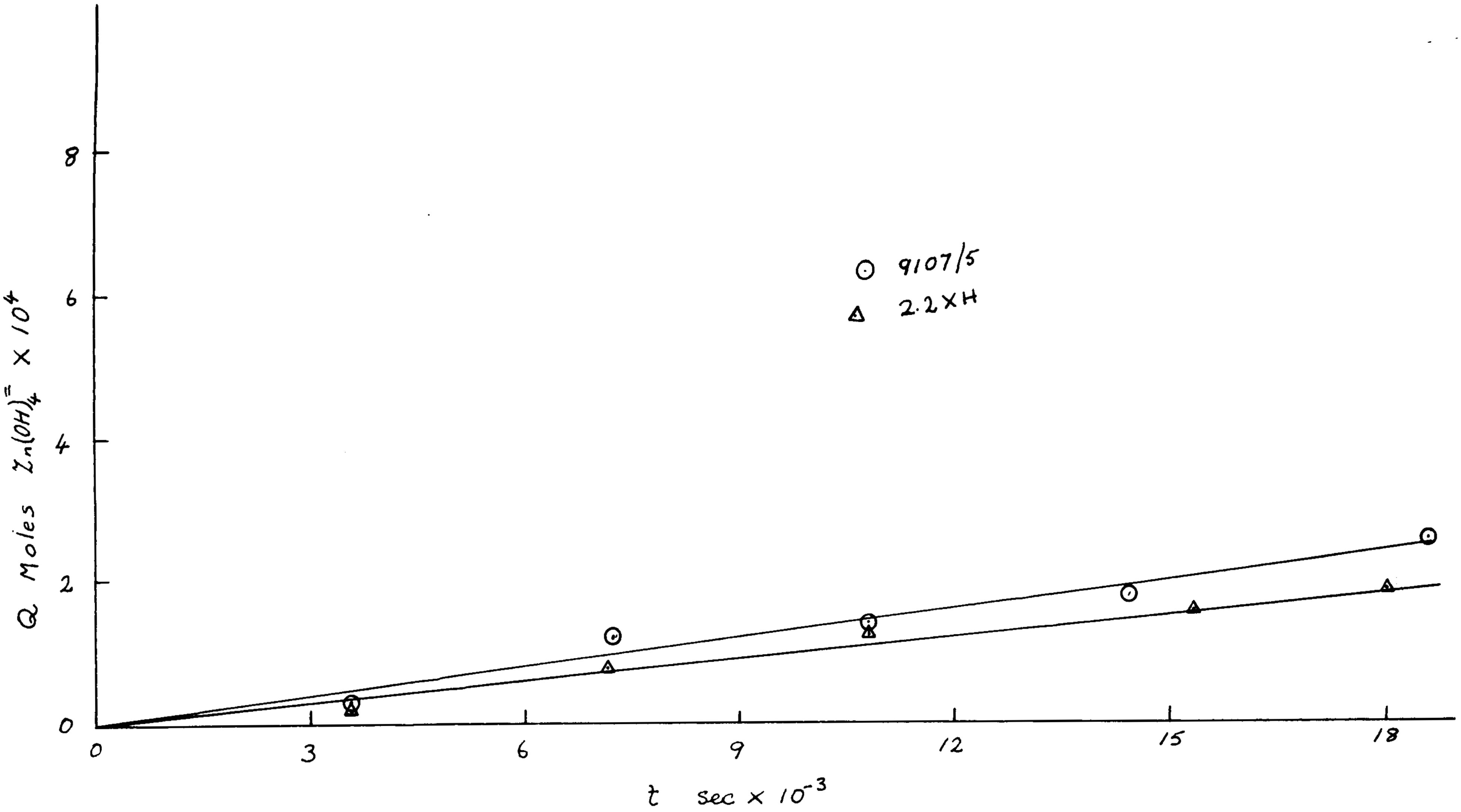

Figure 6. Permeation of Zinc Through 2.2XH (RAI) and 9107-5 (Borden Chemical Co.)

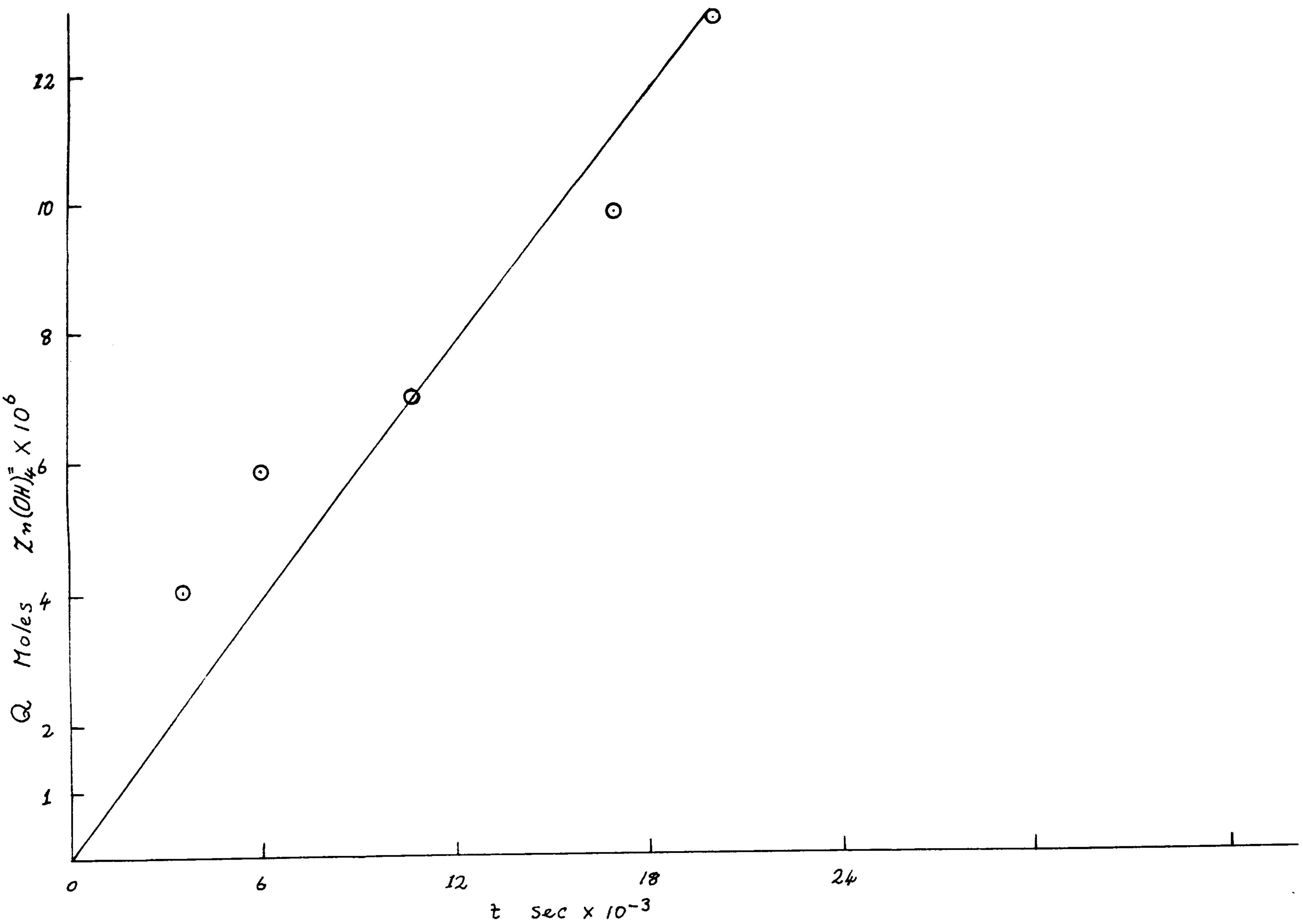

Figure 7. Permeation of Zinc Through C-3 (Borden Chemical Co.)

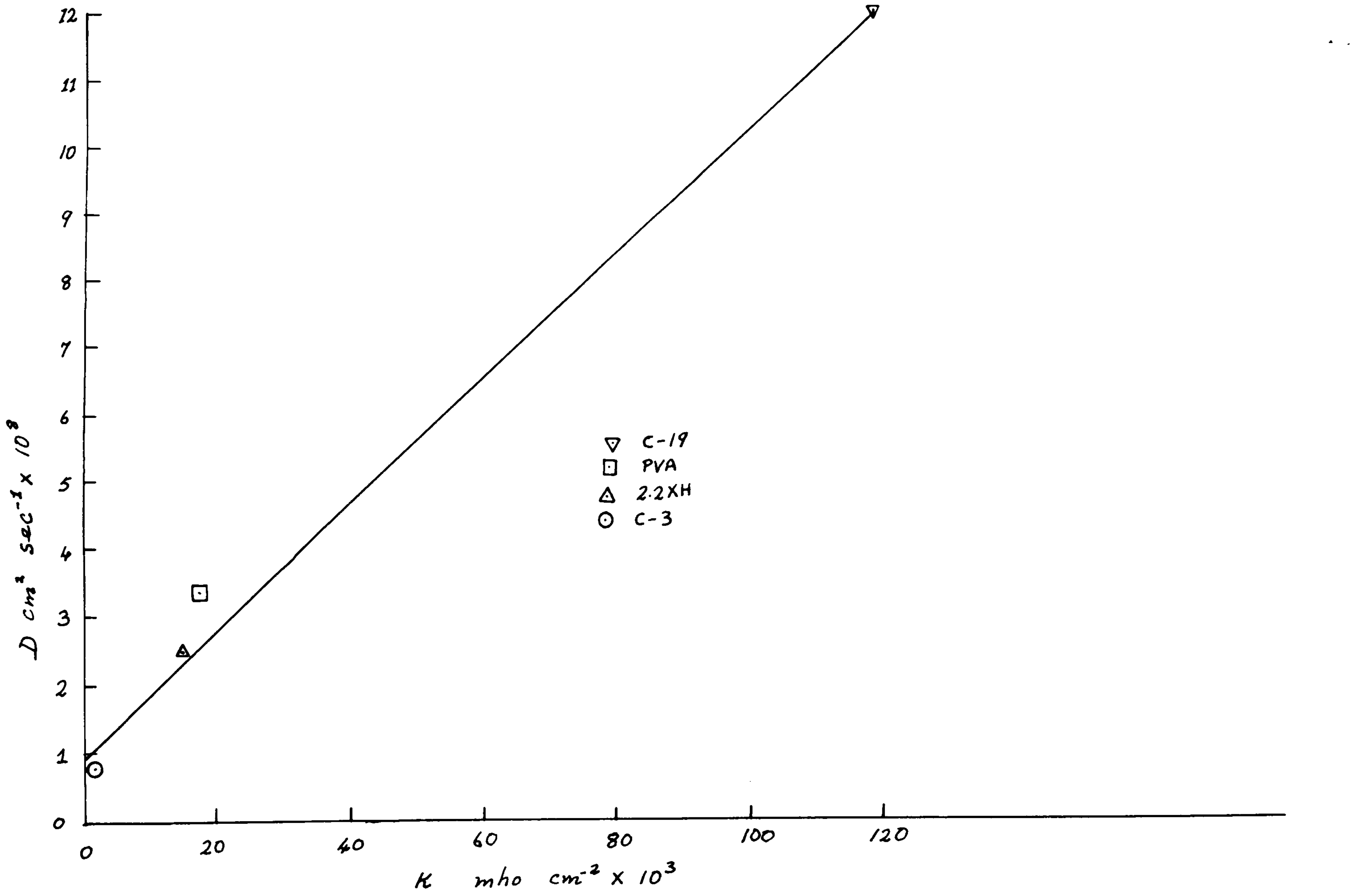

Figure 8. The Diffusivity of Zinc in Separators Versus the Conductivity of the Separator in the Electrolyte

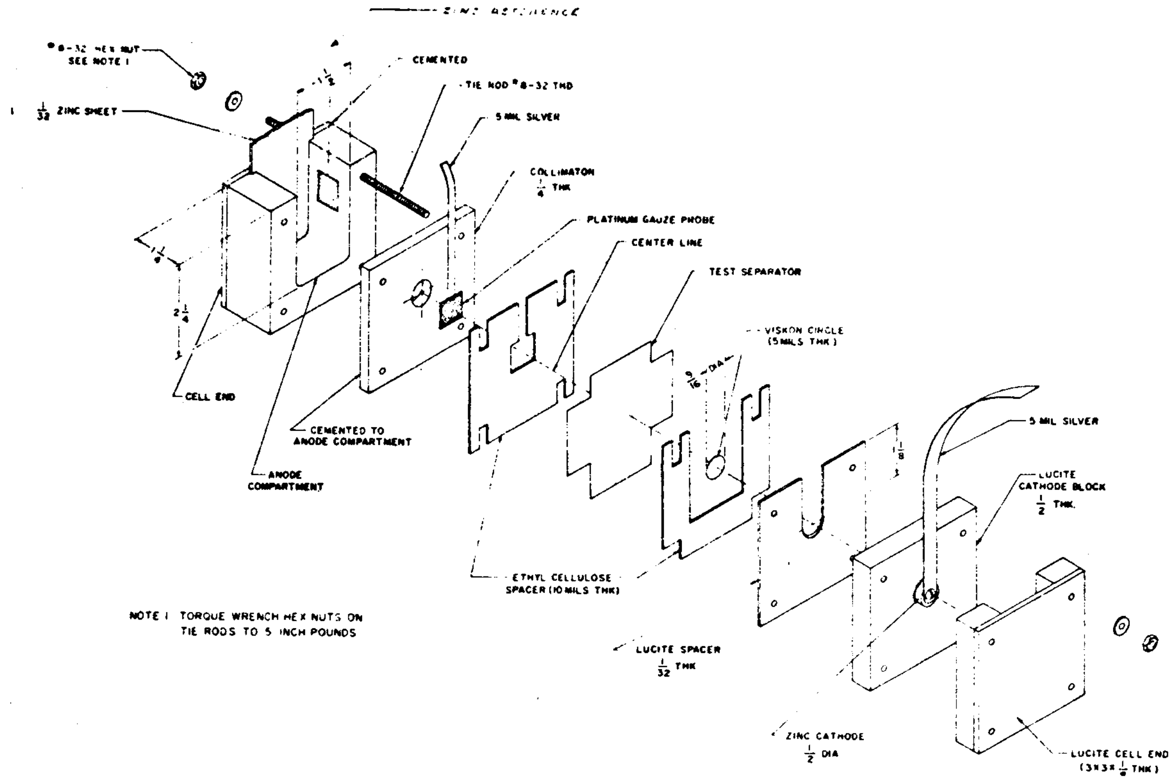

Figure 9. Zinc Penetration Test Cell (Exploded View)

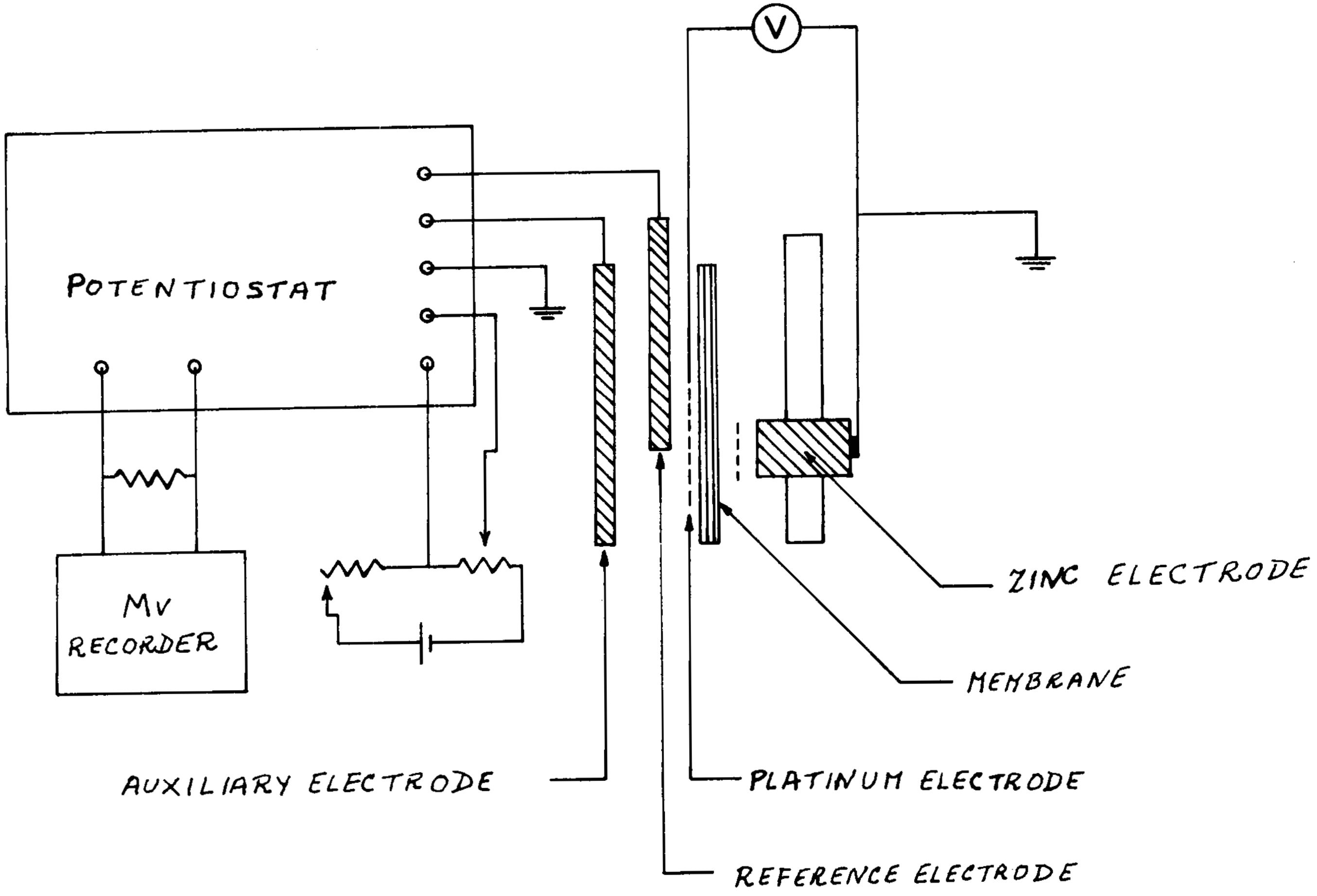

Figure 10. Schematic Representation of the Electrical Set-Up for the Zinc Penetration Test