THE MODIFICATION OF FLEMION MEMBRANES FOR USE IN ENERGY GENERATING DEVICES

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ABSTRACT

Flemion is a perfluorocarboxylated polymer somewhat similar to Nafion. The structure of Flemion was altered by converting the methylester functional group to an acyl group and then acylating the benzene ring of dibenzyl-18-cr-6 ether thereby attaching it as a pendent to the polymer chain. Pyridinium heptachloroaluminate served as the reaction medium and as the Friedel-Crafts catalyst for the acylation reaction. The crown ether was complexed with LiCl to produce a solid electrolyte with mobile anions. A second solid electrolyte, in the fast ionic conductor range, was produced by saturating the lithium carboxylate form of the Flemion with crown ether and then complexing the dissolved ether with LiCl.

INTRODUCTION

In an earlier study, (1) we modified Nafion 901,(2) which is a perfluorinated polymer membrane that contains both sulfonic acid and carboxylic acid pendant groups, in an attempt to convert it from a cationic conductor to an anionic conductor whose mobile species is the Cl\(^{-}\) ion. As a Cl\(^{-}\) ion conductor the membrane would have many uses, one of which would be as the separator to prevent chlorine gas in the cathodic compartment from reacting with the methylethylimidazolium chloride electrolyte in the Al/Cl\(_2\) molten salt battery.(3) A key step in the modification of the membranes's structure was the conversion of the sulfonic and carboxylic acid functional groups to sulfonyle and acyl chlorides.
respectively. This was done by reacting the membrane with \( \text{SOCl}_2 \), but regardless of the conditions used, some of the sulfonic acid groups always remained unreacted. We therefore decided to completely avoid the sulfonic acid problem by switching to Flemion,\(^4\) a membrane containing only methyl ester functional groups which could be readily converted to carboxylic acids.

Flemion is a perfluorocarboxylated polymer membrane somewhat similar to Nafton. It is prepared by copolymerizing tetrafluoroethylene and carboxylated perfluorovinyl ether \(5,6\) and is manufactured by Asahi Glass Company Ltd. Because of its high ionic conductivity and comparative inertness, as well as its ability to reject anions such as \( \text{OH}^- \) and \( \text{Cl}^- \), Flemion has been widely used in the chlor-alkali industry as the membrane separating the anodic and cathodic compartments in chlor-alkali cells. The chemical structure of Flemion is shown schematically below:

\[
-(\text{CF}_2-\text{CF}_2)_x-(\text{CF}_2-\text{CF})_y-
\]

\[
(\text{OCF}_2-\text{CF})_m-(\text{CF}_2)_n-\text{COOCH}_3
\]

where \( m \) is 0 or 1 and \( n \) has values between 1 and 5.

The principal objective of the present research was to attach dibenzo-18-crown-6-ether \( \text{(CE)} \) as a pendent hanging from the polymer chain and then complex the crown ether with \( \text{LiCl} \). The \( \text{CE-LiCl} \) complex was shown to be a fast ion conductor in the solid state with the mobile species being the \( \text{Cl}^- \).\(^7,8\) The \( \text{LiCl-CE} \) complex is shown in Fig. 1. We thought that if all of the acyl chlorides could be converted to \( \text{CO-CE} \) s, and if the structure of the \( \text{LiCl-CE} \) complex was essentially the same in the membrane as it was in the solid, the membrane itself would become a \( \text{Cl}^- \) conductor and reject cations. Moreover, if the extent of several of the reactions could be controlled, it would be a relatively simple matter to produce a polymeric electrolyte with mobile cations and anions; in effect a polymeric molten salt. This material would also have many uses in energy generating devices and in electrolysis cells.

**EXPERIMENTAL DETAILS**
Flemion sheet, 0.145mm thick, was furnished by Asahi Glass Ltd. Coupons of this material, between approximately 1 and 2 cm², were used for most of the chemical reactions. The Flemion was converted to the carboxylic acid form by immersing the coupon first in concentrated sodium hydroxide for 16 hrs at 90 °C and then in 1 M HCl at room temperature for 24 hrs.

The carboxylic acid was next converted to an acyl group by refluxing the membrane in thionyl chloride for approximately 12 hrs. The FTIR spectrum of the acylated membrane (Fig. 2) together with a Mohr titration of the acidic solution formed by the membrane reacting with water:

\[
R_f\text{-COCl} + \text{H}_2\text{O} \rightarrow R_f\text{-COOH} + \text{HCl} \quad [1]
\]

indicated that essentially all of the carboxylic acid groups were converted to acyl groups.

The Flemion acyl chloride membrane was immersed in pyridinium heptachloroaluminate, a room temperature molten salt, at 40 °C. Dibenzo-18-cr-6 was added to the melt and allowed to react with the membrane for as long as 36 hrs. After the allotted reaction time, the membrane was removed from the melt and thoroughly washed in water. In addition to quenching the reaction, this technique converted unreacted acyl sites to carboxylic acids. The membranes were then dried under vacuum to constant weight.

The extent of the reaction of \(R_f\text{-COCl}\) with the crown ether was monitored by measuring the membrane’s weight increase and by measuring the membrane’s UV-vis spectrum with an HP-8452A diode array spectrophotometer.

A second series of CE acylations were carried out by first dissolving the CE in warm methanol and then immersing Flemion, whose methyl esters had been converted to carboxylic acids, in this solution for approximately 24 hrs. The CE diffused into the Flemion saturating it. The methanol was removed by evaporating it under vacuum at 70 °C for approximately 12 hrs. The CE containing membrane was refluxed for approximately 12 hrs in SOCl₂ and subsequently treated as in the first series of experiments. The SOCl₂ did not react with the CE.

All molten salt and acylation reactions were carried out in a controlled atmosphere glove box, the atmosphere being the boil-off from liquid nitrogen. The acylated
membranes were never exposed to the atmosphere because water in the air would eventually convert the acyl groups back to carboxylic acids.

The ac conductivities of the dry membranes were measured with a Jones bridge at 1000 Hz.

Transference numbers for the mobile ions in the dry membranes were measured with a Tubandt cell similar to the one described by Bottelberghs (9), but with three Flemion coupons in place of the three solid electrolyte pellets. That is, one LiCl complexed piece of Flemion was the anodic compartment, a second piece of supposedly identical Flemion the central compartment and a third piece the cathodic compartment. Weight changes of the anodic and cathodic compartments along with chemical analysis of the copper electrodes allowed the Li⁺ and Cl⁻ transference numbers to be calculated.

RESULTS AND DISCUSSION

The chemical reactions necessary to convert the methyl ester form of Flemion to the acyl chloride form are:

\[ R_{f}-\text{COOCH}_3 + \text{NaOH} \rightarrow R_{f}-\text{COONa} + \text{CH}_3\text{OH} \]  \[2\]

\[ R_{f}-\text{COONa} + \text{HCl} \rightarrow R_{f}-\text{COOH} + \text{NaCl} \]  \[3\]

\[ R_{f}-\text{COOH} + \text{SOCl}_2 \rightarrow R_{f}-\text{COCl} + \text{SO}_2 + \text{HCl} \]  \[4\]

The reaction between the Flemion acyl chloride and the CE is:

\[ R_{f}-\text{COCl} + \text{Al}_2\text{Cl}_7^- \rightarrow R_{f}-\text{CO}^+ + 2\text{AlCl}_4^- \]  \[5\]

The mechanism for this reaction is most likely:

\[ R_{f}-\text{COC1} + \text{Al}_2\text{Cl}_7^- \rightarrow R_{f}-\text{CO}^+ + 2\text{AlCl}_4^- \]  \[6\]
Rf-CO$^+$ + CE $\rightarrow$ RfCO-CE$^+$ \[7\]

Rf-CO-CE$^+$ $\rightarrow$ RfCO-CE + H$^+$ \[8\]

H$^+$ + AlCl$_4^-$ $\rightarrow$ HCl + AlCl$_3$ \[9\]

AlCl$_3$ + AlCl$_4^-$ $\rightarrow$ Al$_2$Cl$_7^-$ \[10\]

In this mechanism, the pyridinium heptachloroaluminate serves as both medium and catalyst for the Friedel-Crafts reaction.

Reacting the Flemion acyl chloride directly with the CE in pyridinium heptachloroaluminate (Eq.5) produced membranes with a maximum of 5% of the acyl sites bonded to crown ethers. A shift of 12 nm in the absorption maximum in the CE’s UV-vis spectrum from what it was when the CE was simply dissolved in the membrane, but not reacted, indicated a chemical bond had formed, almost certainly between the CE’s benzene ring and the acyl group. Moreover, the acylated CE could not be removed from the membrane whereas the dissolved CE diffused out of the membrane when it was immersed in warm methanol. Fig. 3 and Fig. 4 show the spectra of the dissolved and bonded CE’s respectively. Curiously enough, CE’s would bind to nearly all of the acyl sites in Nafion 901 membranes under similar conditions.(1)

The CE bonded Flemion coupons were immersed in aqueous LiCl solutions. The LiCl diffused into the membrane and formed a complex with the CE similar to that shown in Fig. 1. Evidence for complexation took the form of a significant change in the FTIR spectrum of Flemion-CE after the LiCl was added and the membrane dried under vacuum. For example, the transmittance peak at 1566 cm$^{-1}$ disappeared after the CE was complexed. In addition, the electrical conductivity (Table 1) of the LiCl complexed membrane was considerably higher than that of the CE bonded Flemion alone or the Flemion carboxylic acid containing LiCl. A dc of ten volts was placed across this membrane which was held between a copper anode and a platinum cathode. After several hours, the copper turned green indicating the formation of CuCl$_2$ and confirming that the complexed CE in the Flemion had similar properties to the solid CE-LiCl complex. Some Li also plated out at the cathode and was detected by wetting it and measuring the pH of the water, which was always basic. The transference numbers of this material were not measured.
There are several possible explanations for the consistently low yields of bonded CE's, but the most plausible is that most of the reaction occurred at, or near, the surface of the membrane and not in the interior. The morphology of the membrane (10) is such that the carboxylic acid groups, and by inference the acyl groups, arrange themselves along the inner surface of cylindrical channels running through the membrane, as shown in Fig. 5a. The acylated CE's block the entrance to these channels thereby preventing further acylations in the interior of the channel, as shown in Fig. 5b. Since under all reaction conditions used to date, the acyl groups at the mouth of a channel reacted prior to the acyl groups in the channel's interior, high yields of bonded CE's could not be obtained.

Because immersing the Flemion acyl chloride in pyridinium heptachloroaluminate containing CE gave low yields of bonded CE's, and because it was assumed the reason for this low yield was that the mouths of the channels through the membrane were blocked by bonded CE's, it was decided to circumvent this problem by first saturating the Flemion carboxylic acid membrane with CE and then refluxing this membrane in SOCl₂ to produce an acylated material whose channels were already filled with CE's. This membrane would be expected to acylate both interior and surface CE's. Pieces of this material were then immersed in the molten salt to which a small quantity of CE was added to discourage diffusion of the CE out of the membrane. As a standard, neat Flemion acyl chloride coupons were also added to the same solution. After several minutes the pyridinium heptachloroaluminate solution turned purple, as did the membranes with incorporated CE. However, the blank acylated membranes remained clear, even after several weeks in the melt. After being removed from the purple melt, the clear membrane's UV-vis spectrum showed that the CE had bound to the membrane as before.

Washing the purple membrane in water for several days did not remove the purple color nor change the membrane's weight, indicating the purple compound was too large to exit the membrane or was trapped by surface bonded CE's, not unlike a portcullis in the entrance to a castle. These membranes remained purple for several months, even when exposed to the atmosphere. The fact that the neat membrane remained clear indicated that the purple compound could not enter the membrane, either because it was too large or because the membrane's channels were again blocked by CE's at their entrances.
The nature of this purple compound is currently under investigation, as are similar highly colored compounds found to form between CE and either BF$_3$ or FeCl$_3$. Both FeCl$_3$ and BF$_3$ are Lewis acids and Friedel-Crafts catalysts.

The CE saturated carboxylic acid membranes were complexed with LiCl as described above and dried under vacuum. The ionic conductivity was found to be exceedingly high (Table 1). Because this material exhibited such high conductivity, samples of the original membrane were hydrolyzed in concentrated LiOH and then saturated with CE. These membranes were then complexed with LiCl, dried under vacuum and their conductivities measured. The ionic conductivity was even greater than that of the LiCl-CE complexes in Flemion carboxylic acid and well within the fast ion conductor range. A plausible reason for the higher ionic conductivity is that there are at least two energetically nearly equivalent sites for the Li$^+$ ion: on the carboxylate and in the crown. This means there is a constant ion exchange occurring. In the carboxylic acid membrane, a similar exchange between H$^+$ and Li$^+$ probably produces some HCl, thereby removing charge carriers from the electric field.

The Li$^+$ and Cl$^-$ transference numbers in the membrane were measured using the Tubandt cell described above. The data obtained is given in Table 2. The average of two separate experiments gave $t^+ = 0.6$ and $t^- = 0.4$ indicating the membrane is a solid electrolyte with mobile anions and cations.

CONCLUSION

The structure of Flemion has been altered so as to produce a material bonded to CE’s which are probably oriented around entrances to channels through the membrane. A second material has been produced that is a fast ion conductor with mobile anions and mobile cations. A series of highly colored compounds formed between CE and Lewis acids such as BF$_3$, C$_5$H$_6$NAI$_2$Cl$_7$ and FeCl$_3$ have been found.

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Table I: The Specific Conductance of Various Materials

| #  | Material                               | k (Ω cm)^{-1} |
|----|----------------------------------------|---------------|
| 1  | Unmodified Flemion Membrane            | 0             |
| 2  | Hydrolyzed Flemion Membrane            | 4.23 x 10^{-5}|
| 3  | Complex of LiCl with CE-Flemion        | 1.30 x 10^{-5}|
| 4  | Crown Ether-LiCl                       | 1.59 x 10^{-4}|
| 5  | Flemion(H+) Containing LiCl            | 6.57 x 10^{-5}|
| 6  | Flemion(H+) Containing CE-LiCl         | 1.18 x 10^{-4}|
| 7  | Flemion(Li+) Containing CE-LiCl        | 1.15 x 10^{-3}|
| 8  | Complex of LiCl with CE-Nafion         | 2.73 x 10^{-3}|

Table II. Weight Changes of the Anodic and Cathodic Membranes in the Tubandt Cell

| #  | ΔWt of Cathodic | ΔWt of Anodic | t^+ | t^- |
|----|----------------|--------------|-----|-----|
| 1  | 4.5mg          | 1.0mg        | 0.53| 0.47|
| 2  | 3.1mg          | 1.4mg        | 0.69| 0.31|

Fig. 1: Li Cl Crown Ether Complex
Fig. 2: FTIR Spectrum of Acylated Flemion

Fig. 3: CE Dissolved in Flemion
Fig. 4: CE Bonded to Flemion
