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ZINC/NICKEL OXIDE BATTERY MEMBRANE
SEPARATOR STUDIES: FINAL REPORT

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Zinc/Nickel Oxide Battery Membrane Separator Studies

by

Douglas N. Bennion
Jerald S. Bradshaw

FINAL REPORT

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to

Lawrence Berkeley Laboratory
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from

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Summary

During this contract, fourteen different macrocyclic compounds were synthesized for possible use in anionic exchange membranes. Several of these compounds were polymerized with polyvinylbenzyl chloride. Two others were used in polyvinyl alcohol membranes.

Work continued to develop a suitable polymer material for the membranes. It was found that polyvinyl alcohol could be cross-linked using a crown-ether dialdehyde as a cross-linking agent to produce a membrane with high ionic conductivity (0.02 mho/cm) and reasonable short-term stability in strong caustic solution at room temperatures. Selectivity of the membrane for hydroxide ions was essentially the same as that in the solution itself. The reason for this was thought to be due to the high water concentration in the membrane.

Two new fabrication methods for polypropylene membranes were investigated and developed. One method involved dissolving the polypropylene powder together with a KOH/crown-ether complex in boiling 1,1,2,2-tetrachloroethane and then evaporating the solvent. With the second technique, a paste of the polypropylene-KOH/crown ether complex-tetrachlorothane mixture was spread in a thin film on a glass plate. The film was placed in an acetone bath to exchange out the tetrachloroethane, and then placed in a dilute KOH/water bath to exchange out the acetone. Membranes made using the first technique showed conductivities of 7×10^{-7} mho/cm to 1.1×10^{-4} mho/cm. These low values were thought to be due to uneven distribution of macrocyclic compounds in the membrane and its low porosity.

Development of a two-dimensional code of a zinc-nickel oxide cell was begun and work is continuing on the code.

Introduction

The purpose of this research is to investigate mass transport processes and their control in alkaline batteries. It has been hypothesized that anionic-exchange membranes would be helpful in decreasing electrode shape change, dendrite formation, and voltage losses in battery systems where semipermeable membranes are used. Consequently, this work was undertaken to 1) develop anionic-exchange membranes which are stable in strong caustic solutions; 2) determine transport and thermodynamic properties of these membranes; 3) demonstrate performance of these membranes in cell tests; 4) develop a computer code that models a zinc-nickel oxide cell; and 5) use the measured transport and thermodynamic properties of these membranes to predict cell performance, comparing these results to those obtained in cell tests.

Anionic-exchange membranes were synthesized by incorporating crown ether and similar compounds into polymer membranes. The principle by which these membranes should work is as follows. The crown-ether compounds are large cyclic molecules which have an electron-rich inner cavity. By introducing a large cation (such as potassium) into this cavity, it is entrapped, thus becoming a fixed positive site. With such fixed positive sites in a membrane, and with the proper polymer membrane structure, anions (such as hydroxide) would move with relative freedom through the membrane, while flow of cations would be much more restricted. The direction of flow of water through the membrane is normally in the same direction as the transport of cations. By increasing hydroxide transport, the transport of water should reverse and go with the hydroxide. All of this would reduce membrane osmotic pumping and undesired movement of positive species such as Zn^{2+} and K^{+}. This would serve to reduce both dendrite formation and electrode shape change associated with zinc electrodes.

Although work has proceeded in all of the areas mentioned earlier, the work performed thus far has largely centered in synthesis of the macrocyclic compounds and membrane development. The basic plan of membrane development and testing has been to 1) synthesize a number of macrocyclic compounds; 2) fabricate membranes with these compounds and test them for ionic conductivity as an initial screening to identify promising candidates; 3) measure the hydroxide transference number of these promising membrane candidates; and 4) measure thermodynamic and transport parameters of several of these membranes.

Difficulty has been encountered in finding a suitable polymer membrane material. Thus far three different candidates have been used, with a number of different preparation methods having been investigated. Problems with the polymers have been: 1) low ionic conductivity (water concentration in the membrane is low); 2) high water concentration; 3) poor long range stability; and 4) low selectivity. Many membranes have been tested for ionic conductivity and the hydroxide transference number has been measured in two of them. As yet a full set of measurements of thermodynamic and transport properties have not been made.

This report emphasizes the efforts made during the second year of the study. During the first year (1) 16 different crown-ether compounds were synthesized. One of these compounds was incorporated into membranes made of either polypropylene or vinyl chloride-vinylidine chloride. Polypropylene membranes were made by complexing the crown-ether with either KOH or KSCN, coating polypropylene powder with the crown-ether-salt complex, and pressing the mixture in a heated press. The vinyl chloride-vinylidine chloride membranes were made by dissolving the same crown-ether-salt complex with the copolymer in tetrahydrofuran, pouring the mixture into a flat dish and evaporating the solvent. Ionic conductivities of these membranes ranged from

5.0×10^{-11} mho/cm for pure polypropylene to 4.0×10^{-4} mho/cm for a polypropylene membrane containing a KOH/crown-ether complex.

A one-dimensional computer code modelling a zinc-nickel cell was also written during the first year. Although a two-dimensional code is needed to fully predict electrode shape change, this one-dimensional code is adequate to describe discharge behavior of the cell and the effect of membrane transport parameters on cell potential and transference number of different ionic species.

During the second year polyvinyl-alcohol was tested as a membrane material. Ionic conductivities of several of these membranes were measured and found to be in the acceptable range for battery applications (0.03 mho/cm). These membranes absorbed an enormous amount of KOH/water solution (up to six times their dry weight). The hydroxide transference number in two of these membranes were measured. It was found that they exhibited essentially the same selectivity for hydroxide as the solution with no membrane present. In addition, these polyvinyl-alcohol membranes tended to degrade after several weeks in strong KOH/water solution at room temperature.

During the past year, work also continued with the polypropylene membranes to improve their conductivity. Three additional macrocyclic compounds were synthesized for use in membranes, and work was begun on a two-dimensional code modelling the zinc-nickel system.

In this report the synthesis of the macrocyclic compounds will be described first. Membrane fabrication and testing will then be treated, followed by discussion of code development.

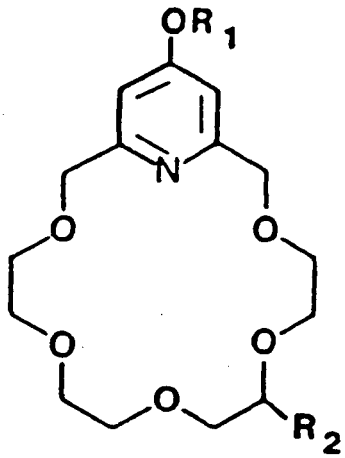
Synthesis of Macrocyclic Compounds

Compounds 1 - 12 (shown in Figure 1) were prepared during this past year. The synthesis of compounds 1 - 7 is described in at least five papers. One paper has been published (2), two are in press (3,4), and two others are being prepared (5,6). Compounds 1 and 8 were reacted with polyvinylbenzyl chloride to give polymers 11 and 12, respectively. We plan to form the polymer containing 5 in the same manner. Compounds 4, 7 and 10 can be copolymerized with propylene or styrene to form a polymeric material containing these metal-cation complexing agents. The incorporation of potassium-complexed polymers 11 and 12 into polypropylene would give a more even distribution of salt in the polymer and thus a higher transport of anions.

Membrane Fabrication and Testing

Polypropylene Membranes As described earlier, polypropylene membranes were previously made by melting a mixture of the crown-ether that was complexed with either KOH or KSCN and polypropylene, and then pressing the melt in a mold. It was found that membranes with crown-ether-KOH salts produced membranes with the highest conductivities, so the KSCN complex was not further studied.

It was also found that these polypropylene membranes exhibited conductivities that were too low for practical applications. The low conductivities could possibly be explained by the hydrophobic nature of polypropylene and uneven distribution of the macrocyclic molecules throughout the membrane. Since water was present in the membrane only in relatively low concentrations (less than 1% of the membrane dry weight), the mobility of ionic species would be reduced. Before melting, the KOH-crown ether salt was only coated onto the polypropylene powder, and not intimately mixed with the

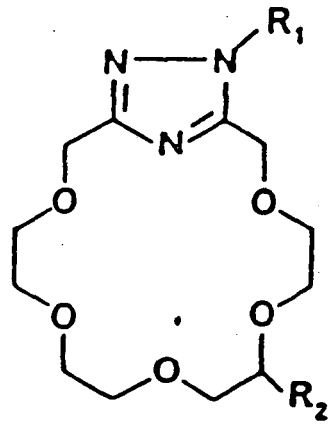


1, R_1, R_2= H

2, R_1 = H, R_2 = C_8H_{17}

3, R_2 = H, R_1 = C_8H_{17}

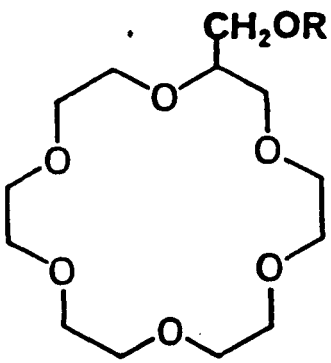
4, R_2 = H, R_1 = $CH_2CH{=}CH_2$



5, R_1 = R_2 = H

6, R_1 = H, R_2 = C_8H_{17}

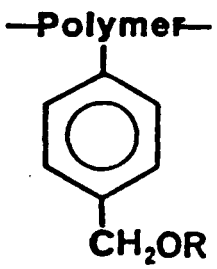
7, R_2 = H, R_1 = $CH_2CH{=}CH_2$



8, R = H

9, R = $CH_2CHC_{10}H_{21}$ (OH)

10, R = $CH_2CH{=}CH_2$



11, R = PYRIDINO 18-CR-6 (#1 ABOVE)

12, R = 18-CR-6 (#8 ABOVE)

Figure 1. Macrocyclic Compounds

polymer. The time that the powder was heated in the press may not be sufficient for the macrocyclic molecules to diffuse into the polypropylene. There could also be a thermodynamic limitation; i. e. the macrocycles may tend to aggregate; and 3) closed membrane structure, resulting in lower ionic mobilities. The actual reason for low conductivities is probably a combination of all three of these factors.

Two fabrication methods were devised to avoid the difficulties mentioned above. It was found that polypropylene can be dissolved with the crown-ether complex in 1,1,2,2-tetrachloroethane (TCE). Consequently a new fabrication technique was developed. The polypropylene and crown ether-KOH complex were introduced into the TCE, and the mixture was boiled until all of the solids were dissolved. The mixture was then placed in a shallow flat-bottomed dish, and the solvent was evaporated in a constant-temperature oven set at 120° C (20° C below the boiling temperature of TCE). The resulting film was then carefully peeled from the pan.

It was found that the concentration of polymer in the solvent, as well as the initial pan temperature had an effect on membrane quality. By choosing low concentration and low initial concentration, it was possible to prepare uniform membranes.

Membranes prepared using this technique showed conductivities of between 7×10^{-7} to 1.1×10^{-4} mho/cm. It was thought that the reason for these low conductivities was 1) the very closed structure of the polymer, which caused low ionic mobility through the membrane; and 2) again, uneven distribution of the macrocycles throughout the membrane. Due to the lower solubility of the polypropylene as compared to the crown-ether, as the solvent evaporated from the mixture, the first precipitate was almost entirely polypropylene. Later, the macrocyclic compounds precipitated. Thus, a layer of almost pure

polypropylene was formed, which proved to be an effective barrier to movement of ionic species. We believe the polymers containing macrocyclic ligands (11 and 12) could alleviate these problems by having the macrocycle more evenly distributed throughout the membrane.

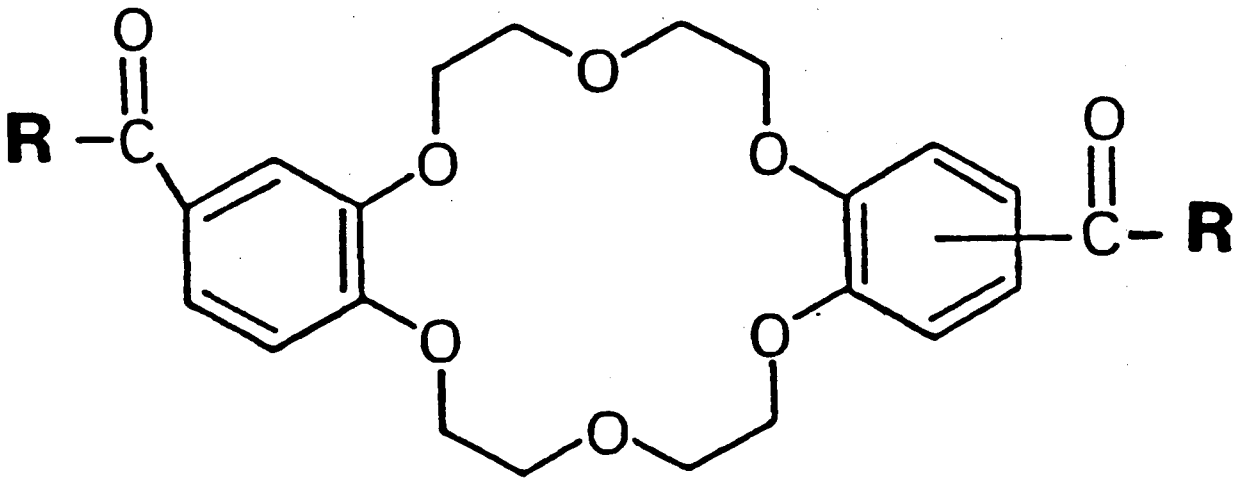
A third membrane fabrication technique was tried to provide a more open membrane structure and even distribution of macrocyclic compounds. The crown ether-KOH-polypropylene mixture in TCE was prepared as before, in the highest concentration possible. A quantity of the viscous mixture was placed on a glass plate with raised edges approximately 0.7-mm high. A channel 0.7-mm deep was thus created. A flat edge was placed along the top of the channel, and the viscous mixture was allowed to slide under the channel to create a layer of viscous mixture of uniform thickness. Before the solvent evaporates, the plate with the viscous layer is immersed in acetone to exchange the TCE for acetone. After the acetone had had sufficient time to replace the TCE in the film, the film was then placed in a dilute KOH/water solution. The acetone was replaced by KOH and water in this step. The first membranes made in this manner did indeed have an open structure, but they did not have sufficient mechanical strength for testing. This technique shows some promise, as polypropylene appears to be one of the few materials with long-term stability in aqueous KOH solutions. Further refinement of this technique could produce an optimum balance of mechanical strength, openness of structure and ionic conductivity.

Polyvinyl Alcohol Membranes A search of the literature showed that Sheibley and coworkers (7,8) have found that polyvinyl alcohol (PVA) membranes can be made stable in aqueous solutions by cross-linking PVA with dialdehydes. The uncross-linked PVA is soluble in water. Although the cross-linked membranes are promising in their own right, it was hypothesized that by

using crown ethers with either two methylketo groups or two aldehyde groups (see Figure 2) as the cross-linking agent, a membrane with both high ionic conductivity and selectivity for hydroxide ions could be easily fabricated. Accordingly, a modification of the methods developed by Sheibley et al. (7,8) was used. The procedure is described below.

A quantity of the crown-ether that is sufficient to produce a desired theoretical amount of cross-linking (2-5% of all alcohol groups reacted) was added to PVA. This mixture was then dissolved in an ethanol/water (70/30) solution by heating. Ten weight percent glyoxylic acid was added and the entire mixture was refluxed for 20 - 65 minutes. After heating, the viscous solution was poured into a petri dish (sprayed with a Teflon mold-release agent) and allowed to air-dry overnight. When dry, the petri dish was placed in an oven at 115 C for 20 - 30 minutes. The film was then carefully removed from the petri dish. Using this method a number of membranes were fabricated.

The membranes produced in this manner were yellow in color, and when first made were quite stiff (although not brittle). When soaked in 4.0 M KOH/water solution, they became soft and floppy within minutes. The membranes also absorbed 2 - 6 times their dry weight when placed in such a solution. Although the presence of water in the membrane facilitates ionic transport and is desirable, it is almost certain that these membranes absorbed too much water. The presence of too much water in a membrane would cause undesirable swelling, increasing the mobility of the cations to a point where no selectivity for anions would be achieved. By comparison, a Nafion membrane studied in this laboratory absorbed 0.03 times its dry weight of a 4.0 M NaOH/water solution (9), and the polypropylene membranes containing macrocyclic compounds absorbed 0.01 times (or less) of their dry weight of a 4.0 M KOH/water solution.



A, R=CH_3

B, R=H

Figure 2. Crown Ether Compound Synthesized for Use in Polyvinyl Alcohol Membranes

The ionic conductivity of several of these membranes were tested in a 4.0 M KOH/water solution. Conductivities ranged from 0.01 - 0.03 mho/cm, well within the acceptable range for application in battery systems. These values are in the same range as the conductivities of a Nafion membrane studied in this laboratory (9). The highest conductivity measured for a polypropylene membrane in this study was 0.0005 mho/cm.

The hydroxide transference number for one of these membranes was measured by performing an electrodialysis experiment. The measured transference number for hydroxide was 0.69, essentially the same value as that of hydroxide ion in KOH/water solution without the membrane. This seems to lend evidence to the idea that too much swelling of the membrane had occurred.

It was thought that perhaps a membrane with a higher degree of cross-linking would yield a tighter structure that is subject to less swelling. A membrane with 50 wt. % of compound B shown in Figure 2 (a dialdehyde crown ether) was fabricated. When soaked in a 6.0 Molar KOH/water solution, it absorbed 1.02 times its dry weight - probably still excessive, but less than the previous PVA membranes. The hydroxide transference number of this membrane was measured in an electrodialysis experiment. The result was 0.71 - again, essentially the same as that in KOH/water solution without the membrane. This would seem to be due to the large amount of membrane swelling. It would be desirable to reduce the amount of solution uptake by this membrane by a factor of 30.

An important aspect of any membrane to be used in alkaline batteries is their long-term stability in caustic solutions. It was observed that these membranes did tend to degrade after several weeks of sitting in concentrated KOH/water at room temperature. The stability of PVA could possibly be improved with higher degrees of cross-linking. Publication of this work is in process (10).

Code Development

As mentioned previously (1), a one-dimensional code that models a zinc-nickel system has been written and is functional. However, in order to predict two-dimensional phenomenon such as electrode shape change, current distribution and dendrite formation, work has proceeded to develop a two-dimensional code. Accordingly, numerical methods similar to those of Newman (11) (developed for one-dimensional systems), are being developed for two-dimensional use (12,13). Finite-difference formulations of the two-dimensional problem are being made presently. In addition to the finite-difference approach, a finite-element code is being developed as well. The advantage of finite-element formulation is its ability to handle irregular-shaped grids, such as could occur when dendrites are formed or electrode shape change occurs. Alkire et al. (14) have been successful in modelling electrodes using the finite-element approach. Recently Sani reported that actual dendrite formation and electrode shape change have been predicted using this technique (15). Neither of the codes have been completed yet. Sub-routines for solving the sparse matrices which result from the two- or three-dimensional finite-difference or finite-element formulation of the cell model have been developed (13). This work will be further described later (16).

Conclusions and Recommendations

Work on the polypropylene membranes has shown that a more open structure and higher ionic conductivity must be achieved for these membranes to succeed. More uniform dispersion of macrocyclic molecules must also be achieved.

The polyvinyl alcohol membranes have exhibited high conductivities. They also show a tendency to absorb too much water and degrade after several weeks in KOH/water solution. As yet little selectivity for hydroxide has been observed.

It is felt that the next efforts in developing the macrocycle-containing polymer membranes should be in obtaining a suitable polymer membrane material. The materials investigated were not suitable. There is reason to believe that perhaps both polypropylene and polyvinyl alcohol can be made to work, and that new polymers may be developed which are stable in KOH/water, sufficiently conductive and able to contain or bind the macrocycles. Further research is needed to find a suitable polymer base for these membranes. Once a suitable polymer membrane material is found the ionic transport behavior of these membranes can be investigated.

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Journal Publications from this Work

1. Nakutsuji, Y., Bradshaw, J.S., Tse, P-K, Arena, G., Wilson, B.E., Dalley, N.K., Izatt, R.M., "New Proton-Ionizable Macrocyclic Ligands. Synthesis, Basicity, Reactions, and Structures of Two Azo Crown Ethers containing the 4-Hydroxypyridine Group," J. Chem. Soc., Chem. Commun., 749 (1985).

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7. Bennion, D.N., LaFollette, R.M., "Modelling of Zinc-Electrode Processes in Alkaline Batteries," in preparation.

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