RECENT PROGRESS IN THE DEVELOPMENT OF THE RADIATION-GRAFTED PSI MEMBRANE

H.P. Brack, F. N. Büchi, J. Huslage, and G. G. Scherer
Paul Scherrer Institut
General Energy Research, Electrochemistry
CH-5232 Villigen, Switzerland

ABSTRACT

Radiation grafting can be used to combine the proton-conducting properties of a partially para-sulfonated polystyrene graft component with the thermal and chemical stability of fluoropolymer base films together in membranes suitable for application in Polymer Electrolyte Fuel Cells (PEFC) and other electrochemical devices. Earlier the performance and lifetime of our radiation-grafted membranes were greatly improved after the introduction of our double crosslinking membrane preparation concept and our optimization of the content of the comonomers, divinylbenzene and triallylcyamurate, which are able to introduce crosslinking to the membrane. We now report on further progress with these membranes with respect to (i) the improvement of the PEFC polarizability by using new thinner radiation-grafted membranes, (ii) the improvement of the mechanical properties by changing our irradiation procedure and base polymer type, (iii) testing at higher temperatures (80-85 °C), (iv) long term testing in excess of 5000 hours at 60 °C, and (v) further insight into the degradation of these membranes in the PEFC application as a result of our post-mortem spectroscopic analysis of membranes.

INTRODUCTION

Radiation-Grafting Method

Radiation-grafting can be used to combine the desirable properties of two disimilar polymers in a graft copolymer structure. For example, the chemical and thermal stability of commodity fluoropolymers can be combined with the ion-exchange or proton-conducting properties of partially para-sulfonated polystyrene to yield materials useful for electrochemical devices, e.g., fuel and electrolysis cells, batteries, and sensors. Our membrane preparation method is shown schematically in Figure 1.

The radiation-grafting method offers several advantages for the preparation of ion-exchange or proton-conducting membranes for electrochemical applications. For example, the materials and methods are widely available and can be low cost. Such
commodity base fluoropolymer films as poly(ethylene-alt-tetrafluoroethylene), or ETFE, currently cost less than $5.00/m² for 50 μm thick film (1) and technical grade styrene currently costs less than $1.00/kg in bulk quantities (2). A liter of styrene is about as much monomer as is found in 10 m² of a typical radiation grafted film. Industrial-scale electron beam irradiation of bulk film quantities can be purchased for less than $1.00/m² (3), and can be carried out for less than $0.10/m² based on actual operating costs for those purchasing an electron beam irradiation system (4). These prices are provided only to give a crude indication of the commercial viability of the radiation-grafting method, and we are still in the process of estimating the additional costs of special material handling in our preparation method such as material cooling or packing under inert atmosphere and the sulfonation step for a production-scale preparation. It is clear, however, that partially-sulfonated polystyrene-based ion exchange materials find widespread application (5), and, similar to our radiation-grafting method, they are often prepared (5) using chlorosulfonic acid to sulfonate the polystyrene-based precursor after it has been processed into its final bead or film form.

Other advantages of the radiation-grafting method include: (a) Radiation-grafted membranes are readily crosslinked to control swelling, solubility, gas crossover, and degradation by adding an appropriate radically polymerizable crosslinker like divinylbenzene to the grafting mixture. (b) The base polymer is already in the form of a flat thin dense film. Therefore, no extrusion or solution casting of the solid electrolyte is required. This is an advantage because ion-containing polymers often have high melting points and melt viscosities due to the presence of strong hydrogen bonding and/or Coulombic interactions (6). In addition sulfonic acid groups are not stable at temperatures above about 180 °C (7) so that polymers containing sulfonic acid groups can not be readily melt processed without undergoing degradation. (c) Electron beam irradiation is a clean method and does not require an initiator or catalyst, and (d) the initiation reaction can be readily controlled by choice of the irradiation dose, dose rate, and atmosphere. In addition, electron beam irradiation finds widespread industrial application in polymerization, crosslinking, and sterilization.
Radiation-Grafted PEFC Membranes

Our early radiation-grafted PSI membranes were based on sulfonated polystyrene as the graft component and poly(tetrafluoroethylene-co-hexafluoropropylene), or FEP, as the base polymer (8). At that time performance and lifetime of these membranes (in terms of a stable in-situ membrane resistance) in Polymer Electrolyte Fuel Cells (PEFCs) were limited to 125 mW/cm² and less than 500 hours. Membrane lifetime in the PEFC was improved by adding divinyl benzene to our grafting mixture in order to crosslink our radiation-grafted membranes (9). As a result of the crosslinking through DVB, lifetimes were increased up to about 1,000 h or more and the open circuit voltage of cells operated with thinner (70-80 µm thick) radiation-grafted membranes increased from 793 up to 971 mV. Unfortunately, the crosslinking also increased the membrane specific resistance from 10.3 up to 36 Ωcm, and thus the ohmic losses in the PEFC. As Wang and Capuano correctly state in their recent publication (10), the polarization performance of PEFCs containing these radiation-grafted membranes crosslinked using DVB alone was poorer than that of similarly tested PEFCs containing Nafion 117. Wang and Capuano fail to mention however that in that same year we reported that the performance and lifetime of our radiation-grafted membranes were greatly increased after the introduction of our double crosslinking membrane preparation concept and optimization of the content of the crosslinking comonomers (11-13). We reported at that time (11) that a maximum power density of 385 mW/cm² was achieved with our optimized membranes and that this value exceeded by 60% that obtained with PEFCs containing Nafion 117 membranes under the same operating conditions (30 cm² cell active area, Nafion-impregnated E-Tek electrodes with a platinum loading of 0.8 mgcm⁻², 60 °C, H₂ and O₂ at atmospheric pressure).

In the following year (14) we reported that our radiation-grafted membranes were able to operate five or six times longer (about 700 h) than two commercially available radiation-grafted membranes from Pall RAI Manufacturing Co., R-1010 and R-4010, without significant degradation in terms of an increase in the in-situ membrane area resistance. Those tests were carried out as described. Recently Wang and Capuano successfully demonstrated (10) long-term testing of these same Pall RAI R-1010 and R-4010 membranes over about 1,000 h. It should be noted however that both cell temperature of 50 °C and active areas of 5 cm² are significantly lower and smaller than those used in our experiments.

In addition, Wang and Capuano used post-mortem infrared spectroscopy to investigate the degradation processes occurring over the lifetime of in the PEFC application (10). They measured the transmission spectra of membranes that had been tested for various times in PEFCs or soaked for various times in H₂O₂ solution. Unfortunately the region of 925 to 1100 cm⁻¹ in their spectra of the untreated H⁺-form of the membranes was completely obscured by a broad strong absorbance feature and no distinct bands were observable. In general, after testing in a PEFC, bands at 1009 and 1039 cm⁻¹ that they assigned to the C-H aromatic in-plane vibration and the S=O symmetric stretching vibration became observable. The absorbance of these two bands was lower in the membranes that were tested longer in a PEFC or exposed longer to H₂O₂ solution.

Electrochemical Society Proceedings Volume 98-27

54
More than 30 years ago Hodgdon and co-workers (15) investigated the degradation of sulfonated polystyrene membranes in fuel cells. Based on ex-situ degradation studies, they proposed that degradation was primarily caused by (i) weak peroxide linkages introduced into the backbone during polymerization and (ii) by attack of HO2· radicals generated at the fuel cell anode on the α-H of the sulfonated polystyrene. Bûchi and co-workers (9) carried out HPLC analysis of the product water from PEFCs containing radiation-grafted, sulfonated polystyrene-based membranes. The 4-hydroxy- and 4-carboxybenzensulfonic acids and other non-identified benzenesulfonic acids that they found in the product water were consistent with the latter mechanism proposed by Hodgdon and co-workers (attack of in-situ generated radicals at the α-hydrogen positions). Bûchi and co-workers (9) observed differences between the spectra of the dried K+-exchanged form of untested and PEFC-tested FEP-based radiation-grafted membranes that were similar to those reported more recently by Wang and Capuano (9). In the work of Bûchi and co-workers (9) the absorbance of the bands at 1009 and 1039 cm⁻¹ due to the sulfonated polystyrene-based graft component decreased after membrane testing in a PEFC but that the intensity of the C-F absorption band at 982 cm⁻¹ due to the CF₃ group of the FEP base polymer remained unchanged.

Unfortunately, the results of Wang and Capuano (10) are not so easily interpreted because Zundel has shown in his extensive fundamental infrared spectroscopic investigations of sulfonated polystyrene-based membranes that both of these bands at 1009 and 1039 cm⁻¹ are highly dependent on the hydration level of the acid form of the membrane (16). Zundel’s spectral measurements of membranes at various hydration levels show that the band at 1009 cm⁻¹ decreases considerably in intensity upon drying due to strong coupling between the aromatic and sulfonic acid vibrational modes. Likewise Zundel showed that the band at 1039 cm⁻¹ also decreases systematically with drying. Unfortunately, Wang and Capuano make no mention (10) of drying the membrane samples prior to spectroscopic analysis. Therefore some of the spectral changes that they reported over this narrow frequency range may be due to not only degradation losses of the sulfonated aromatic groups but also simply to drying out of the membrane in the application or prior to spectroscopic analysis. In addition, they did not report any analysis of spectral features due to the base polymer component of the Pall RAI membranes. In general, post-mortem analysis by transmission mode (through the membrane thickness) infrared measurements of the acid form of radiation-grafted and other PEFC membranes is extremely difficult due to the very strong absorbances of many of the vibrational modes of the sulfonic acid, aromatic, and fluorinated groups and the strong hydration level dependence in the case of the first and sometimes second type of vibrational modes. These problems in the post-mortem spectroscopic analysis of radiation-grafted and other PEFC membranes are addressed in the present work and the post-mortem analysis of membranes based on the partially fluorinated base polymer ETFE are reported.

In addition, we report here on further progress in the development of our PSI radiation-grafted membranes with respect to (i) the improvement of the mechanical properties by changing our irradiation procedure and base polymer type, (ii) the
improvement of the PEFC polarizability by using new thinner radiation-grafted membranes, (iii) long term testing in excess in excess of 750 hours at a temperature of 80 °C, and (iv) long term testing in excess of 5000 hours at 60 °C.

EXPERIMENTAL

Membrane preparation and characterization
Nowoflon ET-6235 (ETFE) films from Nowofol GmbH of Siegsdorf, Germany (25, 50, and 100 µm thick) and Teflon FEP films from DuPont of Circleville, OH, USA (25, 50, and 75 µm thick) were used as base polymer films. Our membrane preparation method has been reported earlier (17-18) and is shown schematically in Figure 1. Some important preparation parameters include: (i) polymer film pre-irradiation by electron irradiation under N₂ atmosphere (e⁻/N₂) at a dose rate of 15.1 kGy/s or gamma irradiation in air (g/air) at a dose rate of 5.9 kGy/h; (ii) subsequent grafting with a solution of 3.5 M styrene (Fluka purum grade), 0.33 M divinylbenzene (Fluka technical grade, 70-85 % active), and 0.19 M triallylcyanurate (Fluka purum grade) in benzene for 4.5 h at 60 °C; (iii) sulfonation of the graft component using a solution of chlorosulfonic acid, and (iv) generation of the water-swollen acid form of the membrane by treating the sulfonated films in (a) NaOH(aq), (b) HCl (aq), and then approximately 90 °C de-ionized water. The membranes prepared in this manner from the above ETFE and FEP base polymer films are designated here as ETFE-25, ETFE-50, ETFE-100, FEP-25, FEP-50, and FEP-75 depending on the base polymer film type and its thickness.

Stress-strain measurements of the radiation-grafted films and sulfonated and water-swollen membranes were carried out according to DIN 53455 using a jaw speed of 10 mm/min. Infrared analysis of the films and the dried acid form and the dried K⁺-form of the membranes was carried out at a resolution of 1 cm⁻¹ in the Attenuated Total Reflectance (ATR) mode using a 45° ZnSe crystal and in the transmission mode on a Perkin Elmer System 2000. FT-Raman spectra of the films and membranes were measured with a Bruker IFS 55/S Equinox Raman FRA 106/S spectrometer at a resolution of 2 cm⁻¹ using a laser intensity of 420 mW, 256 scans, and a Ge-detector. An aluminum mirror was placed in the light path behind the membrane sample in order to obtain spectral information through the film and membrane thicknesses.

Fuel Cell Testing
Membranes were tested in fuel cells using our previously reported methods (8). Membranes were tested in stainless steel cells with active areas of 30 cm² and graphite cells with active areas of 100 cm². Test parameters include: (a) nominal cell temperatures of 60 °C (some single cell experiments with active areas of 30 cm² were carried out at a nominal cell temperature of 80 °C), (b) humidified H₂ and O₂ gases at 1 atm, and (c) Nafion-impregnated E-TEK electrodes having a Pt loading of 0.8 mg/cm². The stability
of the membranes over their lifetime in the PEFCs was evaluated by monitoring the in-situ membrane area resistances measured by a current pulse method (19). The performance of the membranes over their lifetime in the application was evaluated based on the polarization characteristics of the PEFCs.

RESULTS AND DISCUSSION

Membrane Mechanical Properties

Previously we used γ-irradiation in air for the pre-irradiation of our perfluorinated FEP base polymer films. Membranes produced using this procedure were brittle and suffered from poor mechanical properties and breakage in cells having active areas much larger than 30 cm². The irradiation procedure was optimized and changed to e-beam irradiation in inert gas atmosphere and partially fluorinated poly(ethylene-alt-tetrafluoroethylene), or ETFE, base polymer films were used instead of perfluorinated FEP films. Membranes produced using this modified irradiation process and partially fluorinated base fluoropolymer films show improved mechanical properties, both ex-situ and in cells having active areas of 100 cm². The ex-situ characterized mechanical properties typical of these membranes are shown in Figure 2. This improvement in mechanical properties has been ascribed (18) to the lesser extent of chain scission occurring when (i) the pre-irradiation step is carried out more rapidly using the higher dose rate electron beam source, (ii) the pre-irradiation is carried out under inert atmosphere, and (iii) partially fluorinated films are used instead of perfluorinated ones.

![Figure 2 : Mechanical properties of swollen 125 μm FEP-based and 70 μm ETFE-based membranes.](image)

Membrane Ion-Exchange Capacities and Swelling Properties

The ion-exchange capacities (IEC) of the PSI radiation-grafted membranes and Nafion membranes are compared in Table I. The IEC values of the PSI radiation-grafted membranes are considerably higher than those of the Nafion membranes on both a mass
(mEq/g) basis, as shown in Table I, and volume (mEq/cm³) basis. For example, the IECs of the water-swollen PSI membranes are over 200 mEq/cm³, while the Nafions are less than 50 mEq/cm³. An important factor is that our membranes are crosslinked so that they can have higher acid group contents than Nafion without excessive swelling. In addition each side chain in Nafion has only one sulfonic acid group. Presumably the grafted chains in our membranes are many monomer units in length and each styrene unit is sulfonated. The higher IEC of our radiation-grafted membranes on a mass basis is also partly a result of the fact that only the main chains (base polymer) in our membrane are partially or fully fluorinated (ETFE or FEP, respectively), whereas in Nafion both the main chain and side chain are fluorinated. The crosslinking in our radiation-grafted membranes restricts their volumetric expansion during swelling and thus favors a higher IEC value on a volumetric basis.

| Membrane   | Thickness /μm | IEC /mEqg⁻¹ | Water swelling /mass % | Water/acid concentration ratio (H₂O/RSO₃H) |
|------------|---------------|--------------|------------------------|--------------------------------------------|
| FEP-25     | 41            | 2.0          | 22                     | 6.4                                        |
| FEP-50     | 85            | 1.9          | 27                     | 7.9                                        |
| FEP-75     | 125           | 1.8          | 33                     | 10                                         |
| ETFE-25    | 39            | 2.4          | 27                     | 6.2                                        |
| ETFE-50    | 84            | 2.3          | 29                     | 7.0                                        |
| ETFE-100   | 152           | 2.4          | 44                     | 10                                         |
| Nafion N-112 | 60            | 0.91        | 37                     | 22                                         |
| Nafion N-115 | 150           | 0.91        | 37                     | 22                                         |
| Nafion N-117 | 200           | 0.91        | 37                     | 22                                         |

As a result of their crosslinking, many of the PSI radiation-grafted membranes swell to a lesser extent in water on a mass basis than Nafion (Table I). It is difficult to readily compare the swelling properties of these different membranes due to their different structures and extents of fluorination. For this reason, the water content in terms of the number of water molecules per acid group in the water swollen membranes (referred to as here as water/acid concentration ratio) is also given in Table I. These values are also lower for our crosslinked radiation-grafted membranes than for the uncrosslinked Nafion membranes. The mass-based water swelling of the ETFE-based membranes are higher than those of their FEP-based counterparts. This difference in swelling is largely a result of the higher extent of fluorination and thus repeat unit weight in the case of the FEP-based membranes because the water/acid concentration ratios are nearly identical for membranes of the same thickness but based on the two different base polymers. For each radiation-grafted membrane type, FEP- or ETFE based, the swelling decreases on a mass.
basis or in terms of the water/acid concentration ratio as the membranes become thinner. This lower extent of swelling in the thinner membranes has been ascribed (18) to gradients in the concentration of the grafted monomers through the membrane thickness. Thus the thinner membranes have a higher relative content of the larger crosslinking monomer DVB than the thicker membranes do, and thus the thinner membranes are more effectively crosslinked and swell to a lesser extent.

Testing in PEFCs

Thinner Membranes. The in-situ characterized properties of our membranes and the comparably thick Nafion membranes are summarized in Table II. The thinner radiation-grafted membranes have lower area resistances than their thicker counterparts (Table II) and thus there is an increase in the PEFC performance with the thinner membranes, as shown by the maximum power densities in Table II and by the polarization curves in Figure 3. Unfortunately, we are not able yet to take complete advantage of the decrease in membrane thickness because the specific resistance of our membranes increases as they become thinner. As mentioned earlier, we have ascribed this effect to inhomogeneities in the grafted monomer distribution through the membrane thickness (18), and we are examining ways of overcoming this challenge. The type of base polymer film, perfluorinated FEP or partially fluorinated ETFE, does not appear to influence the polarization performance of the PEFC, as shown in Figure 4. In spite of the increase in specific resistance as our membranes become thinner, both the polarization curves in Figure 4 and the summarized maximum power densities in Table II indicate that, under the same operating conditions, the polarization characteristics of PEFCs containing our radiation-grafted membranes are comparable or better than those of PEFCs containing Nafion membranes of similar thickness.

![Figure 3: Performance of 40 and 125 μm thick radiation-grafted FEP-25 and FEP-75 membranes in a H₂/O₂ fuel cell at 60 °C and 1.0 bar (absolute) gas pressure.](image1)

![Figure 4: Performance of 40 μm thick radiation-grafted ETFE-25 and FEP-25 membranes in a H₂/O₂ fuel cell at 60 °C and 1.0 bar (absolute) gas pressure.](image2)
Table II  *In-Situ* Characterized Membrane Properties: 60 °C, 1 atm. H₂ and O₂

| Membrane   | Area Resistance / (mΩ cm²) | Specific Resistance / (Ω cm) | Maximum power densities / mW cm⁻² |
|------------|-----------------------------|------------------------------|----------------------------------|
| FEP-25     | 65                          | 16                           | 550                              |
| FEP-75     | 120                         | 9.6                          | 450                              |
| ETFE-25    | 66                          | 17                           | 490                              |
| ETFE-50    | 96                          | 11                           | 470                              |
| ETFE-100   | 135                         | 9                            | 390                              |
| Nafion N-112 | 70                         | 11                           | 440                              |
| Nafion N-115 | 150                        | 10                           | 380                              |
| Nafion N-117 | 190                        | 9.5                          | 270                              |

**Long-Term PEFC Testing.** We have recently obtained reproducible membrane cell lifetimes (in terms of *in-situ* membrane resistance) of greater than 5000 hours at 65°C with our radiation-grafted PSI membranes as shown in Figure 5. In this test the PEFC was restricted to operating at voltages greater than about 650 mV and thus in the cell operating region characterized by useful electrical efficiencies and low heat generation. Over this period of time the membrane resistance increased only by about 0.5 %/100hr, qualitatively indicating that the loss of proton-conducting groups has not been too extensive. More recently, we have begun tests under similar operating conditions at higher temperatures. An example of a long-term test currently in progress at 80 °C is shown in Figure 6. The membrane resistance and the cell current and voltage do not exhibit any large-scale changes indicating that the membrane remains fairly stable during the first 1200 hours of this experiment.

**Post-Mortem Membrane Analysis**

Transmission mode FTIR measurements were carried out on membranes after their testing in fuel cells was finished. The absorbance of the acid-form of the membranes was too high to yield useful spectra even when the membranes were first dried under vacuum at 80 °C and rapidly transferred to the spectrometer (not shown). Better spectra were obtained by exchanging the membranes into their K⁺-exchanged form, but the absorbance of many of the bands of interest were still greater than 2 (less than 1% of the light transmitted) even for the thinnest 40 μm membranes. Useful infrared spectra (all absorbances less than 2) were obtained by measuring in the Attenuated Total Reflectance (ATR) mode. In contrast, FT-Raman measurements were readily measured through the film thickness by placing an aluminum mirror in the light path behind the sample.
Figure 5: In-situ membrane resistances of FEP-75 membranes during long-term testing in a H₂/O₂ fuel cell at 60 °C and 1.0 bar (absolute) gas pressure.

Figure 6: In-situ membrane resistance of FEP-75 membrane and cell voltage during long-term testing in a H₂/O₂ fuel cell at 80 °C and 1.0 bar (absolute) gas pressure. Current density 0-916 h 0.35 A/cm², < 916 h 0.28 A/cm².
Raman spectra of an ETFE base polymer film and an uncrosslinked grafted film and untested and PEFC-tested K+-form membranes prepared from this base polymer are shown in Figure 7. Aromatic bands at about 3050 (C-H stretch), 1600 (quadrant ring stretching), 1130 and 1000 (C-H bending coupled with ring motions) and 785 cm⁻¹ (C-H wag), and aliphatic bands at 2900 cm⁻¹ (C-H and CH₂ stretch) are found in the spectra of the grafted film (Figure 7b) but not in that of the base polymer (Figure 7a). After sulfonation in the spectrum of the untested membrane a strong absorption band develops at 1125 cm⁻¹ due to the stretching vibration of the RSO₃⁻ anion. This uncrosslinked membrane was next tested in a PEFC. The cell performance was stable for several hundred hours, and then the membrane resistance increased and the cell performance diminished (in terms of polarization properties and power) with further testing. After about 500 hours of testing, the membrane was removed from the PEFC and analyzed. The membrane was observed to have some white regions in the active area. The spectrum of one of these white regions is shown in Figure 7e and appears to be identical with that of the unmodified ETFE base polymer (Figure 7a). The spectra of one of the active area regions having a normal transparent light brown color is shown in Figure 7d and it is essentially identical to that of the untested membrane (Figure 7c). The partially fluorinated base polymer ETFE did not appear to undergo degradation even in the most heavily degraded white region. These Raman spectral results were found to correlate well with infrared spectral changes observed in ATR mode FTIR spectroscopic investigations and ion-exchange capacity measurements on regions of the untested and tested membrane. These results indicate that while some regions of the active area analyzed suffered a complete loss of the sulfonated polystyrene graft component, at least in this particular PEFC test, other regions suffered little degradation. Wang and Capuano reported (10) that they found differences in the extent of degradation of different regions of their membranes in their post-mortem analyses also. We are continuing to investigate this in-situ membrane degradation.
As we reported earlier based on in-situ membrane resistance and cell polarization measurements during long-term PEFC testing, the in-situ stability of our membranes prepared using the double crosslinking concept (DVB and TAC) is much better than that of uncrosslinked radiation-grafted membranes (11-13). For example, spectroscopic analysis and ion-exchange capacity measurements were carried out also on a crosslinked ETFE-50 membrane after about 500 hours of testing in a PEFC under the same operating conditions (Figure 8). In contrast to the characterization results on the uncrosslinked membrane, no evidence of significant degradation or inhomogeneities in the doubly crosslinked membrane was found by FTIR-ATR or FT-Raman spectroscopic analysis or ion-exchange capacity measurements. It is important to note that in some of our present cell and stack designs, mechanical breakage of the membrane during cell operation can be a problem with either thinner Nafion membranes or the thinner PSI crosslinked radiation-grafted membranes. In these cases, mechanical failure, probably due to swelling stresses near the active area (swollen membrane)/gasket (non-swollen) border in the PEFC (14,18) often seem to be solely responsible for the membrane failure. We are currently examining ways to alleviate this problem by still further improving the mechanical properties of our crosslinked membranes and our our cell and stack designs.

Figure 8. FT-Raman spectra: (a) 50 mm ETFE film, (b) grafted film, (c) untested membrane, and (d) tested active area of membrane.

**CONCLUSIONS**

The polarization performance of PEFCs containing our radiation-grafted membranes has been improved by the development of thinner membranes based on thinner base polymer films. Membrane mechanical properties have been improved through the use of
partially fluorinated ETFE films as base polymers. Long-term testing of our membranes has been carried out for periods of more that 5,000 hours at 60 °C and more than 1400 hours at 80 °C. Post-mortem membrane analysis by means of FT-Raman spectroscopy indicate that membrane degradation is limited to the sulfonated polystyrene-based graft component, even when the partially fluorinated base polymer ETFE is used. Future research efforts will be devoted to improving the mechanical properties and chemical stability of our membranes even further.

ACKNOWLEDGMENTS

Financial support for this work by the Swiss Federal Office of Energy (BFE); electron beam irradiation by Mr. C. Günthard of Studer AG, CH-4658 Däniken; gamma irradiation by Mr. M. Steinemann of the Paul Scherrer Institute (PSI) Hot Laboratory; Melt Flow Index (MFI) measurements on irradiated fluoropolymers by Professor H.G. Bühler and Mr. M. Wyler and Mr. M. Benz of Technikum Winterthur Ingenieurschule (TWI), CH-8401 Winterthur; characterization of membrane mechanical properties by Dr. Ch. Löwe and Mr. Ch. Walder of the Swiss Federal Laboratories for Materials Testing and Research (EMPA), CH-8600 Dübendorf, membrane preparation by Ms. F. Geiger of PSI, are all gratefully acknowledged.

REFERENCES

1. Personal communication, R. Hodann, Nowofol Kunstoffprodukte GmbH, Siegsdorf, Germany, July 1998.
2. Personal communication, E. Chamot, Chamot Labs., July 1998.
3. Personal communication, C. Günthard, Studer AG, Däniken, Switzerland, August 1998.
4. Personal communication, J. Chrusciel, Energy Sciences Inc., Wilmington MA, USA, July 1998.
5. F.D. Dardel and T.V. Arden in Ullmann's Encyclopedia of Industrial Chemistry, Fifth ed., B. Elvers, S. Hawkins, M. Ravenscroft, and G. Schulz Eds., Vol. A 14, p. 393.
6. R.A. Register and R.K. Prud'homme in Ionomers: Synthesis, structure, properties, and applications, M.R. Tant, K.A. Mauritz, and G.L. Wilkes, Eds., Chapman and Hall, London, 1997, Chapter 5.
7. G.E. Boyd, B.A. Soldano, O.D. Bonner Ind. Eng. Chem., 58, 456 (1954).
8. F.N. Büchi, B.Gupta, M. Rouilly, P.C. Hauser, A. Chapiró, and G.G. Scherer, Proceedings of the 27th IECEC Conference, 3, 3.419 (1992)
9. F.N. Büchi, B.Gupta, O. Haas, and G. G. Scherer, Electrochim. Acta, 40(3), 345 (1995).
10. H. Wang and G.A. Capuano, J. Electrochem. Soc., 145(3), 780 (1998).
11. F. N. Büchi, B. Gupta, O. Haas, and G. G. Scherer, J. Electrochem. Soc., 142, 3044, (1995).
12. M. Rota, H. P. Brack, F. N. Büchi, B. Gupta, O. Haas, and G. G. Scherer, Extended Abstracts, 187th Meeting of the Electrochemical Society, Reno, NE, 1995, Vol. 95-1, p. 719.
13. F. N. Büchi, B. Gupta, G. G. Scherer European Patent Application 94 924 184.8-2111
14. G. G. Scherer, H. P. Brack, F. N. Büchi, B. Gupta, O. Haas, M. Rota; Hydrogen Energy Progress XI, Proceedings of the 11th World Hydrogen Energy Conference, Stuttgart, Germany, June 1996; Vol. 2, p 1727.
15. R. Hodgdon, J. R. Boyack, and A. B. LaConti, in Advance Development and Laboratory Technical Report, No. 65DE5, General Electric Co., West Lynn, MA, USA, 1966.
16. G. Zundel, Hydration and Intermolecular Interaction, Infrared Investigations with Polyelectrolyte Membranes. Academic Press, New York, 1969.
17. B. Gupta, F. N. Büchi, G. G. Scherer, J. Polym. Sci.: Part A: Polym. Chem. 32, 1931 (1994).
18. H. P. Brack and G. G. Scherer Macromol. Symp. 126, 25 (1997).
19. F. N. Büchi, A. Marek, G. G. Scherer, J. Electrochem. Soc. 142(6), 1895 (1995).