NEAR INFRARED SPECTROSCOPY OF ANIONIC CONDUCTING POLYMER MEMBRANES

David S. Newman, Guangping Bi, Deanne L. Snavely, John Dubsky, Frank Zamborini and Thomas S. Cina
Department of Chemistry
Bowling Green State University
Bowling Green, OH 43403

ABSTRACT

Flemion is a perfluorocarboxylated polymer somewhat similar to Nafion and is widely used in the chlor-alkali industry as the separator between anolyte and catholyte compartments of the electrolysis cell. The structure of Flemion was altered by converting the methylester functional group to an acyl group and then acylating the benzene ring of either dibenzo-18-cr-6 ether or benzo-18-cr-6 ether under Friedel-Crafts conditions, thereby attaching the crown ether to the Flemion as a "pendent". The bonded crown ether was then complexed with alkali metal halides to produce a solid electrolyte with mobile anions. Fluorescence spectroscopy, near IR spectroscopy, mid IR spectroscopy, UV-Visible spectroscopy and chemical analysis were used to assay the various reactions. A combination of fluorescence spectroscopy and near IR spectroscopy allowed us to unambiguously decide whether crown ethers were bonded to the membrane, dissolved in the membrane, or both.

INTRODUCTION

Flemion [1] is a perfluorocarboxylated polymer membrane which is prepared by copolymerizing tetrafluoroethylene and carboxylated perfluorovinyl ether [2,3]. Flemion is manufactured by Asahi Glass Ltd. of Japan. The chemical formula for Flemion is:

$$-(CF_2\cdot CF_2)_x\cdot(CF_2\cdot CF)_y\cdot OCF_2\cdot CF_m\cdot(CF_2)_n\cdot COOCH_3$$

where m is 0 or 1 and n has values between 1 and 5. The average molecular weight of a methylester containing unit of Flemion is approximately 700 amu. The methylester group on the Flemion is readily hydrolyzed to a carboxylic acid. The carboxylic acid form of Flemion is widely used in the chlor-alkali industry as the membrane separating the anodic and cathodic compartments of chlor-alkali cells because of its chemical inertness, its high cationic conductivity in aqueous media, and its ability to reject anions such as Cl^- and OH^-.

The reason anions cannot readily pass through the membrane, but cations can, is that, in aqueous media, especially at high pH, the carboxylic acid is partially dissociated leaving a negatively charged pendant group which repels other negative charges while allowing positively charged species, such as Na^+ ions, to hop from site to site within the membrane. However, when completely or nearly completely dry, neither the carboxylic acid form of Flemion (Fl-COOH) nor the sodium salt of the carboxylated Flemion (Fl-COONa) exhibit high ionic conductivity.
There are many potential applications for a material with properties similar to FL-COOH, but which conducts anions such as Cl\(^-\) and OH\(^-\) and rejects cations. Among the more intriguing of these applications is as the separator in the Al/Cl\(_2\) methylethylimidazolium chloride-AlCl\(_3\) battery [4] and in the production of a Na\(_2\)SO\(_4\) salt splitter using both the anionic and cationic conducting forms of Flemion [5,6]. Therefore, the principal objective of our Flemion research was to convert it to an anion conducting membrane, while still retaining its other desirable properties. This objective was achieved by hanging a positively charged pendant group on the Teflon backbone rather than a negatively charged species.

The approach taken for introducing a positively charged species was to attach a crown ether (CE) as the pendant group hanging from the polymer chain and then complexing the CE with an alkalai metal halide, the assumption being that the alkalai metal ion would lock in the crown and the halide would carry the current. This approach differs from that used in the fabrication of Neosepta in which a basic nitrogen group is the pendant and this group acquires a positive charge by bonding to a proton in acidic media. In an earlier study, we were able to bond dibenzo-18-cr-6-ether (DBCE) to Flemion, using a series of reactions, the last one of which was a Friedel-Crafts acylation of the benzene ring of DBCE using the ambient temperature molten salt, pyridinium heptachloroaluminate, as both the reaction medium and as a Friedel-Crafts catalyst. The bonded DBCE was then complexed it with LiCl [6]. We found that this material was a solid electrolyte, with an electrical conductivity, $\kappa$, equal to $1.3 \times 10^{-5}$ S/cm. This conductivity was only an order of magnitude lower than that of the lithium chloride salt of DBCE which was shown to be a fast ion conductor in the solid state with the mobile species being the Cl\(^-\) ion [7,8]. Although the transport numbers of the membrane were not measured, the assumption was that the Cl\(^-\) ions and not the Li\(^+\) ions were mobile.

In the FL-DBCE study [6] and again in this study, indications were that an ether was bonded to only about 5% of the possible sites on the Flemion, although the evidence was inconclusive. A possible reason for this was that, in the molten salt, the Flemion formed channels which were blocked or clogged by the large DBCE and the C\(_5\)H\(_6\)N\(_2\)Cl\(_7\). It is known that Nafion forms channels in aqueous media [9,10] and direct evidence for channel formation in Flemion using transmission electron microscopy has been found and will be reported on elsewhere. In the present study, we used BF\(_3\) in ether as the F-C catalyst and both DBCE and benzo-18-cr-6-ether (BCE) as pendant groups. The assumption being that the FL-BCE - LiCl complex would have properties similar to those of the FL-DBCE-LiCl complex, but because of the smaller size of both the catalyst and BCE, we would be able to bond more CE s to the Flemion. However, ascertaining the extent to which the CE bonded to the Flemion remained troublesome so we set out to develop analytical techniques to assay the extent of the various reactions and changes in membrane morphology that resulted from these reactions. The techniques used were FTIR and near IR spectroscopy, Fluorescence spectroscopy, UV-Vis spectroscopy, mercuric nitrate titration, and weighing the polymer coupons before and after each reaction, but the technique that proved most interesting, and the technique we report on here, was near IR spectroscopy.
EXPERIMENTAL DETAILS

Flemion sheet, which was 0.145 mm thick, was supplied by Asahi Glass Ltd. Coupons of this material, usually between 3 and 8 cm² were used for most of the experiments. The Flemion was converted to FI-COOH by immersing the coupon first in 50 w% NaOH for 16 hrs at 90 °C and then soaking it in 1 M HCl for 24 hrs at room temperature. The FI-COOH was then converted to the acyl containing Flemion, FICOCl, by refluxing the coupon in SOCl₂ for 16 hrs. The coupons of FICOCl were rinsed in diethyl ether to remove excess SOCl₂. One coupon of this material served as a "standard". It was immersed in a known quantity of de ionized water and allowed to shake in a continuous rotation tumbler for 24 hrs. The purpose of this step was to convert all acyl groups back to carboxylic acid and HCl. The HCl released, was titrated using a standard mercuric nitrate titration (CAWW method 325.3) [11]. The moles of HCl equaled the moles of acyl groups in the membrane. The FICOCl coupons were next refluxed in 40 ml of BF₃/ether to which approximately 0.2 g of crown ether, CE, had been added, for 16 hrs. Upon completion of the reflux, the coupons were each immersed in a known quantity of deionized water to convert any unreacted acyl groups to -COOH and HCl. The HCl was then titrated as before. It was assumed that the difference between the number of acyl groups in the standard coupon and the number of unreacted acyl groups in the coupon that had undergone the BF₃/ether Friedel-Crafts reaction, was equal to the number of CEs that had been bonded to the Flemion.

Briefly, the mercuric nitrate titration consists of an acidified Cl⁻ containing sample being titrated with Hg(NO₃)₂ in the presence of mixed diphenylcarbazone-bromphenol blue indicator. The end-point of the titration is the formation of a blue-violet mercury-diphenylcarbazone complex. This is a modern version of the older, and more difficult, Mohr titration.

The FICO-DBCE and FICO-BCE coupons were complexed by soaking them in aqueous LiCl solutions of various concentrations ranging from saturated to 1 M for approximately 24 hrs.

All transfer and weighing operations were done in a controlled atmosphere Kewaunee glove box which used the boil-off from liquid nitrogen as the atmosphere and had a moisture content less than 10 ppm. Before and after each reaction, the coupons were dried and weighed on an analytical balance with 0.01 mg precision.

Spectra were taken of the membranes directly and no attempt was made to reduce the membrane's thickness or to dissolve the Flemion. Both the near IR and the mid IR spectra were obtained with a Mattson 6020 spectrophotometer. The fluorescence spectra were obtained with a Perkin-Elmer LS-5B luminescence spectrometer which automatically optimizes its sensitivity for each sample. The actual absorbance is observed by the operator at the time of analysis via a digital display. The carboxylic acid form of Flemion was used as the blank.

Electrochemical Society Proceedings Volume 96-7
RESULTS AND DISCUSSION

The series of reactions used to convert the FI-COOCH$_3$ to FI-COBCE were:

\[
\text{FI-COOCH}_3 + \text{NaOH (aq)} = \text{Fl-COONa} + \text{CH}_3\text{OH} \quad [1]
\]

\[
\text{Fl-COONa} + \text{HCl (aq)} = \text{Fl-COOH} + \text{NaCl (aq)} \quad [2]
\]

\[
\text{Fl-COOH} + \text{SOCl}_2 = \text{Fl-COCl} + \text{SO}_2 + \text{HCl} \quad [3]
\]

\[
\begin{align*}
\text{BF}_3 & \quad \text{R}_4\text{COCl} + \text{BCE} \rightarrow \text{R}_4\text{CO-BCE} + \text{HCl} \quad [4]
\end{align*}
\]

Thin layer chromatography indicated that only one product formed when acetyl chloride reacted with BCE in ethyl ether. This product was most likely the BCE acylated at the 3 or 4 position rather than at the 2 or 5 position, because the latter site is far more hindered. It was therefore assumed that in the more crowded Flemion, only one product formed and this was the BCE bonded to the carbonyl group at the 3 or 4 position of the CE's benzene ring.

The mechanism for Eq. [4] is probably

\[
\text{Fl-COCl} + \text{BF}_3 = \text{Fl-CO}^+ + \text{BF}_3\text{Cl}^- \quad [5]
\]

\[
\text{Fl-CO}^+ + \text{BCE} = \text{Fl-CO-BCE}^+ \quad [6]
\]

\[
\text{Fl-CO-BCE}^+ = \text{Fl-CO-BCE} + \text{H}^+ \quad [7]
\]

\[
\text{H}^+ + \text{BF}_3\text{Cl}^- = \text{HCl} + \text{BF}_3 \quad [8]
\]

Gaseous HCl was isolated and identified in the reaction between BF$_3$ and coupons of Fl-COCl. In addition to reactions [5] through [8], a side reaction occurs producing a complex of some sort which causes the membrane to turn purple. The exact structure of this complex is not yet known, but when purple acylated coupons of Fl-CO-BCE were refluxed in 50 ml of approximately 1 M LiCl, much of the purple color disappeared and the LiCl solution was found to contain BCE and have a pH near 1. This indicated the colored complex was trapped in the membrane, but not bonded to it and that it probably dissociated in water into intact BCE and BF$_3$. 

Electrochemical Society Proceedings Volume 96-7 56
The complexing of the Fl-CO-BCE with LiCl can be described by the equation:

\[
\text{R}_4\text{CO} \quad \text{LiCl} \quad \text{R}_4\text{CO} \quad \text{Li}^+ \quad \text{Cl}^- \quad [9]
\]

The extent to which Eqs. [4] or [9] went to completion in the membrane varied considerably and was extremely difficult to assay. The usual FTIR spectra that are used to identify typical chemical bonds and other structural features of a species, were of only limited use in our experiments because of the thickness of the membrane. Most of the membranes absorbed too much light for the spectra to be anything more than a rough indication that a given reaction occurred. The same was true for the UV-Vis spectra. The membranes absorbed too strongly in the UV range. We therefore resorted to near IR spectroscopy because the overtones or second harmonics of quenched mid-IR absorptions appear in this region. [12,13]. Fig. 1 shows the near IR spectrum of bonded BCE and Fig. 2 shows the near IR spectrum of the same BCE that had diffused into the Fl-COOH without any chemical reaction taking place. Fig. 3 shows the near IR spectrum of carboxylated Flemion with no CE present. It is obvious from these spectra that there is a qualitative difference between the spectrum of the dissolved CE and that of the bonded CE in the 4100 -4450 cm\(^{-1}\) region of the spectrum. The bonded CE exhibits a distinct five sharp peak pattern which we think is an overtone of some harmonic motion of the carbonyl-benzene bond. The near IR spectrum of Fl-DBCE was obtained and is shown in Fig. 4. An almost identical five peak pattern appears. In order to prove that this is due to a feature of the Fl-CO-Benzene bond and not an overtone of the crown's motion, pyrene and benzene were bonded to the membrane under Friedel-Crafts conditions and the near IR spectra obtained. Both the benzene (Fl-CO-Benzene) and the pyrene (FICO-Pyrene) gave a virtually identical pattern to that of the bonded BCE in the 4100-4450 cm\(^{-1}\) region indicating we had indeed discovered the "signature" of the carbonyl-benzene bond. The near IR spectrum of Fl-CO-pyrene is shown in Fig.5.

The combination of techniques which seemed to give the most unambiguous qualitative results and which allowed us to readily distinguish between a CE molecule that was bonded to the Flemion and a CE molecule that had diffused into the Flemion without forming a chemical bond when both were present, turned out to be a combination of fluorescence spectroscopy and near-IR spectroscopy. A CE molecule that had diffused into the membrane without being bonded to it could readily be identified by its fluorescence spectrum whereas the fluorescence of both the bonded BCE in Fl-CO-BCE and the bonded DBCE in Fl-CO-DBCE was quenched under the conditions of our experiments. The reason why the fluorescence quenched is not known and is currently under investigation. Fig. 6 shows the fluorescence spectrum of BCE dissolved in Fl-COOH and Fig. 7 shows the fluorescence spectrum of the same molecule dissolved in methanol. In order to prove that the CE is bonded and not dissolved, the following protocol is followed. The near IR spectrum and the fluorescence spectrum of the membrane are taken. If there is fluorescence and no CO-Benzene overtone in the 4360 to 4434 cm\(^{-1}\) range, the CE has diffused into the membrane without being bonded to it. If we do not get a fluorescence spectrum and we do get the characteristic overtone spectrum, the molecule is bonded and not dissolved. If we get both spectra, some CE is dissolved in the membrane and some is bonded to it.
CONCLUSION

We have successfully bonded BCE and DBCE to Flemion membranes and complexed these CE's with LiCl to form electrolytes with mobile anions. We have developed analytical techniques to assay the many reactions involved. We have produced solid electrolytes with mobile anions and cations and solid electrolytes with mobile anions only. We are currently in the process of measuring the transference numbers of the various membranes and well as using these membranes to develop a Na$_2$SO$_4$ salt splitter.

ACKNOWLEDGMENT

We wish to thank the NSF-REU program at Bowling Green State University for its continuing support.

LIST OF REFERENCES

1. Flemion is a registered trademark of the Asahi Glass Company, Ltd. Japan
2. H. Ukahashi, M. Yamabe, in Perfluorinated Ionomer Membranes; A. Eisenberg, H.L. Yeager, Editors, American Chemical Society: Washington, DC, 1982: ACS Symposium Series No. 180
3. E. Blatt, W.H.F. Sasse, A.W.H. Mau, J. Phys Chem, 92, 4151 (1988)
4. F.M. Donahue, J.S. Wilkes, J.S. Reynolds, G. Fredric, in: Proceedings of the Fifth International Symposium on Molten Salts; M. Saboungi, D.S. Newman, K.E. Johnson, D. Inman, Editors, The Electrochemical Society Softbound Proceedings Series, pv-86-1, pp332-343, Pennington NJ 1986
5. J.D. Genders, D. Hartsough, J. Thompson, Novel Approaches To Salt Splitting, Extended Abstracts 94-1 185th Electrochemical Society Meeting, May 22-27, 1994
6. Abstract # 704. Ch. Kot, M-M. Letord, Production of Sodium Hydroxide and Sulfuric Acid From Sodium Sulfate Solutions, ibid, Abstract # 705
7. D.S. Newman, S. Li, T. Howard, L. Hunt. in : Proceedings of the Eight International Symposium on Molten Salts, R.G. Gale, G. Blomgren,H Kojima, Editors, The Electrochemical Society Softbound Proceedings Series, PV-92-16, pp 250-261 Pennington, NJ, 1992
8. D.S. Newman, D. Hazlett, K.F. Mucker; Solid State Ionics, 3/4 389 (1981)
9. M. Fujimoto, T. Nogami, H. Mikawa, Chem. Let. 547-550, 1982
10. M.W. Verbrugge, R.F. Hill, J. Electrochem. Soc. 137, 893(1990)
11. S. W. Capeci, P.N. Pintauro, R.F. Hill, ibid, 136, 2876(1989)
11. United States Environmental Monitoring and Support Laboratory, *Methods For Chemical Analysis of Water and Wastes*, Ohio, March 1983.

12. K.A. Bunding Lee, *Applied Spectroscopy Reviews*, 28(3), 231(1984)

13. W. F. McClure, *Analytical Chemistry*, 66, 43 A (1994)

---

**Fig. 1.** Near-IR Spectrum of Bonded BCE

**Fig. 2.** Near-IR Spectrum of BCE that has Diffused Into Fl-COOH
Fig. 3. Near-IR Spectrum of Fl-COOH

Fig. 4. Near-IR Spectrum of Bonded DBCE

Electrochemical Society Proceedings Volume 96-7
Fig. 5. Near-IR Spectrum of Fl-CO-pyrene

Fig. 6. Fluorescence Spectrum of BCE Diffused into Fl-COOH

Fig. 7. Fluorescence Spectrum of BCE Dissolved in Methanol