MODIFICATION AND CHARACTERIZATION OF THIN POLYMER FILMS FOR ELECTROCHEMICAL APPLICATIONS

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Abstract: Proton-conducting polymer membranes are utilized as the solid electrolyte in low temperature polymer electrolyte fuel cells (PEFC), which are efficient energy converters. We have selected the process of radiation grafting and subsequent sulfonation to prepare novel membranes because of its feasibility as a low cost production method. Investigations of the two first preparations steps, i.e., irradiation and grafting, lead to insight concerning the optimization of these two steps and the dependence of the final membrane properties on the various preparation parameters.

INTRODUCTION

Ionically-conducting thin polymer films can be utilized as *solid electrolytes* in electrochemical devices, e.g., fuel and electrolysis cells, batteries, and sensors. Fuel cells are promising energy converters due to their potentially high efficiency and their environmental friendliness (Ref. 1). In a fuel cell, a fuel, e.g., hydrogen, and an oxidant, e.g., oxygen from air, are electrochemically converted to water, thereby generating electricity and heat.

$$H_2 + O_2 \rightleftharpoons H_2O + \text{electricity} + \text{heat}$$

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Acidic fuel cells are CO_2 tolerant, and therefore air can be used as the oxidant. This is an important advantage for any terrestrial application.

In the low temperature (≤100 °C) polymer electrolyte fuel cell (PEFC) a *proton-conducting polymer membrane*, typically 25 to 100 µm thick, acts as both *electrolyte* and *separator* (Ref. 2). Fig. 1 shows a part of a PEFC in a typical plate and frame arrangement for a fuel cell stack, in which several cells are connected in series. Plate and frame configurations are common in many other electromembrane processes, for example, in electrodialysis, so the problems encountered in fuel cell stacks and discussed here are applicable to many other electrochemical systems.

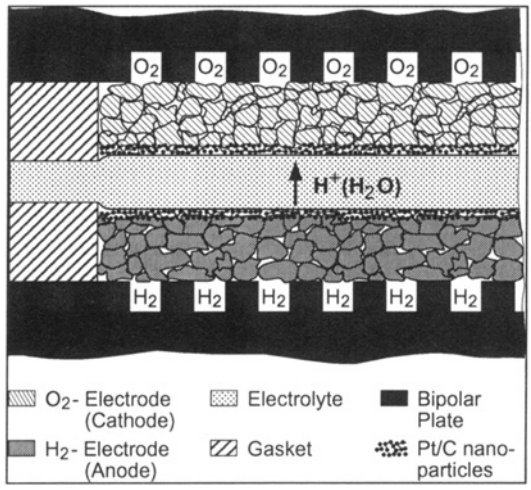

Fig. 1 Polymer Electrolyte Fuel Cell (not to scale)

Within the active area of current flow the polymer electrolyte is sandwiched between two gas diffusion electrodes (H_2-anode, O_2-cathode), each consisting of a PTFE-impregnated carbon structure (e.g. cloth, paper). The electrode surfaces that are bonded to the membrane are activated by nano-particles of platinum, which are highly dispersed on carbon to obtain a high platinum surface area at low platinum loadings (≤1 mg Pt cm^{-2}). The part of the membrane within the active area of current flow has to be hydrated to facilitate high proton conductivity and, therefore, to minimize the ohmic loss due to the electrolyte resistance. Hydration of the membrane during cell operation is achieved by humidifying the reactant gases.

Outside of the active area the membrane is sandwiched between gaskets that separate the anode and cathode compartment from each other and from the environment. This part of the membrane dries out during operation and, therefore, is thinner than the hydrated (swollen) membrane area within the active area under current flow. A bipolar plate separates the anode side of one cell from the cathode side of the neighboring cell. Each side (surface) of the bipolar plate contains flow channels for the respective reactant gases.

As stated previously, the membrane functions both as electrolyte and gas separator. This means that the membrane should possess those properties shown in Table I in order to fulfill this dual function. Some of these properties can be easily quantified, such as the specific resistivity. Others such as the surface acidity depend, for example, on the design of the membrane/electrode interface. The desired mechanical properties depend strongly also on the cell geometry and design. Therefore, only qualitative criteria can be stated for most of these properties.

Tab. I Membrane properties required for PEFC applications

flat, non-reinforced
dense, no pores
not brittle when dry
thickness of 25 - 100 µm
low gas crossover in hydrated state
strong acid, $-SO_3H$
specific resistivity < 10 Ωcm (80 °C)
area resistance < 0.1 Ωcm^2 (80 °C)
high surface acidity
electro-osmotic transport $H_2O/H^+ \cong 1-3$
thermal and hydrolytic stability (up to 100 °C)
oxidative stability
reductive stability

A minimum hydration level of the membrane, typically 10 to 20 water molecules per sulfonic acid site ($H_2O/-SO_3H$), is necessary to achieve the desired specific resistivity value in Table I (Ref. 3). This hydration also determines the electro-

osmotic water flow from the anode to the cathode side of the membrane, which is balanced by back diffusion of water from the cathode to the anode (Ref. 4). Typically one or both of the reactant gases are humidified so that the membrane remains hydrated.

Water management in the fuel cell system is important and has consequences on the overall efficiency of the system (Ref. 5). Water content also influences surface acidity (Ref. 6), gas permeation (Ref. 7), and mechanical properties (Ref. 8). Membrane hydration can also affect membrane degradation in the fuel cell application since it affects gas crossover. Gas crossover in the fuel cell can result in the formation of highly reactive hydroxyl radicals. These radicals are believed to initiate membrane degradation, for example, by the extraction of labile α-hydrogens in membranes based on sulfonated polystyrene (Ref. 9).

THE RADIATION GRAFTING PROCESS : GENERAL IMPLICATIONS FOR MEMBRANE PREPARATION

There is a strong incentive to develop novel low cost proton-conducting polymer membranes because the currently available materials do not meet the cost requirements. We have selected the radiation grafting process to prepare low cost novel solid electrolytes for application in polymer electrolyte fuel cells. Although this process has been scaled up by others to the pilot-plant and industrial level for the production of membranes used in other applications, very little has been described in the open literature about fundamental investigations of the individual preparation steps. Essentially, this is a three step process, consisting of irradiation, grafting, and sulfonation, to convert a non-conducting commodity polymer film into a proton-conducting membrane (Fig. 2).

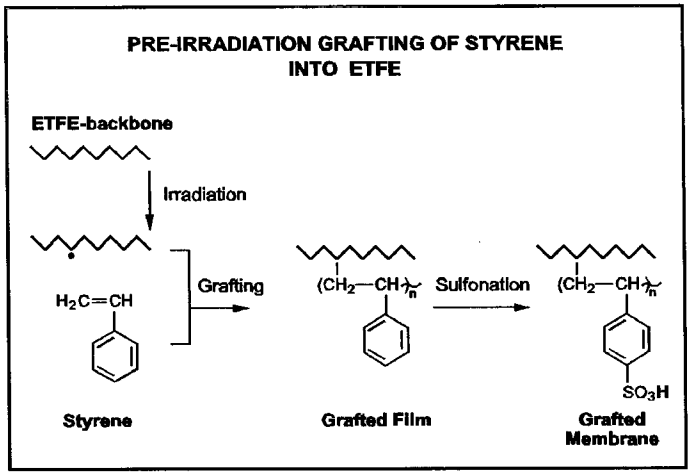

Fig. 2 Membrane Preparation by Pre-Irradiation Grafting

The grafting of a pre-irradiated film by a monomer, in which the film does not swell, is illustrated schematically in Figure 3.

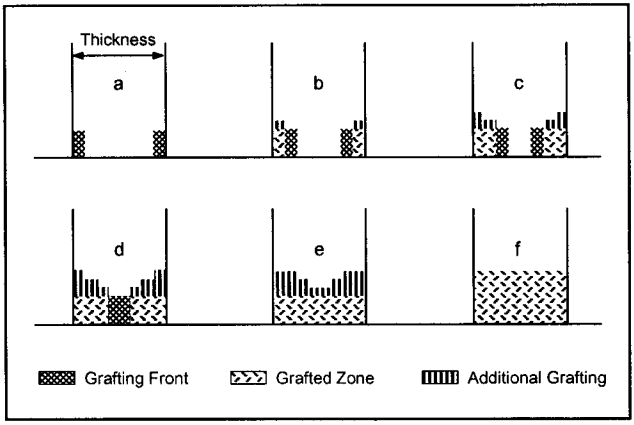

Fig. 3 Grafting Front Mechanism

Monomer grafting begins only at the surface of the irradiated film (Figure 3a) and later penetrates into the interior (Figure 3c), depending on the solubility, diffusion coefficient, and reactivity of each of the graft monomer components, e.g., styrene

and divinylbenzene (DVB). A homogeneous graft level across the membrane thickness has to be achieved so that the film has a high bulk proton-conductivity (Figure 3e-f) and not just conductivity in the near surface regions (Figure 3a-d).
We present here some of our results concerning mainly the characterization of the two first preparation steps, irradiation and grafting, and of some important membrane properties. These investigations were carried out using poly(tetrafluorethylene-*co*-hexafluorpropylene), or FEP, and poly(ethylene-*alt*-tetrafluorethylene), or ETFE, base polymer films and styrene, divenylbenzene (DVB), and triallylcyanurate (TAC) as the grafting monomers. One has to bear in mind that the starting materials in our film modification process are technical products and their properties are largely determined by their production processes. The next sections will provide and discuss examples of how aspects of these industrial processes for the preparation of our starting materials can have important influences on both the preparation and properties of our radiation-grafted membranes.

IRRADIATION OF FEP AND ETFE FILMS

Irradiation of polymers leads to the formation of radical or ionic species due to heterolytic or homolytic bond scission reactions. These reactions can have several consequences (Ref. 10) including : (a) the dominance of either chain scission or crosslinking reactions and the resulting changes in the polymer molecular weight, and (b) the formation of such oxidative degradation products as acid fluoride, carboxylic acid, alcohol, and hydroperoxide groups if even traces of oxygen are present during, or in some cases, after the radiation processing. Two irradiation sources are used in our investigations: a cavity-type Co^{60} source, which emits gamma irradiation at 1.17 and 1.33 MeV (mean value of 1.25 MeV) and a linear electron accelerator with an electron energy of 2.5 MeV. The different nature of the two types of irradiation, photons versus charged particles, results in very different penetration depths for the two different irradiation methods. However for a typical base film thickness of 100 µm or less, the radical formation is expected to be homogeneous throughout the thickness for both gamma irradiation and 2.5 MeV

electron irradiation. The dose rates of the two radiation sources are quite different however, 6 kGy/h for the gamma-chamber and 15 kGy/s for the linear electron accelerator. Thus samples are exposed to the respective radiation for very different periods of time to accumulate the same dose, e.g., 10 h versus 4 s for a dose of 60 kGy. Typical accumulated doses for pre-irradiation grafting range from 10 to 100 kGy. This brings up a further problem, the atmosphere in which the sample is irradiated. While for short exposure times (electron irradiation) the exclusion of oxygen can be fairly well controlled, the much longer exposure time in the gamma-chamber complicates the exclusion of oxygen, especially when plastic sample containers are used instead of glassware. In the following section we will distinguish between irradiation under inert atmosphere (N_2) and air.

We have characterized our samples both prior to and subsequent to the irradiation step. In our membrane preparation method, pre-irradiated samples are stored prior to grafting at -80°C, either packed in aluminum foil in the case of the samples that have been irradiated in air or still packed in heat-sealed, low permeable polyamide/polyethylene composite bags under inert atmosphere in the case of the other samples.

Infrared Spectroscopic Investigations

We have used FT-IR spectroscopy to investigate the changes occurring in our FEP and ETFE base polymer films upon irradiation and during their subsequent storage. Lunkwitz and co-workers (Ref. 11) have used FT-IR spectroscopy to study the effects of electron irradiation in air on PTFE and FEP powders. Their goal of improving the adhesive properties of fluoropolymer surfaces is based on a reaction scheme in which carbon-based radicals react with oxygen in the air to form oxy-and peroxy-radicals and peroxide bridges. These functional groups will undergo β-scission reactions upon a second excitation to form acid fluoride groups and, after subsequent hydrolysis reactions, carboxylic acid groups. The improved adhesive and wetting properties of these fluoropolymers when they are irradiated in air has been ascribed to the formation of acid fluoride and carboxylic acids. All of the acid fluoride and carboxylic acid groups that are formed, of course, are end groups resulting from chain scission reactions in the case of PTFE. These desirable

reactions of radicals with oxygen and subsequent chain scission in the case of the work of Lunkwitz and co-workers are, however, extremely undesirable in our pre-irradiation grafting method because : (1) oxy- and peroxy-radicals and peroxides are much less reactive than carbon-based radicals (Ref. 12) and (2) chain scission reactions lead to loss of such desirable properties as mechanical strength and flexibility (Ref. 10). Nonetheless Lunkwitz and co-workers have developed a method for quantifying the content of acid fluoride and carboxylic acid groups in irradiated fluoropolymer films and have studied a useful system with which we can compare our results.

The spectra of an FEP film before and after irradiation is shown in Figure 4. The absorbance bands at 1885 cm^{-1}, 1812 cm^{-1}, and 1775 cm^{-1} are assigned (Ref. 11) to acid fluoride, isolated carboxylic acid, and hydrogen-bonded carboxylic acid groups, respectively.

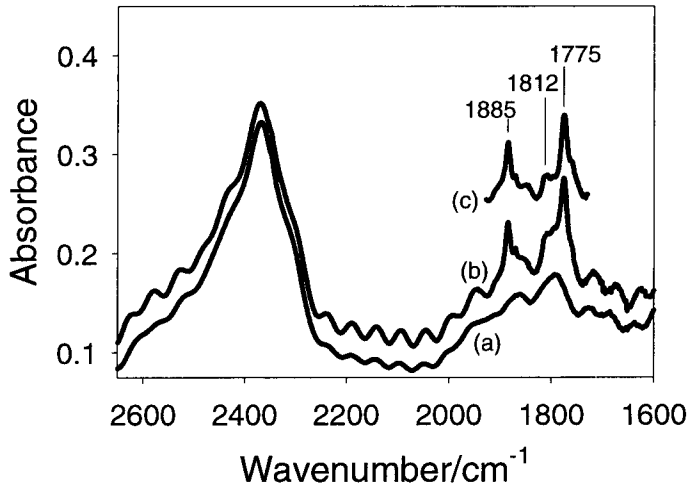

Fig. 4 Mid-infrared spectra of (a) unirradiated 75 μm FEP film, (b) the same FEP film after 150 kGy gamma irradiation in air and subsequent storage at room temperature in air for two days, and (c) the results of the spectral subtraction of spectrum (a) from (b).

Our work to date indicates (Ref. 13) that (1) acid fluoride groups are the dominant degradation product formed during irradiation with low doses and high dose rates in

air. Carboxylic acid groups are formed in addition only during irradiation with high total doses and low dose rates in air (γ/air). The total summed concentrations of acid fluoride and carboxylic acid groups for various irradiation treatments is shown in Figure 5 for irradiated FEP films, and it : (2) increases with increasing irradiation dose, (3) increases for the same irradiation dose as : e^-/N_2 << e^-/air < γ/air, and (4) remains constant during storage at or below room temperature.

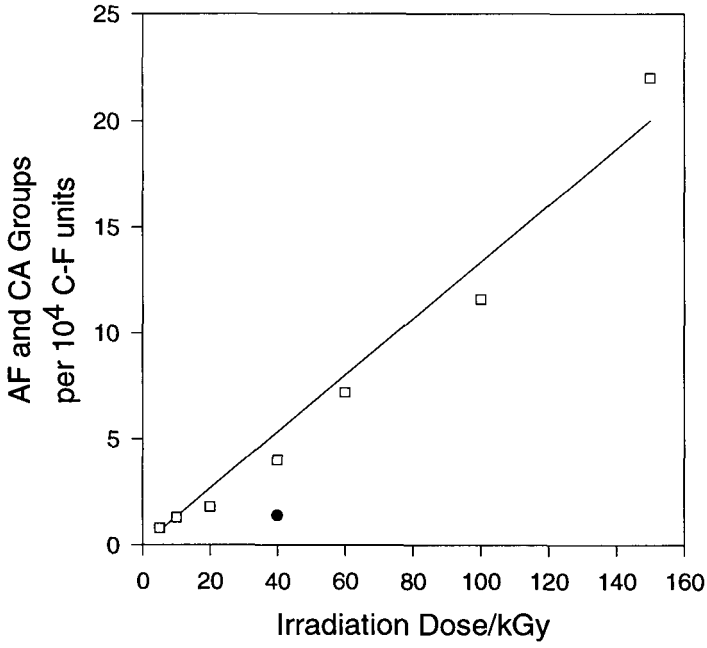

Fig. 5. Concentration of acid fluoride (AF) and carboxylic acid (CA) groups per 10^4 C-F units in (□)γ/air and (●) e^-/air irradiated 75 μm FEP films. The content of AF and CA groups in the 40 kGy e^-/N_2 irradiated films was below the detection limit.

Carboxylic acid groups are formed only during γ/air radiation processing (1) because it requires the presence of water vapor (air) in the irradiation atmosphere and time for water vapor to diffuse into the film and react with acid fluoride groups. In particular, water is expected to have only a very low solubility in hydrophobic fluoropolymer films. The dependence of the summed concentrations on dose (2)

and irradiation method (3) arises because the formation of acid fluorides requires an excitation to form a radical, followed by reaction of the radical with oxygen, and finally a second excitation to provide the activation energy for the β-scission reaction. Higher irradiation doses (2) provide for the formation of a greater concentration of initial radicals and for more subsequent excitations. The reaction conditions are most favorable during γ/air irradiation (3) because it has the longest irradiation times and is carried out under an oxygen containing atmosphere. The reaction conditions are less favorable during e^-/air irradiation because the irradiation time is shorter, and the reaction conditions are even less favorable during e^-/N_2 irradiation because of the combination of short irradiation times and the possible presence of only trace oxygen levels.

Upon storage of the irradiated FEP films at room temperature in air and darkness (4), the acid fluoride groups undergo hydrolysis to form carboxylic acid groups, but the sum of the acid fluoride and carboxylic acid concentrations remains constant. β-scission reactions do not occur under these conditions because the activation energy is high enough to require either light or higher temperatures for initiation.

In contrast, few acid fluoride or carboxylic acid groups have been found to form (Ref. 12) upon irradiation of ETFE films, even in the case of γ/air irradiated ETFE. The dominant mid-infrared spectral changes are instead due to the development of (1) an anomalous band at 2342 cm^{-1}, shown in Figure 6 and tentatively assigned here to the allyl radical, and (2) absorption bands in the O-H stretching region near 3300 to 3600 cm^{-1} (not shown) due to peroxide and alcohol groups (Ref. 14).

This anomalous absorption band at 2342 cm^{-1} has not been observed to date in any irradiated FEP films, and it has the following characteristics : (1) it is not present in the spectrum of ETFE films directly after irradiation, (2) it develops and intensifies during storage under oxygen-free conditions, (3) for the same irradiation and storage conditions, it is more intense for samples that have received a higher irradiation dose, and (4) it disappears rapidly upon exposure to air at room temperature. Characteristics 1-4 are similar to those reported for the allyl radical from ESR investigations of irradiated PE and ETFE (Ref. 15). In those investigations resonance stabilized allyl radicals were reported to form from the initially isolated single carbon based radicals by means of hydrogen migration reactions.

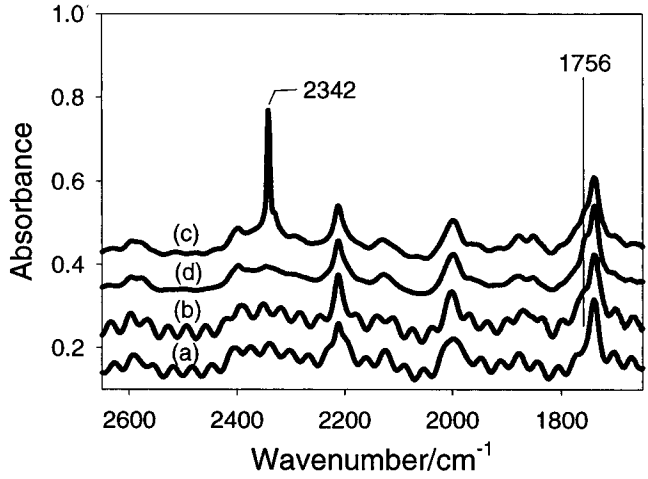

Fig. 6 FTIR spectra of 100 μm ETFE films : (a) unirradiated, (b) directly after irradiation with 40 kGy γ/air, (c) sample (b) after storage for 1 week at -80°C in inert atmosphere, and (d) sample (c) after 1 hr at 25°C in air.

Only comparatively small changes are observed in the carbonyl region in Figure 6, and the most prominent is the appearance of a shoulder at 1756 cm^{-1}. The difference between the interference fringes observed in the spectra in Figures 4 and 6 arises because the irradiated sample was large in area compared to the infrared beam cross-section of the spectrometer and there can be variations in the sample thickness and surface planarity over this larger sample area.

In the O-H stretching region of the mid-infrared region two bands are observed to develop in the spectra of ETFE films upon irradiation. They are an absorption band at 3360 cm^{-1} assigned to hydrogen-bonded hydroperoxide and alcohol groups and another at 3545 cm^{-1} assigned to hydroperoxide and alcohol groups that are not involved in hydrogen bonding. The content of hydroperoxide groups that are active in grafting can be quantified from a difference spectrum obtained by subtracting the spectrum of a grafted film from that of its pre-irradiated precursor film. For example, the concentration of hydroperoxide groups that are reactive in the grafting of a 20 kGy γ/air pre-irradiated 100 μm ETFE film has been determined (Ref. 13) to be

$8.3x10^{-3}$ M and $7.2x10^{-3}$ M based on the reported extinction coefficients (Ref. 14) of hydroperoxide groups.

Our investigations of irradiated FEP and ETFE films using FT-IR spectroscopy indicate that the irradiation process leads to the formation of quite different species in the two fluoropolymers. The next section will look at how the molecular weights of these two polymers are affected by radiation processing.

Melt Flow Index (MFI) Measurements

Melt flow index (MFI) measurements can be used to obtain qualitative, and in some cases, quantitative information concerning the molecular weight of polymers. Measurements of the MFI of irradiated fluoropolymer films can thus be used to determine whether chain scission or crosslinking reactions dominate as a result of the radiation processing. Representative MFI values of our unirradiated and irradiated FEP and ETFE films are given in Table 2. The irradiated samples were allowed to equilibrate with air at room temperature for one week prior to their analysis. The term pre-conditioned in our work means that the samples have been evacuated and purged with inert gas in several cycles prior to irradiation under inert atmosphere.

Tab. 2. Melt flow indexes (MFI) of 75 µm FEP and 100 µm ETFE films measured according to DIN 53'735 using a mass of 1 kg at 372°C and 300°C, respectively.

Irradiation	MFI of FEP in g/10 min	MFI of ETFE in g/10 min
unirradiated	1.3	1.1
40 kGy γ/air	8.1	9.4
40 kGy e^-/air	4.9	3.3
*2x20 kGy e^-/air	7.0	3.6
40 kGy e^-/ N_2 (pc)	4.2	0.8
*2x20 kGy e^-/ N_2 (pc)	4.2	0.8

*irradiation carried out in two steps separated by about 5 min.

pc = pre-conditioned (see text)

From the results given in Table 2 it can be seen that :
(1) irradiation of FEP under air or inert atmosphere near room temperature leads to a higher MFI value, indicating that chain scission dominates in all cases;
(2) the extent of chain scission occurring in irradiated FEP and ETFE films can be reduced by (a) using electron irradiation instead of gamma irradiation in the case of film irradiation in air, (b) using only one irradiation step in the case of e^-/air irradiation, and (c) carrying out the radiation processing under inert atmosphere;
(3) carrying out the irradiation stepwise instead of in a single step under rigorously oxygen-free conditions does not appear to greatly affect the MFI of FEP or ETFE;
and (4) ETFE will crosslink during irradiation at room temperature if the irradiation is carried out under rigorously oxygen-free conditions.
The results of our investigations using infrared spectroscopy and melt flow index measurements are consistent with each other. The maximum amount of base polymer degradation was determined by both methods to occur during the γ/air radiation processing of FEP base films. No degradation was found to occur during the e^-/N_2 radiation processing of ETFE films based on (1) the absence of bands due to carbonyl, alcohol, or hydroperoxide groups in the mid-infrared spectra of irradiated films and (2) the lack of increase in the MFI of the films upon irradiation indicating that significant chain scission has not occurred. On the basis of these results the mechanical properties of grafted films and membranes prepared from e^-/N_2 pre-irradiated ETFE base polymer films are expected to be superior to those prepared from γ/air pre-irradiated FEP films.

THE GRAFTING STEP

It was shown in the previous section that radiation processing of FEP and ETFE films can lead to very different reaction courses depending on the (1) film type; (2) irradiation source, and such irradiation conditions as (a) dose rate, (b) number of irradiation dose steps and (c) irradiation atmosphere; and (3) subsequent film storage. The second step in our membrane preparation method, the grafting step, is also greatly influenced by these same experimental parameters, and others, as will be discussed next.

Grafting Reaction Yields

The pre-irradiation grafting yields are given in Table 3 of some pre-irradiated films obtained when they are reacted with our grafting solution containing two possible crosslinkers, DVB and TAC (Ref. 16).

Tab. 3. Grafting yields of pre-irradiated films that were reacted with grafting solutions consisting of 3.5 M styrene, 0.33 M divinylbenzene, and 0.19 M triallylcyanurate in benzene, a reaction temperature of 60°C, and a reaction time of 4.5 h.

Comparison			Base Polymer Film	Irradiation Type	Dose in kGy	Graft Level in Mole %
a1	b		75 µm FEP	γ/air	60	23.0±0.5
	b		75 µm FEP	e^-/N_2	40	26
	b	c1	75 µm FEP	e^-/N_2 (pc)	25	23.2±1.2
a2	b	c1	50 µm FEP	e^-/N_2 (pc)	60	23.6±0.9
a3		c1	25 µm FEP	e^-/N_2 (pc)	80	23
a1			100 µm ETFE	γ/air	20	26
		c2	100µm ETFE	e^-/N_2 (pc)	10	30
a2		c2	50 µm ETFE	e^-/N_2 (pc)	18	33
a3		c2	25 µm ETFE	e^-/N_2 (pc)	25	31

pc= pre-conditioned (see text)

The influence of several parameters on the grafting yield are apparent:

(1) *ETFE vs. FEP as Base Polymer Film* : In comparisons a1, a2, and a3 the pre-irradiation method and grafting conditions of grafting solution composition, grafting temperature, and grafting time are held constant. For these conditions, ETFE films graft to a greater extent than FEP films. This behavior is likely due to a greater number of reactive sites available for grafting in the case of ETFE. For example, more radicals are expected to be formed per kGy in the case of ETFE because of the lower bond strengths of C-H bonds compared to C-C and C-F bonds. Also important is that many hydroperoxide groups in ETFE (Refs. 9 and 12) may be

formed from each initial radical present due to auto-oxidation reactions resulting from the presence of trace levels of oxygen. Similar reactions have not been found to occur in FEP films (Ref. 13), probably due to the higher bond strength of O-H and C-F bonds compared to C-H and O-F bonds.

(2) *Pre-irradiation Method* : In comparison b for 75 μm FEP films, the pre-irradiation dose necessary to achieve a particular level of grafting increases as: e^-/N_2 (pc) < e-/N_2 < γ/air. This increase is likely due to (a) the transformation of carbon-based radicals into less reactive (Ref. 12) oxy- and peroxy-radicals, or even acid fluoride groups, in the presence of oxygen, and (b) the loss of reactive radicals due to recombination reactions or their reaction with oxygen during the long irradiation times necessary in gamma radiation processing.

(3) *Base Polymer Film Thickness* : In comparisons c1 for FEP films and c2 for ETFE films, higher irradiation doses are required for thinner films to obtain comparable grafting levels for constant pre-irradiation and grafting processing conditions. This behavior is likely to result from the greater extent of orientation in the machine direction in thinner films (Ref. 17). The extent of orientation could be quite important because the permeability of many polymers decreases (Ref. 18) when they are oriented. The influence of orientation on grafting behavior is shown in more detail in Figure 7, in which (a) the grafting level obtained using constant pre-irradiation and grafting process parameters and (b) the extent of orientation as determined by heat shrinkage measurements are shown as a function of position across a 25 μm thick ETFE film roll width. This is a typical example of how the properties of our commodity starting materials can affect our membrane preparation process.

The extent of grafting has also been found to decrease with increasing molecular weight of the base polymer film (Ref. 19), and this decrease likely also results from lower permeability of the base polymer film. For example, Tuminello (Ref. 20) has reported that polymer permeability decreases with increases in the polymer molecular weight. He attributed this decrease to the greater number of entanglement junctions present in higher molecular weight polymers.

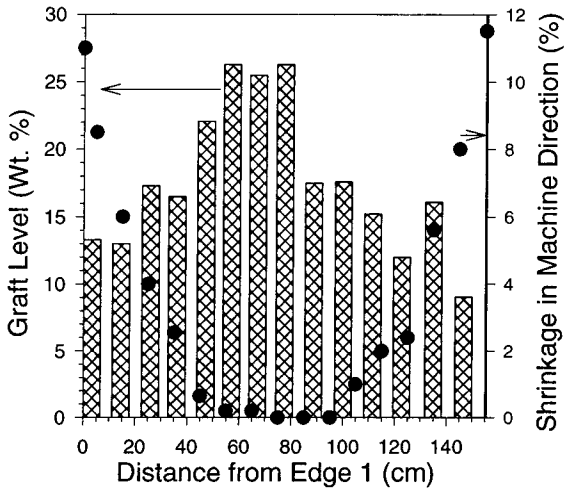

Fig. 7. (●) Shrinkage of an unirradiated 25 μm ETFE film starting film (Ref. 16) and (vertical bars) graft level of the same film after 20 kGy γ/air pre-irradiation as a function of distance from film edge 1. The extruded film roll width is 155 cm and the shrinkage was measured after annealing at 150°C for 5 min. The pre-irradiated films were grafted by reaction with a 50:50 (vol:vol) mixture of styrene and benzene at 60°C for 2.25 h.

The next section will discuss how infrared spectroscopy has been used to obtain information about the relative diffusion rates of monomers during the grafting process by examining the distribution of grafted monomers throughout the grafted film thickness.

Investigations of Grafted Films Using Infrared Spectroscopy

As was discussed in the previous section, diffusion of monomer into the pre-irradiated film is an important part of the grafting process. The diffusion rate depends however not only upon the base polymer film properties but also upon the monomer size and functionalization. These latter aspects lead to complications when more than one grafting monomer is used. We have used infrared

spectroscopy to investigate (Refs. 21 and 22) the grafting behavior when grafting solutions containing two or more monomers are used.

Mid-infrared spectra of FEP films grafted using mixtures of styrene and divinylbenzene (DVB), FEP-*g*-(styrene-*co*-DVB), are shown in Figure 8. Spectra of the entire film thickness and of the near surface region were obtained using transmission and attenuated total reflectance (ATR) measurement configurations, respectively.

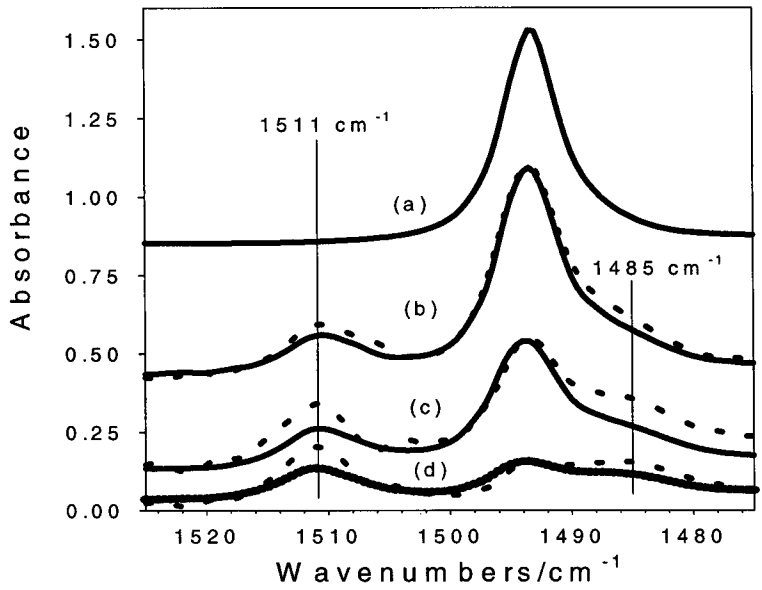

Fig. 8. FTIR absorbance spectra of 80 kGy e^-/N_2 FEP grafted with styrene/divinylbenzene (DVB) reaction mixtures consisting of : (a) 100% styrene (spectrum reduced to 1/3 of original scale), (b) 16.9 mole % DVB, (c) 25.8 mole % DVB, and (d) 76.5 mole % DVB. Our DVB monomer is typically an 80% percent mixture of the two DVB isomers, predominantly m-DVB, and the remainder (20%) is 3- and 4-ethylvinylbenzene (Ref 23). Spectra were obtained in transmission (solid line) and 45° ATR (broken line) measurement configurations. The ATR spectra have been corrected for penetration depth effects and have been arbitrarily scaled to the spectra measured in the transmission configuration.

The bands at 1511 cm^{-1} and at 1494 cm^{-1}, and the shoulder at 1485 cm^{-1} in Figure 8 are assigned (Ref. 24) to the pair of semicircle stretching vibrations of grafted para-substituted, mono-substituted, and meta-substituted benzene rings, respectively. The infrared spectra indicate that the concentration of the grafted DVB relative to that of the grafted styrene is higher in the near surface region than in the film interior. The problem is complicated because the monomers, styrene, m-DVB, and p-DVB, have different reactivities, and the two DVB isomers have different reactivity ratios with styrene (Ref. 25). In spite of these differences, the concentrations of both isomers are lower in the film interior compared to the near surface region. Therefore the larger size of DVB compared to styrene is likely to be responsible for the lower DVB content in the film interior. The diffusion path for grafting in the film middle is longer than the diffusion path for grafting in the near surface region probed by ATR spectroscopy. Thus differences in diffusion rates are expected to lead to more pronounced concentration differences in the interior of the film, especially for thicker base polymer films. For this reason thicker base polymer films are expected to have a lower concentration of grafted DVB in their interior regions compared to those of thinner films. The effect of this variation of graft composition with depth on the properties of the resulting membranes will be discussed later.

MEMBRANE CHARACTERIZATION

In this section we present some results of characterization studies of membrane swelling, surface, and mechanical properties, all of which are important membrane properties for fuel cell applications.

Swelling

The variation in graft composition as a function of film depth discussed in the previous section results in differences in the membrane properties for base polymer films of the same type, FEP or ETFE, but of different thickness, even if they are grafted under the same conditions. A higher concentration of DVB and thus greater

extent of crosslinking in the interior of thinner base polymer films leads to lesser swelling in thinner membranes.

Membrane characterization results are shown in Table 6 for membranes prepared from 75, 50, and 25 μm thick FEP base polymer films. The percent swelling and number of water molecules per acid site (H_2O/-SO_3H) decreases for membranes having the same level of grafting and ion-exchange capacity (IEC) but prepared from thinner pre-irradiated films. Also reported in Table 4 are the results of in-situ measurements (Ref. 26) of the area resistance and specific resistivity of each membrane in fuel cells operating at 60°C. The in-situ area resistances decrease but the specific resistivities increase as the membranes become thinner. This means that the ohmic losses of the fuel cell can be reduced by using thinner base polymer films, and thus decreasing the thickness of the radiation-grafted membranes, but that the ohmic losses do not decrease linearly with decreasing thickness. It is desirable to overcome this problem because lower ohmic losses of the cell tend to increase the power output of the cell.

Tab. 4. Properties of FEP-Based Membranes (e^-/N_2 irradiated, grafted as in Tab. 3)

FEP-based Membrane Thickness in μm	Ion-Exchange Capacity in $mequivg^{-1}$	Swelling in H_2O in wt. %	H_2O/-SO_3H	Area Resistance in $m\Omega cm^2$	Specific Resistivity in Ωcm
125	1.87	32	10	120	9.6
80	1.90	22	6	100	13
41	1.92	22	6	70	17

It is not yet clear how important differences in such properties as the crystallinity and extent of orientation of the different thickness base polymer films are in determining the properties of the corresponding membranes.

Contact Angle Investigations of Membrane Surfaces

In addition to our characterization of the near surface region of grafted films using FTIR-ATR spectroscopy, contact angle measurements have been used to study a

surface depth that is often stated to be characteristic of the first several monolayers, although care must be taken in interpreting their results since dispersive forces in macrobodies may act over much greater distances (Ref. 27). Typical contact angles of water and diiodomethane, surface energies, and surface energy components of ETFE-based grafted films and membranes have been reported previously (Ref. 28) and are given in Table 5. The surface energies have been determined based on a separation of the surface energy into dispersive, γ_d, and „polar" or non-dispersive components, γ_{nd}, and the geometric mean equation (Ref. 29).

Tab. 5. Contact angles and surface energies of ETFE-based radiation grafted films and membranes prepared using γ/air pre-irradiation except as indicated.

Sample No.	Sample	Graft Level in Wt.%	θ_{H_2O} °	$\theta_{CH_2I_2}$ °	γ_d mNm^{-1}	γ_{nd} mNm^{-1}	γ_{total} mNm^{-1}
I	ETFE	N.A.	98	73	18	5	23
II	PS	N.A.	91	35	43	0.4	43
III	ETFE-g-PS	52.9	91	63	24	3	27
IV	ETFE-g-SPS (γ/air)	50.5	70	71	15	18	33
V	ETFE-g-SPS (e^-/N_2)	52.0	78	64	20	10	30
VI	ETFE-g-SPS (XL)	50.1	85	63	22	6	28
VII	ETFE-g-SPS (XL)	76.0	78	66	20	10	30

N.A. = Not Applicable. These materials are not irradiated or grafted. XL= Crosslinked with DVB and TAC. These samples have been prepared using the same grafting solution as in Table 3.

The results show that the ETFE (I), polystyrene or PS (II), and grafted film, ETFE-*g*-PS, (III) films are quite hydrophobic and that the dispersive components of their surface energies are dominant.

The grafted and sulfonated membranes (IV-VII) were first swollen in water and then allowed to equilibrate a short time (several minutes) under ambient atmosphere prior to contact angle analysis. They are much more hydrophilic and the non-dispersive component of their surface energies is relatively much more important than in samples I-III. A comparison of membranes (IV) and (V) indicates that the membrane which was prepared using gamma pre-irradiation in air (IV) is more hydrophilic and has a higher surface energy than a comparable membrane (V) prepared using electron irradiation in nitrogen. This difference is likely due to the formation of such oxidative degradation products as acid fluoride and carboxylic acid groups in films that are irradiated in air, and it thus agrees well with our results discussed earlier in the section on investigations on irradiated films using infrared spectroscopy.

The crosslinked (XL) membrane (VI) is less hydrophilic and has a lower surface energy than its uncrosslinked counterpart (IV). Restricting the mobility of the sulfonic acid groups through crosslinking may limit their interaction with water. A comparison of the results for the crosslinked membranes (VI) and (VII) indicates that the membranes become increasingly hydrophilic and their surface energies increase as their graft level, and thus sulfonic acid content, increases. Subsequent contact angle investigations (Ref. 30) have found that the surfaces of the water swollen membranes are extremely sensitive to their state of hydration, and they can dry out and become much more hydrophobic on a time scale of minutes when exposed to ambient atmosphere. This is in agreement with the results of contact angle investigations on Nafion membranes (Ref. 6). Future investigations using additional measuring liquids will enable us to separate the non-dispersive components of the surface energies into their acid-base contributions (Ref. 31).

Mechanical Properties of Membranes

As was discussed in the introduction, robust fuel cell membranes are required because of the presence of mechanical and swelling stresses in the application. Typical mechanical properties, such as Young's modulus, percent elongation at the break point, and tensile strength, for some of our radiation grafted membranes are reported in Table 6.

Tab. 6. Mechanical properties of membranes prepared by pre-irradiation grafting

Comparison				Membrane	Young's Modulus in N/mm^2	Percent Elongation at Break Point in %	Tensile Strength in N/mm^2
a1b	b1	c1		γ/air 75 µm FEP	7.9x10	1.9x10	6
a2	b1	c1	d	e^-/N_2 pc 50 µm FEP	$1.8x10^2$	10	9
			d	e^-/N_2 pc 50 µm FEP (High XL)	N.M.	<1	2
a3		c1		e^-/N_2 pc 25 µm FEP	N.M.	N.M.	N.M.
a1	b2	c2		γ/air 100 µm ETFE	$1.9x10^2$	2.1x10	4.2x10
a2	b2	c2		e^-/N_2 pc 50 γm ETFE	$4.8x10^2$	2.8x10	2.5x10
a3		c2		e^-/N_2 pc 25 µm ETFE	$3.9x10^2$	2.0x10	1.1x10

N.M. = not measurable (sample too brittle)

pc = pre-conditioned (see text)

The important results can be summarized as follows:

(1) *ETFE vs. FEP Base Polymer Films :* Comparisons a1, a2, and a3 indicate that ETFE-based membranes have superior mechanical properties compared to their FEP counterparts.

(2) *Pre-irradiation Atmosphere :* Comparisons b1 and b2 indicate than the membranes prepared from e^-/N_2 pc pre-irradiated films have better mechanical properties than those prepared from γ/air pre-irradiated films.

(3) *Base Polymer Film Thickness :* Comparisons c1 and c2 show that thinner membranes have poorer mechanical properties than thicker ones. This probably is a result of both the higher pre-irradiation doses required for preparing the thinner membranes and their higher extent of crosslinking with the stiff crosslinker DVB. This shows another challenge involved in preparing thin radiation-grafted membranes.

(4) *Crosslinking :* Comparing the mechanical properties of a highly crosslinked membrane with those of a membrane having a lower degree of crosslinking (d)

shows that mechanical properties can degrade if the level of crosslinking by DVB is too high. This is an important consideration because the chemical stability of our membranes tends to increase with the level of crosslinking by DVB (Ref. 9).

These results indicate that the base polymer film type, FEP or ETFE, and its properties; the radiation processing type, gamma or electron irradiation, and the irradiation atmosphere, oxygen containing or inert; and the nature of the graft component all have a significant effect on the mechanical properties of our radiation-grafted membranes.

CONCLUSIONS

The base polymer film type and its properties have been shown to have a significant effect on the chemistry of the irradiation and grafting steps of the pre-irradiation grafting process. The properties of the final membrane product are highly dependent on the commodity base polymer film type and properties, radiation-processing parameters, and the nature of the graft component.

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