

Aromatic Ionomer Membranes: II. Evaluation as Separators for Advanced Alkaline Water Electrolyzers

A. E. STECK and H. L. YEAGER, *Department of Chemistry, University of Calgary, Calgary, Alberta, T2N 1N4 Canada*, F. W. HARRIS, *Institute of Polymer Science, University of Akron, Akron, Ohio*, R. K. GUPTA, *Daychem Laboratories, Dayton, Ohio*, and A. EISENBERG and E. BESSO, *Department of Chemistry, McGill University, Montreal, Quebec, Canada*

Synopsis

The sorption and transport properties of newly developed aromatic carboxylate polymers have been investigated in the context of their application as membrane separators for water electrolyzers. Conductance measurements of aromatic carboxylates of various equivalent weights have been performed as a function of current density, temperature, and electrolyte environment. Results have been compared with those for Nafion 117. The sorption results in dilute and concentrated solution show large water and electrolyte uptake for the aromatic carboxylate films. Furthermore, relatively large sodium ion self-diffusion coefficients have been found in both dilute and concentrated solution environments. The results of these measurements are characteristic of microporous films. The dc conductance behavior of the aromatic carboxylate ionomers is quite different from that found for nonporous 1150 equivalent weight Nafion membranes. This difference is caused primarily by the microporous structure of the aromatic carboxylates, which results in large membrane specific conductances.

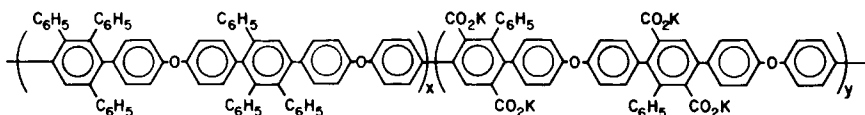
INTRODUCTION

The development of new and more efficient water electrolyzer plants is vital in order to meet the anticipated, enhanced demands for hydrogen as a chemical feedstock, process gas, clean fuel, and an energy carrier. In addition, recent large increases in the cost of fossil fuels have made water electrolysis increasingly attractive for the production of hydrogen. At present, the best method for hydrogen production from water is direct electrolytic water decomposition using potassium hydroxide solution as the electrolyte. All other processes are still far away from technical realization.¹ A recent review of developments in advanced electrolyzer technology² has concluded that significant gains in the efficiency of hydrogen production can be achieved by an increase of the cell operating temperature. The power consumption for operating water electrolysis cells is directly proportional to the cell voltage. Increasing the electrochemical cell operating temperature allows a general improvement of the operating energetics of hydrogen production mainly by reducing the thermodynamic decomposition voltage and electrode overpotentials and by increasing the separator conductance.³ Present electrolyzers normally operate at 60–90°C at ambient pressures

Present address: A. E. Steck, Ballard Technologies Corporation, 1164 15th Street West, North Vancouver, V7P 1M9 Canada

using concentrated KOH electrolytes.⁴ It would be desirable to increase the temperature and pressure of operation to 150–200°C and 30 bar. However, no commercial separators exist at this time which can withstand these extreme conditions for prolonged periods. For example, asbestos diaphragms have been shown to disintegrate at temperatures higher than 100°C.^{5,6} Several new materials are under active investigation including the Nafions and potassium titanate.^{7,8} The former suffers from the disadvantage of being extremely expensive, and only preliminary performance results are available for the latter, so that no critical evaluation can be made at this time. Thus, the successful commercialization of advanced alkaline electrolyzers hinges on a breakthrough in separator technology. Separator materials to be used in alkaline electrolysis cells are expected to have the following properties: good temperature stability (100–200°C), chemical inertness in highly alkaline solution, stability towards oxygen, mechanical strength, good wettability, high ionic conductivity, low electronic conductivity, and reasonable cost of production. At the present time no single material possesses all of these properties.

One excellent possibility for membrane materials in such applications are aromatic ionomers such as the phenylated polyphenylenes containing carboxylate sites. The general formula is given by



Scheme I.

where x and y can be varied to produce materials of different ion exchange capacities. Their synthesis has been described previously.^{9–11} These polymers, which were originally prepared for possible use as windshield materials on supersonic aircraft, can be cast into tough, flexible films that display outstanding chemical and thermal stability.¹⁰ The methods of membrane preparation, preparation of the carboxylated polyphenylenes, and their structural and mechanical properties have been published in a preceding paper.¹¹

Here, the sorption and transport properties of these materials, in the context of their application as membrane separators for alkali water electrolyzers, are reported. Preliminary results have been described elsewhere.¹² Three types of experiments have been employed to evaluate these membranes in solution environments: sorption of water and electrolyte, ionic self-diffusion, and electrical conductance measurements. To be a valuable indicator of the performance of separators in working cells, the conductance measurements were carried out under the severe operating conditions of advanced electrolyzers.

EXPERIMENTAL

Various polyphenylated aromatic carboxylate membranes of 400, 600, and 800 equivalent weight and of approximately 0.015 cm thickness were used in this study. The hydrolysis condition used to convert the ethyl ester films into the ionomer membranes was a 50:50 volume mixture of 13.5*M* aqueous sodium hydroxide and ethylene glycol, heated to 190°C at 30 bar

nitrogen pressure. About 4 days were needed to complete the hydrolysis. Sorption and diffusion measurements were performed using the radio-isotope $^{22}\text{Na}^+$, which was obtained as a carrier-free aqueous solution from commercial sources.

The sorption characteristics of aromatic carboxylate membranes were studied in 5.0 and 11.0M sodium hydroxide solution using the following procedure. A membrane piece of 10 cm² surface area and a thickness of 0.02 cm was immersed in the appropriate electrolyte solution containing $^{22}\text{Na}^+$. The membrane sample was equilibrated under magnetic stirring at a temperature of 80°C for the duration of approximately 16 h. The sample was then removed from the solution, its dimension measured, carefully blotted with ashless filter paper, and then counted in a scintillation counter. The water content of membrane samples were determined by measuring the weight loss after drying the samples at 120°C under vacuum. Completeness of dehydration was monitored by infrared spectroscopy. Details of the procedure involved in the determination of ionic self-diffusion coefficients have been described previously.¹³⁻¹⁵

Conductance measurements for these aromatic carboxylate polymers have been performed as a function of current density (0.5–10 kA m⁻²), temperature (100–180°C), and electrolyte environment. The membrane voltage drop has been determined in a Teflon test cell using reference electrodes which were placed on either side of the membrane. A detailed description of the test cell and the procedure to measure dc conductance has been reported elsewhere.^{15,16} For this study, a minor cell modification has been made in that the nickel oxide reference electrodes were replaced by palladium–silver wire electrodes.^{17,18} These electrodes were built with a 24-gauge palladium (75%)–silver (25%) alloy wire (Johnson Matthey, Inc.) and sealed with a Teflon heat shrinkable tubing so that approximately 3 mm of the uncovered sensing wire was exposed to the solution.¹⁵

RESULTS AND DISCUSSION

Sorption Studies

The ion exchange capacities and water sorption properties of the 400, 600, and 800 equivalent weight polymer films are listed in Table I. The ion exchange capacities (mmol exchange site per g dry polymer) were determined from the sodium ion content of the polymer in dilute solution using $^{22}\text{Na}^+$ radiotracer. The reciprocal values of the exchange capacities are 410, 637, and 870 (g dry Na^+ -form polymer per mole of exchange site), which correspond well to the nominal equivalent weights. Furthermore, it is seen

TABLE I
Aromatic Carboxylate Polymers, Na^+ form, 0.1M NaOH, 25°C

| Nominal equivalent wt | mmol $-\text{CO}_2^-$ /g dry polymer | Wt % H_2O | mmol $-\text{CO}_2^-$ /mL wet polymer |
|-----------------------|--------------------------------------|---------------------------|---------------------------------------|
| 400 | 2.44 | 66 | 1.10 |
| 600 | 1.57 | 32 | 1.25 |
| 800 | 1.15 | 24 | 0.93 |

that these polymer films sorb surprisingly large amounts of water for ion exchange membranes having carboxylate sites. This water sorption behavior suggests possible microporosity, particularly for the 400 equivalent weight ionomer. The water sorption increases with increasing ion exchange capacity as expected. However, the increase of water content with an increase in ionic character of the polymer is so large that other factors would appear to be involved. It is suspected that the extent of microporosity decreases with increasing equivalent weight as well. Since the 400 EW film sorbs far more water than the 600 EW film, the volume concentration of exchange sites is actually smaller for the lower equivalent weight material. The nature of this sorbed water was discussed in the preceding paper.¹¹

Sorption characteristics for these membranes in concentrated sodium hydroxide solution at 80°C are listed in Table II. The sodium ion concentration in the membrane is the sum of exchange site counterions and sorbed NaOH. Extensive electrolyte invasion is evident from these results. In addition, the dehydrating effects of higher concentrations of caustic are reflected in the water contents of the membranes. Electrolyte sorption strongly increases with decreasing equivalent weight of the ionomer. This is contrary to predictions based on the Donnan exclusion principle. The pronounced decrease in sorption of both water and ions with increasing equivalent weight is again an indication of changing porous character of the three materials. The mole ratio of water to sodium ion-coion is also of interest here. This value is generally much smaller in the polymer phase than the respective value in the equilibrating solution for homogeneous nonporous membranes.¹⁹ This can be ascribed to the lower dielectric constant and less aqueous character of the polymer phase. As seen in Table II, the mole ratios of water to sodium hydroxide in 5 and 11*M* solutions are 10.8 and 4.6, respectively. In nonporous ionomer membranes such as the perfluorinated sulfonate and carboxylate, the ratios are about 4.5 and 2 for these two solution concentrations.¹⁹ The aromatic carboxylate polymers show values which are much closer to the solution ratios, which again suggests microporosity.

Sodium Ion Self-Diffusion in Dilute and Concentrated Solution Environments

Sodium ion self-diffusion coefficients in 0.10*M* sodium hydroxide solution were measured at 0, 25, and 40°C. Results are shown in Figure 1, in which

TABLE II
Aromatic Carboxylate Polymers, Na⁺ form, concd NaOH Solution, 80°C

| Equivalent wt | M_{NaOH} | mmol Na ⁺ /mL polymer | Wt % H ₂ O | mmol H ₂ O/mmol Na ⁺ | |
|---------------|-------------------|----------------------------------|-----------------------|--|----------|
| | | | | Polymer | Solution |
| 400 | 5.0 | 3.08 | 44 | 9.2 | 10.8 |
| | 11.0 | 5.88 | 38 | 4.5 | 4.6 |
| 600 | 5.0 | 2.14 | 27 | 7.6 | 10.8 |
| | 11.0 | 4.10 | 26 | 4.2 | 4.6 |
| 800 | 5.0 | 1.57 | 23 | 8.8 | 10.8 |
| | 11.0 | 2.96 | 19 | 4.3 | 4.6 |

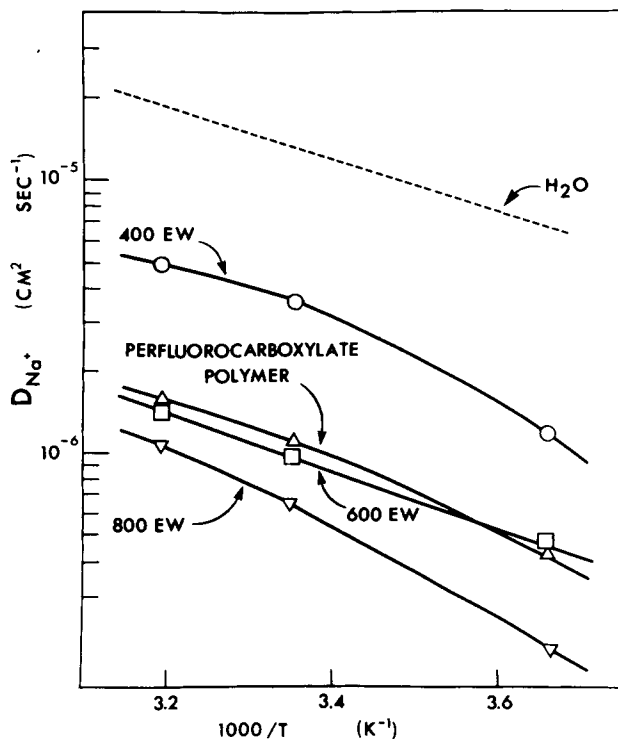


Fig. 1. Arrhenius plots of sodium ion diffusion in aromatic carboxylate polymer films, 0.1M sodium hydroxide solution.

Arrhenius plots of the logarithm of D_{Na^+} are plotted vs. the reciprocal of absolute temperature also shown are values for sodium ion diffusion in water and in a perfluorinated carboxylate polymer membrane.²⁰ The latter material is an ion clustered polymer with excellent ionic diffusion properties, similar to those of perfluorinated sulfonate ionomers.²¹ The aromatic carboxylates are presumably not capable of an ion clustered morphology, but they show relatively large self-diffusion coefficients for all equivalent weights, comparable or even greater than the ones for the perfluorinated carboxylate. Activation energies of diffusion, calculated from the slopes of the lines in Figure 1, are 27, 20, 32, and 22 kJ mol⁻¹ for the 400 EW, 600 EW, 800 EW, and perfluorocarboxylate polymers, respectively. Except for the 800 EW ionomer, all of these values are only slightly larger than that for sodium ion diffusion in pure water in this temperature range, 19.1 kJ mol⁻¹. Thus, a solutionlike diffusion mechanism is inferred.

Similar diffusion characteristics are seen in the more concentrated NaOH solutions in the 70–90°C temperature range, as shown in Figure 2. Again, large diffusion coefficients result compared to the nonporous membrane and activation energies remain in the 20 ± 5 kJ mol⁻¹ region. A large decrease in sodium ion diffusion for 11M NaOH compared to 5M solution is seen only for the perfluorinated sample, due to the more severe effects of membrane dehydration. This is accompanied by a change in diffusional activation energy from 39 to 94 kJ mol⁻¹ for this nonporous membrane.¹⁹

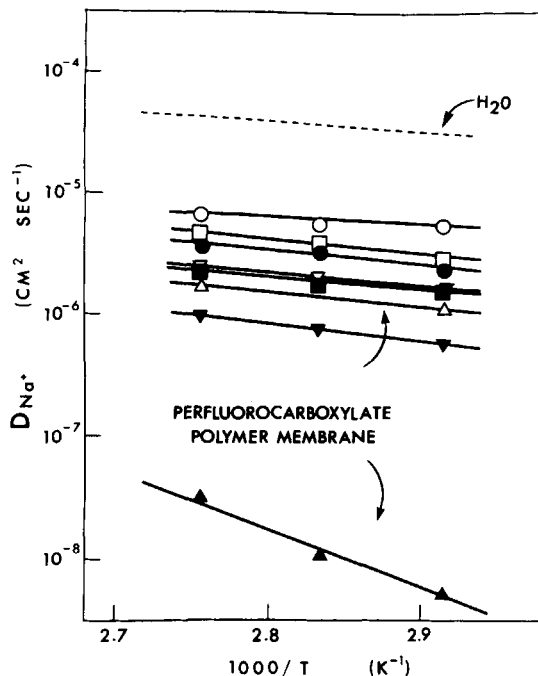


Fig. 2. Arrhenius plots of sodium ion diffusion in aromatic carboxylate polymer films: (○, □, ▽, △) 5 M NaOH; (●, ■, ▼, ▲) 11 M NaOH solution; (○, ●) 400 EW; (□, ■) 600 EW; (▽, ▼) 800 EW; (△, ▲) perfluorinated carboxylate membrane.

DC Membrane Conductance

Specific conductance values for membranes of three equivalent weights in 30% sodium hydroxide solution at a current density of 5 kA m^{-2} are shown in Figure 3. Values are also included for typical asbestos diaphragms at 100°C as well as for the solution and for 1150 EW Nafion. These results clearly demonstrate that the specific conductances of the aromatic carboxylate films behave more like a porous separator such as asbestos than a nonporous membrane film such as Nafion. The specific conductances of aromatic carboxylates are on the average one order of magnitude lower compared to the corresponding free electrolyte. In addition, conductance generally increases with decreasing equivalent weight, which is explained by the higher content of mobile ions of the latter (Table II). The increased electrolyte uptake has been attributed to an increase in generated microporosity with increasing ester content, when these materials are hydrolyzed into the ionomer form.

The decrease in specific conductance with increasing temperature for the 400 EW film is rather unusual. Consequently, experiments have been performed to determine if any decarboxylation occurs during the period of the conductance measurements. The ion exchange capacity of the sample used in the conductance experiment was redetermined and found to be within 2% relative (experimental error) to the original value. In addition, membrane samples of the various equivalent weight ionomers have been equilibrated at 180°C in 30% sodium hydroxide solution at a pressure of 30 bar.

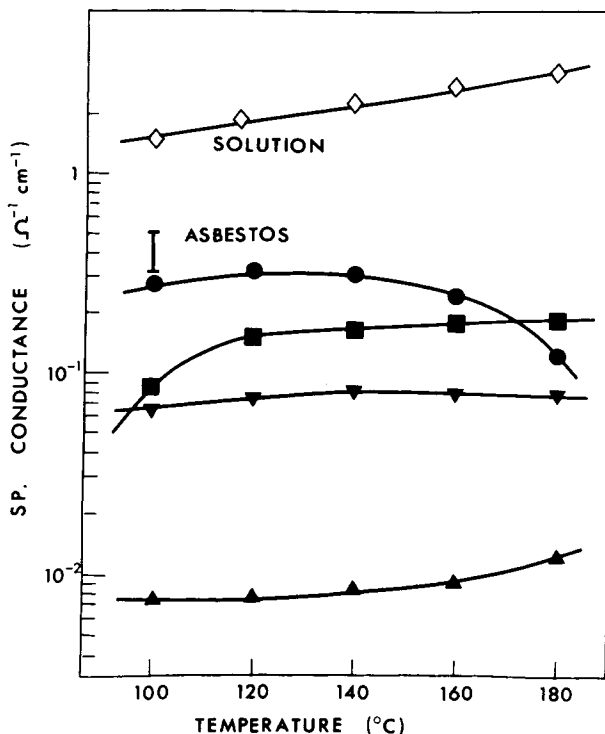


Fig. 3. Specific conductance of polymer films in 30% sodium hydroxide, 5.0 kA m^{-2} : (●) 400 EW; (■) 600 EW; (▼) 800 EW aromatic carboxylate; (▲) 1150 EW Nafion perfluorinated sulfonate membrane.

Samples were taken after 12 days to determine possible changes in sodium ion capacity. Results indicated that no decarboxylation occurred within the time range of the experiment. In order to explore the unusual specific conductance-temperature relation of the 400 EW aromatic carboxylate, the conductance measurements were repeated with a second film of identical history. Results are shown in Figure 4. The closed symbols represent original measurements which were made in order of increasing temperature. The open symbols refer to a second series of experiments which were performed immediately after the first series. It appears that some sort of annealing effect has taken place at the highest temperature, so that values at lower temperatures are subsequently lower. The result is that a cycled 400 EW film performs in a very similar fashion to 600 EW films. This result has a significant practical consequence. Since the 600 EW film is mechanically more stable (less brittle) than the 400 EW film, but shows the same conductance at high temperatures as the latter, it is the more likely candidate for a commercial separator.

The dependence of specific conductance on current density at 160°C is shown in Figure 5. The aromatic carboxylate films show ohmic behavior, even at a current density as high as 10 kA m^{-2} . This behavior could be expected for microporous films. This is in contrast to the results obtained in a comparative study with Nafion perfluorinated sulfonate ionomer of 1150 EW, where the specific conductance increased with an increase in

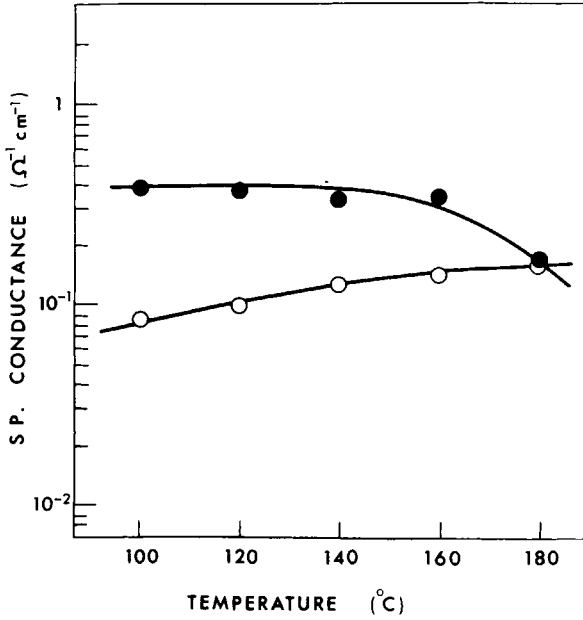


Fig. 4. Specific conductance of 400 EW aromatic carboxylate film in 30% NaOH, 5.0 kA m⁻²: (●) first series of experiments; (○) second series of experiments.

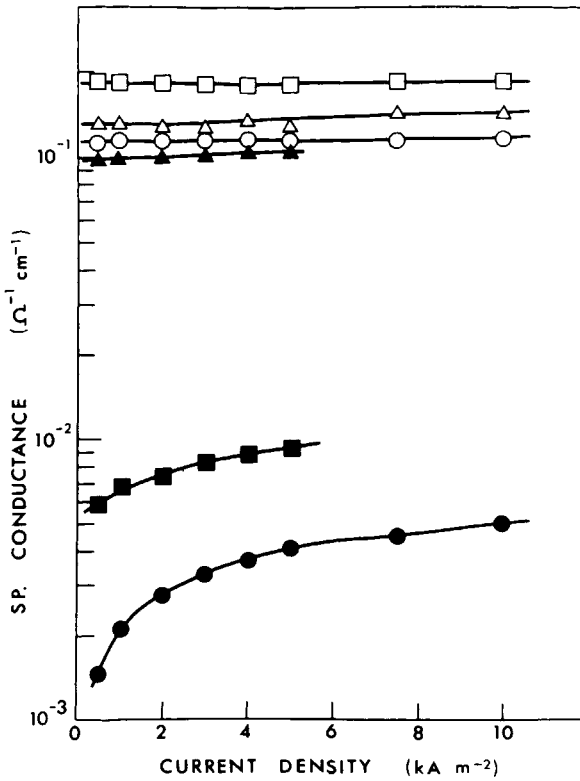


Fig. 5. Specific conductance of a 600 EW (□, △, ○) aromatic carboxylate and 1150 EW Nafion at (■, ▲, ●) at 160°C: (□, ■) 30% NaOH; (△, ▲) 16.9% NaOH; (○, ●) 40% KOH.

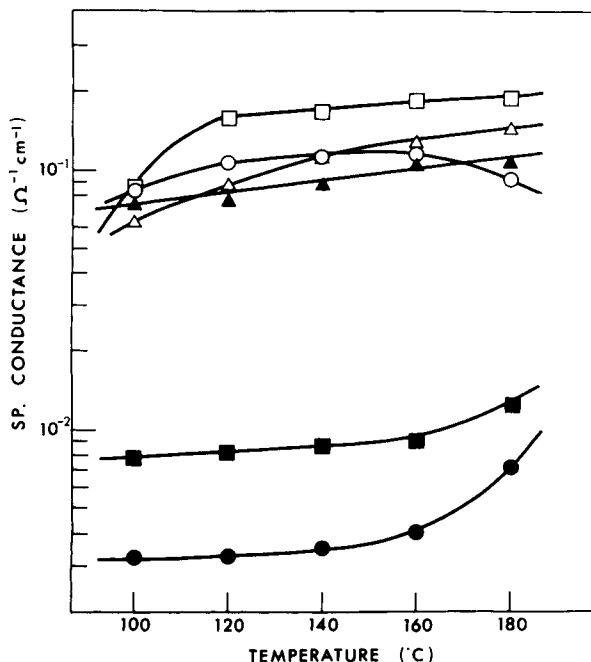


Fig. 6. Specific conductance of a 600 EW (\square , \triangle , \circ) aromatic carboxylate and 1150 EW Nafion (\blacksquare , \blacktriangle , \bullet) at a current density of 5 kA m^{-2} : (\square , \blacksquare) 30% NaOH; (\triangle , \blacktriangle) 16.9% NaOH; (\circ , \bullet) 40% KOH.

current density.¹⁶ The reason for this behavior was ascribed to morphological changes caused by the effects of large amounts of electroosmotically transported water. Also, little dependence is seen on solution concentration for the latter separator, in contrast to the Nafion sample. For nonporous films, the effects of exchange site and counterion dehydration generate a pronounced drop in conductance with increasing solution concentration, mainly due to ion pairing effects. The microporous films do not show this effect.

Figure 6 illustrates the specific conductance of a 600 EW aromatic carboxylate as a function of temperature and different solution environments. Generally, the temperature vs. specific conductance relationship is similar to the one found for Nafion. In 40% potassium hydroxide solution, which is the most dehydrating solution of the three studied, a reduction in membrane conductance is seen from 160 to 180°C. This is similar to the behavior shown by the 400 EW film in other solution environments as well. Probably a similar annealing effect is operative here, induced by high temperature and strongly dehydrating electrolyte solutions.

In general, the dc conductance behavior of the aromatic carboxylate for all equivalent weights is quite different from the one found for nonporous 1150 EW Nafion membranes. This difference is caused primarily by the microporous structure of the aromatic carboxylates, resulting in membrane specific conductances which are only one order of magnitude lower than those in free, concentrated electrolyte solutions.

The authors wish to thank the Research Council of Canada for the financial support provided and Dr. M. Hammerli of NRC for his help with this project.

References

1. J. Divisek and H. Schmitz, *Int. J. Hydrogen Energy*, **7**, 703 (1982).
2. *Hydrogen Manufacture by Electrolysis, Thermal Decomposition and Unusual Techniques*, M. S. Casper, Ed., Noyes Data Corp., Park Ridge, NJ, 1978, p. 111.
3. R. L. LeRoy, C. T. Bowen, and D. J. LeRoy, *J. Electrochem. Soc.*, **127**, 1954 (1980).
4. B. V. Tilak, P. W. T. Lu, J. E. Colman, and S. Srinivasan, in *Comprehensive Treatise of Electrochemistry*, Vol. 2, J. O'M. Bockris, B. E. Conway, E. Yeager, and R. E. White, Eds., Plenum, New York, 1982, Chap. 1.
5. W. B. Crandall and Y. Harada, "Fuel Cell Matrix Studies," Report AD761512, prepared by IIT Research Institute for U. S. Air Force Aerospace Research Laboratories, 1973.
6. P. Godin, R. Graziotti, A. Damien, and P. Masniere, *Int. J. Hydrogen Energy*, **2**, 291 (1977).
7. H. Vandendorre, R. Leysen, and H. Nackaerts, *Int. J. Hydrogen Energy*, **8**, 81 (1983).
8. R. Renaud and R. L. LeRoy, *Int. J. Hydrogen Energy*, **7**, 155 (1982).
9. F. W. Harris, B. A. Reinhardt, and R. D. Case, *Polym. Prepr.*, **19**(2), 394 (1978).
10. F. W. Harris, B. A. Reinhardt, R. D. Case, S. M. Padaki, V. Sudarsanian, and W. A. Feld, "Synthesis and Modification of Carboxylated Polyphenylenes and Phenylated Polyimides," Technical Report AFML-TR-76-9, Air Force Materials Laboratory, Wright-Patterson AFB, OH, 1976.
11. Part I of this work.
12. A. Eisenberg, E. Besso, H. L. Yeager, A. Steck, F. W. Harris, and R. K. Gupta, in *Proceedings of the Eleventh Biennial Polymer Symposium, High Performance Polymers*, Plenum, New York, *Contemporary Topics in Polymer Science*, Vol. 5, Edited by E. J. Vandenberg, Plenum Publishing Corporation, (1984).
13. M. Lopez, B. Kipling, and H. L. Yeager, *Anal. Chem.*, **49**, 629 (1977).
14. H. L. Yeager and B. Kipling, *J. Phys. Chem.*, **83**, 1836 (1979).
15. A. Steck, Ph.D. Thesis, The University of Calgary, Calgary, Alberta, Canada, 1983.
16. A. Steck, and H. L. Yeager, *J. Electrochem. Soc.*, **130**, 1297 (1983).
17. D. J. G. Ives and G. J. Janz, in *Reference Electrodes—Theory and Practice*, Academic, New York, 1961, pp. 112-114.
18. S. Tamotsu, *Denki Kagaku*, **40**(5), 390 (1972).
19. Z. Twardowski, H. L. Yeager, and B. O'Bell, *J. Electrochem. Soc.*, **129**, 328 (1982).
20. H. L. Yeager, Z. Twardowski, and L. M. Clarke, *J. Electrochem. Soc.*, **129**, 324 (1982).
21. H. L. Yeager and A. Steck, *J. Electrochem. Soc.*, **128**, 1881 (1981).

Received May 7, 1984

Accepted October 22, 1984