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Radiation-Grafted Polymer Electrolyte Membranes for Water Electrolysis Cells: Evaluation of Key Membrane Properties

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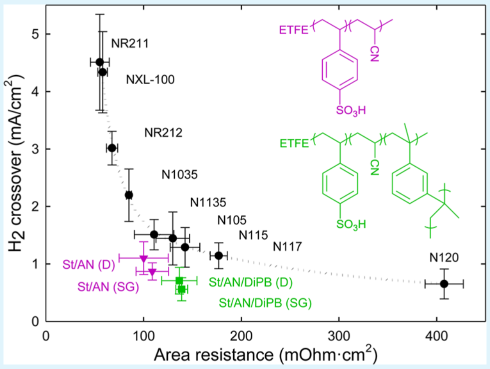
ABSTRACT: Radiation-grafted membranes can be considered an alternative to perfluorosulfonic acid (PFSA) membranes, such as Nafion, in a solid polymer electrolyte electrolyzer. Styrene, acrylonitrile, and 1,3-diisopropenylbenzene monomers are cografted into preirradiated 50 μm ethylene tetrafluoroethylene (ETFE) base film, followed by sulfonation to introduce proton exchange sites to the obtained grafted films. The incorporation of grafts throughout the thickness is demonstrated by scanning electron microscopy/energy-dispersive X-ray spectroscopy (SEM/EDX) analysis of the membrane cross-sections. The membranes are analyzed in terms of grafting kinetics, ion-exchange capacity (IEC), and water uptake. The key properties of radiation-grafted membranes and Nafion, such as gas crossover, area resistance, and mechanical properties, are evaluated and compared. The plot of hydrogen crossover versus area resistance of the membranes results in a property map that indicates the target areas for membrane development for electrolyzer applications. Tensile tests are performed to assess the mechanical properties of the membranes. Finally, these three properties are combined to establish a figure of merit, which indicates that radiation-grafted membranes obtained in the present study are promising candidates with properties superior to those of Nafion membranes. A water electrolysis cell test is performed as proof of principle, including a comparison to a commercial membrane electrode assembly (MEA).



KEYWORDS: *radiation-grafted membrane, polymer electrolyte, Nafion, electrolyzer, fuel cell, gas crossover, resistance, mechanical properties*

1. INTRODUCTION

Fossil fuels have been used as energy sources since the beginning of industrialization.[1] However, the problem of carbon dioxide and the fact that fossil fuels will be depleted in the future drive the search for alternatives.[2−4] Renewable energy is an option for replacing fossil fuels, since it is an environmentally friendly solution and its sources, such as wind and solar energy, are abundant.[5] One of the main challenges is to find suitable means for energy storage due to the intermittent nature of these primary energies.[6] Hydrogen is a potential energy vector in this context, since it offers the prospect of large storage capacities (terawatt hour range) for weeks or months (power-to-gas concept), which also allows for highly efficient reconversion to electricity in hydrogen−oxygen fuel cells.[7−9]

One approach to produce hydrogen from electricity is electrochemical splitting of water: that is, electrolysis.[10] There are three common types of water electrolyzers: alkaline, polymer electrolyte, and solid oxide.[10−12] The alkaline electrolyzer is a mature technology, but its corrosive liquid electrolyte is the main drawback for this type of electrolyzer.[11,13] The solid oxide electrolysis cell (SOEC) is still in the early stage of research and development.[14] It requires high-temperature materials and the cell has limited long-term stability.[11] In addition, SOECs are not necessarily the best devices for intermittent operation due to the lack of thermal and redox cyclability.[15] The polymer electrolyte electrolysis cell (PEEC) is a fairly mature technology yet with room for improvement in various areas, such as catalyst reduction/substitution, membrane improvement, and low-cost and corrosion-resistant current collectors and separator plates.[12,16]

The proton-conducting membrane as the electrolyte in a PEEC plays an important role in the efficiency and durability of the system. Thick perfluorosulfonic acid (PFSA) membranes, such as Nafion N115 (ca. 127 μm) and N117 (ca. 178 μm), are commonly used in PEECs.[12,17−19] However, thick membranes create relatively large ohmic resistances, which become the dominant loss term at high current densities.[20] Cost is also one of the main disadvantages of these perfluorinated materials.[21,22] In addition, these membranes are not suited for temperatures

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above 90 °C due to loss of mechanical integrity.[23] Therefore, further research is required to improve the membranes or find alternative materials.[12]

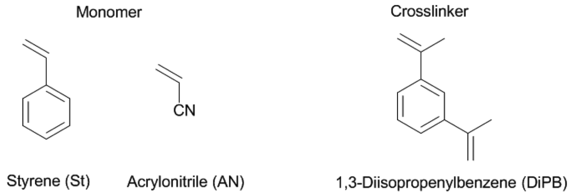
Proton conducting membranes have been intensively studied for polymer electrolyte fuel cell (PEFC) applications.[24] Despite the similar chemistry of the membranes used today for fuel cell and electrolyzer, the requirements for the two applications are somewhat different. Electrolyzers operate under fully hydrated conditions, whereas fuel cells typically operate under partially humidified conditions.[25] The concomitant different hydration states of the ionomer may affect its properties and performance.[12,26−29] Moreover, unlike fuel cells, electrolyzers may operate at high differential pressure of over 100 bar; hence mechanical and gas barrier properties of the membranes become more crucial.[20]

For electrolyzer applications, Nafion membranes have been mixed or doped with SiO_2, TiO_2, sulfated ZrO_2, and phosphoric acid to allow higher operating temperature.[30−33] Skulimowska et al.[34] used short side chain PFSA membranes, such as Aquivion and its composites, and tested them at temperatures up to 120 °C. Despite these approaches, the inherent limitations of PFSA membranes, for example, high gas permeability, remain. Hydrocarbon membranes, such as polybenzimidazoles (PBI), poly(ether ether ketones) (PEEK), poly(ether sulfones) (PES), and sulfonated polyphenyl quinoxaline (SPPQ), are considered as alternatives to Nafion membranes, since they are of potentially lower cost than PFSA membranes.[33,35−37]

Ion-conducting membranes prepared by radiation-induced grafting are another promising option. Advantages of the radiation-induced grafting method are its versatility and a potentially low-cost fabrication process.[38] The properties of radiation-grafted membranes can be readily modified by varying the composition and architecture of the graft copolymer.[39] An adequate monomer/comonomer selection or combination can be chosen to obtain a membrane with desired properties. To the best of our knowledge, up to now only Masson et al.[40] and Scherer et al.[17] have developed radiation-grafted membranes for water electrolyzer applications, whereas numerous studies can be found for fuel cell applications.[41−48] Masson et al.[40] produced the membrane by radiation-induced grafting of styrene groups onto a polyethylene (PE) matrix, and Scherer et al.[17] grafted α,β,β-trifluorostyrene onto ethylene tetrafluoroethylene (ETFE) and styrene onto poly(tetrafluoroethylene) (PTFE), followed by sulfonation of the aromatic ring.

In this work, radiation-grafted membranes based on 50 μm ETFE film were synthesized. ETFE was selected as base film because it demonstrates low mechanical degradation upon electron beam irradiation, unlike PTFE.[44] In addition, ETFE has better thermal stability than PE. The combination of styrene (St), acrylonitrile (AN), and 1,3-diisopropenylbenzene (DiPB) is chosen for grafting monomers (Scheme 1). Styrene is used as a precursor for the subsequent introduction of sulfonic acid functional groups. It is selected instead of α,β,β-trifluorostyrene, since it has better grafting kinetics and lower cost. The shortcomings associated with polystyrene, that is, limited oxidative stability, are sought to be compensated by adequate choice of comonomers. The nitrile group in acrylonitrile improves gas barrier properties when incorporated into polymer materials.[49−51] Despite its susceptibility to hydrolysis, acrylonitrile is chosen instead of methacrylonitrile (MAN) as a model compound, because MAN was not commercially available in Europe and could not be shipped to Europe during this study for regulatory reasons. Incorporation of a cross-linker, such as 1,3-diisopropenylbenzene, leads to formation of a polymer network with interconnected chains, which effectively improves the chemical stability of the membrane.[39] Moreover, unlike the more common divinylbenzene, 1,3-diisopropenylbenzene has the advantage to yield a more homogeneous cross-linker distribution in the grafted films.[52] The obtained membranes were characterized in terms of ion-exchange capacity (IEC), water uptake, gas barrier properties, area resistance, and mechanical properties, and they were compared to a selected range of commercial Nafion membranes. Scanning electron microscopy/energy-dispersive X-ray spectroscopy (SEM/EDX) analysis of the membrane cross-section was used to map the distribution of the graft component across the sample thickness.

Scheme 1. Grafting Monomers and Cross-Linker Used in This Work



2. EXPERIMENTAL SECTION

2.1. Chemicals. DuPont Nafion NR211, NXL-100, NR212, N1035, N1135, N105, N115, N117, and N120 membranes were used as reference membranes.

DuPont Tefzel ETFE 200 LZ (1.7 g/cm^3) and Saint-Gobain Norton ETFE (1.70−1.76 g/cm^3) of 50 μm thickness were used as base films for preparation of radiation-grafted membranes. The reagents for membrane preparation were styrene (≥99%, Sigma−Aldrich), acrylonitrile (≥99%, Aldrich), 1,3-diisopropenylbenzene (97%, Aldrich), 2-propanol (≥99.7%, VWR), acetone (≥99.8%, VWR), dichloromethane (≥98%, VWR), and chlorosulfonic acid (98%, Fluka).

Potassium chloride (≥99%, VWR) and potassium hydroxide solution for 1000 mL, $c(KOH) = 0.1$ mol/L (Titrisol, Merck), were used for measurement of ion-exchange capacity. The potassium hydroxide solution is diluted prior to use to obtain a concentration of 0.05 mol/L. Deionized water with a resistivity of 18.2 MΩ·cm is obtained from a Purelab Ultra MK2 Scientific Instrument (ELGA Labwater).

Johnson Matthey ELE-0162 gas diffusion electrodes with a platinum (Pt) loading of 0.4 mg of Pt/cm^2 were used for determination of hydrogen crossover and area resistance in a single cell used for fuel cell testing. Hydrogen, oxygen, argon, and nitrogen (Messer, Lenzburg, Switzerland) of at least 99.995% purity were used as received.

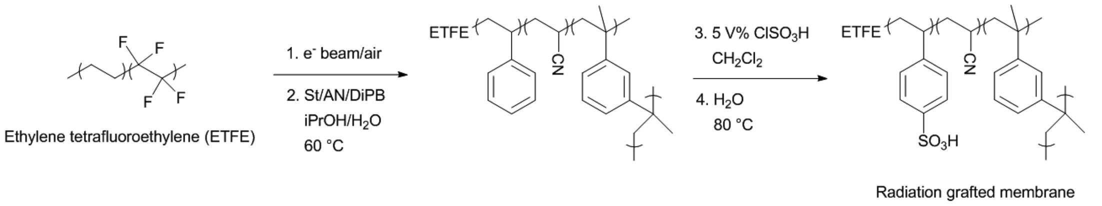
Iridium oxide (IrO_2) black and Pt black were used as catalysts to produce the membrane electrode assembly (MEA) for a preliminary electrolysis cell test. The catalyst loading was 2.03 mg of Ir/cm^2 at the anode and 1.05 mg of Pt/cm^2 at the cathode.

2.2. Instruments. Acid−base titrations were performed on a Metrohm SM Titrino 702. A thickness gauge, Heidenhain ND287, was used to determine the thickness of films and membranes.

All scanning electron micrographs were taken with a field emission scanning electron microscope (FE-SEM), Carl Zeiss Ultra 55 with SmartSEM V05.06 software. Energy-dispersive X-ray analysis was performed with a compatible accessory, EDAX TSL, AMETEK with EDAX Genesis Version 6.02 software. A Leica EM SCD500 high-vacuum sputter coater was used for FE-SEM sample preparation.

Hydrogen gas crossover experiments were performed electrochemically in a two-electrode cell setup operated in the driven cell mode. The cell had an active area of 29.16 cm^2 with graphite flow fields and

Scheme 2. Reaction Scheme for Synthesizing Radiation-Grafted Membranes



stainless steel current collectors. Temperature was controlled with Jumo dTRON 16.1 compact microprocessor controllers. The gas feeds were regulated by a Brooks model 5850E mass-flow controller for hydrogen and model 5850S for nitrogen gas. An Agilent E3633A DC power supply was used to set the cell potential and measure the current response.

With the same setup but with hydrogen and oxygen feeds, area resistance of the membranes was measured on a Tsuruga model 3566 digital AC milliohm meter at 1 kHz frequency. The cell was operated with a Hewlett-Packard 6050A electronic load in constant current mode. Cell voltage was measured with a Hewlett-Packard 34970A data acquisition unit.

Tensile tests were performed in a Zwick/Roell materials testing machine, BT1-FR005TE.A50 with testXpert V12.0 software.

The preliminary electrolyzer test was conducted in a customized electrolyzer test station at SINTEF Materials and Chemistry, Trondheim, Norway, by use of cell hardware from Baltic FuelCells GmbH with an active area of 25 cm^2. The cell hardware had parallel flow field channels made of titanium (Ti) at the anode side and carbon at the cathode side. At the anode, a polished Ti porous sinter from GKN was used as current collector, while at the cathode a carbon paper gas-diffusion layer (Freudenberg C6) was used.

2.3. Base Film Treatment.

The 50 μm ETFE films from DuPont or Saint-Gobain were cut into pieces of 14 cm × 16 cm. First they were washed in ethanol and dried in vacuum at 80 °C. Then they were electron-beam-irradiated under ambient conditions with a dose of 1.5 kGy. The irradiation was performed at Leoni-Studer AG (Däniken, Switzerland) with an acceleration voltage of 2.10 MeV. Subsequently, the films were stored at −80 °C until further use.

2.4. Membrane Preparation.

Radiation-grafted membranes were prepared by immersing a preirradiated ETFE film in a nitrogen-saturated reaction mixture containing water (10 vol %), 2-propanol (70 vol %), and monomer (20 vol %) placed in a glass reactor. Afterward, the reactor was placed in a water bath at 60 °C for a predefined amount of time to reach the desired graft level of 40% (Scheme 2, steps 1 and 2). A graft level of 40% is targeted, as this yielded in earlier studies a volumetric ion-exchange capacity similar to that of Nafion with an equivalent weight of 1100 g/mol.[45] The grafted film was rinsed with 2-propanol and then immersed in acetone under stirring overnight to remove residual monomer and homopolymer. Finally, it was dried at 80 °C under vacuum and reweighed to determine the graft level (GL), defined as

$$\mathrm{GL} = \frac{W_g - W_0}{W_0} \times 100\% \tag{1}$$

where W_g represents the weight of the grafted film and W_0 is the weight of the film before grafting.

Combinations of styrene (St), acrylonitrile (AN), and 1,3-diisopropenylbenzene (DiPB) as grafting monomers were investigated. The St/AN volumetric ratio was 40/60, which corresponds to molar fractions of $X_{St} = 0.28$ and $X_{AN} = 0.72$ in the solution and $X_{St} \approx 0.4$ and $X_{AN} \approx 0.6$ in the grafted film. The reactivity ratios of St and AN are $r_{St} = 0.52 \pm 0.06$ and $r_{AN} = 0.25 \pm 0.05$.[45] The ternary monomer mixture St/AN/DiPB contained 5 vol % DiPB with respect to the total monomer content. The total monomer content in the reaction mixture for each combination was maintained at 20 vol %. Finally, the grafted film was functionalized with sulfonic acid groups by immersing the film into 5 vol % chlorosulfonic acid and 95 vol % dichloromethane solution at room temperature for 6 h (Scheme 2, step 3). Afterward, the membrane was placed consecutively into two water baths at room temperature for 1 h each and finally in a water bath at 80 °C for 16 h for hydrolysis of sulfonyl chloride to form sulfonic acid (Scheme 2, step 4).[53] Sulfonyl chloride as the intermediate in this reaction is not shown in Scheme 2. Then the membrane was stored in a box filled with deionized water or dried under ambient conditions and stored until further use.

2.5. Nafion Pretreatment.

Nafion NR211, NXL-100, NR212, N1035, N1135, N105, N115, N117, and N120 were pretreated prior to experiment in order to obtain their fully hydrated forms. After removal of the coversheets from solution-cast NR211, NXL-100, and NR212, the membranes were immersed in a water bath at 90 °C for 1 h. Nafion membranes prepared by extrusion (without coversheets) were pretreated with a 32.5 vol % nitric acid (HNO_3) solution at 90 °C for 1 h to remove impurities and reprotonate the sulfonic acid groups. Afterward, they were washed twice with 600 mL of deionized water and immersed consecutively in three water baths at 90 °C for 1 h. The pH of the water bath was 7 at the end. Finally, all membranes were stored in boxes filled with deionized water.

2.6. Evaluation of Membrane Properties.

2.6.1. Bulk Properties. Samples for measurement of ion-exchange capacity (IEC) and water uptake were prepared by punching six discs with diameter of 2 cm from the fully hydrated membrane sample. For each type of membrane, three measurements were performed. For each IEC measurement, two discs were placed in 45 mL of 0.5 M KCl solution and the solution was stirred overnight. The number of H^+ released after the ion exchange with K^+ was determined by titration to pH 7 with 0.05 M KOH titrant. IEC is calculated according to

$$\mathrm{IEC} = \frac{n(\mathrm{H}^+)}{W_{\mathrm{dry}}} = \frac{c(\mathrm{KOH})V(\mathrm{KOH})}{W_{\mathrm{K}} - [M(\mathrm{K}^+) - M(\mathrm{H}^+)][c(\mathrm{KOH})V(\mathrm{KOH})]} \tag{2}$$

where $n(\mathrm{H}^+)$ is the number of moles of protons, W_{dry} is is weight of dry membrane in H^+ form, $c(\mathrm{KOH})$ is the concentration of KOH titrant, $V(\mathrm{KOH})$ is the volume of added KOH solution during titration, and W_{K} is the weight of dry membrane in K^+ form. $M(\mathrm{K}^+)$ and $M(\mathrm{H}^+)$ are the molar masses of K^+ and H^+, respectively.

The degree of sulfonation is the ratio of measured to theoretical IEC:

$$\text{degree of sulfonation} = \frac{\mathrm{IEC}}{\mathrm{IEC}_{\mathrm{theor}}} \times 100\% \tag{3}$$

$\mathrm{IEC}_{\mathrm{theor}}$ can be calculated as follows:[47]

$$\mathrm{IEC}_{\mathrm{theor}} = \frac{\mathrm{GL}}{\left(M_{\mathrm{St}} + \frac{X_{\mathrm{AN}}}{X_{\mathrm{St}}} M_{\mathrm{AN}}\right)(1 + \mathrm{GL}) + \mathrm{GL}(M_{\mathrm{StSA}} - M_{\mathrm{AN}})} \tag{4}$$

where X is the molar fraction of the respective monomer unit in the grafted polymer and M is the molar mass of styrene (St), styrenesulfonic acid (StSA), or acrylonitrile (AN) monomer as indicated by the subscript.

Water uptake is determined as follows:

$$\text{water uptake} = \frac{W_{\mathrm{wet}} - W_{\mathrm{dry}}}{W_{\mathrm{dry}}} \times 100\% \tag{5}$$

where W_{wet} is the weight of fully hydrated membrane. Hydration number λ is calculated from the IEC and water uptake values:

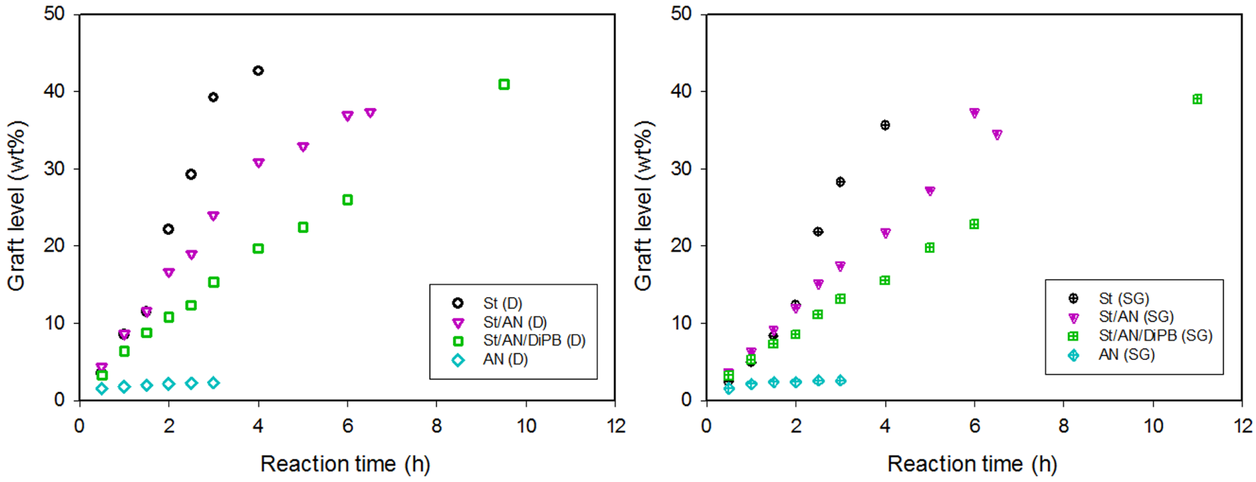


Figure 1. Reaction kinetics for cografting of styrene, acrylonitrile, and 1,3-diisopropenylbenzene into ETFE 50 μm from DuPont (D, left) and Saint-Gobain (SG, right) base film with irradiation dose 1.5 kGy.

$$\lambda = \frac{n(H_2O)}{n(SO_3H)} = \frac{\text{water uptake}}{(\text{IEC})[M(H_2O)]} \qquad (6)$$

where $n(H_2O)$ and $n(SO_3H)$ are the number of moles of water and sulfonic acid groups in the membrane and $M(H_2O)$ is the molar mass of water.

2.6.2. Gas Crossover. Hydrogen crossover was determined electrochemically in a single-cell configuration with fuel cell electrodes by feeding one side with hydrogen and the other with nitrogen, applying a potential between the two sides, and measuring the observed hydrogen crossover current density. The measurements were performed at 80 °C, 2.5 bar absolute gas pressure on both sides, 200 mL (n)/min gas flow rate, and 100% relative humidity. [Note that (n) refers to normal conditions, that is, 273 K and 1013 mbar (1 atm); thus mL (n)/min is identical to sccm, standard cubic centimeters per minute.]

2.6.3. Area Resistance. Area resistance of the membrane was measured in the same single cell on a fixed-frequency (1 kHz) AC milliohm meter at a current density of 0.2 A/cm^2 with fully humidified hydrogen and oxygen gases, temperature of 80 °C, gas pressure of 2.5 bar absolute, gas stoichiometry of 1.5/1.5, and minimum flow of 200 ml (n)/min. The area resistance at this low current density was chosen as reference point to minimize the influence of the electro-osmotic drag of water, especially for the thicker membranes, such as N117 and N120.

2.6.4. Mechanical Properties. Mechanical properties of the membranes were assessed by tensile tests performed at room temperature under ambient and fully hydrated conditions. The ASTM D 882 protocol was used as measurement standard. Prior to measurements, the membranes were cut into 10 cm × 1 cm stripes. For measurement under ambient conditions, tensile tests were conducted with five samples, and in the case of fully hydrated membranes, 10 samples were tested to ensure reproducibility. The gauge length was 5 cm and the cross-head speed was 500 mm/min. Membranes were sprayed with water during measurements under fully hydrated condition.

Uncertainties and error bars associated with experimental data represent one standard deviation of the mean, and the laws of error propagation are applied to estimate uncertainties of calculated quantities derived from experimental data.

2.7. Electrolyzer Test. The electrolysis cell, with MEA based on the radiation-grafted membrane or commercial MEA, was clamped by a pneumatic piston at 3 bar. [Note that unfortunately, for reasons of confidentiality, the supplier and specifications of the commercial MEA used as benchmark cannot be disclosed.] The cell was conditioned at 80 °C with a water flow rate of 500 mL/min deionized water on both anode and cathode for 30 min. Polarization curves were recorded galvanostatically (20 min/point).

3. RESULTS AND DISCUSSION

3.1. Membrane Bulk Properties. Preparation of radiation-grafted membranes depends on many factors, such as irradiation dose, preparation procedures, base film, monomer, comonomer(s), solvents and additives, and reaction temperature and time. Figure 1 shows the dependency of graft level on reaction time, base film type, and monomers and monomer combinations. The graft level increases with increasing reaction time, as expected. Measurement of reaction kinetics is necessary to establish the correct reaction time for obtaining a film with desired graft level. The experiments were performed at least twice to ensure reproducibility. Reactions with base films from different suppliers demonstrate dissimilar grafting kinetics. The DuPont (D) base film tends to have faster grafting kinetics than the one from Saint-Gobain (SG). Different monomers and combination of monomers also entail different kinetics. Styrene alone grafts the fastest. In contrast, acrylonitrile has the slowest kinetics. The combination of styrene and acrylonitrile (St/AN) grafts much faster than AN, which is in agreement with previously reported findings for grafting onto 25 μm ETFE base film.[45]

Addition of 1,3-diisopropenylbenzene cross-linker to the St/AN system slows down the kinetics. The target graft level for St/AN and St/AN/DiPB membranes is 40%, which yields a slightly higher IEC value than that of the Nafion membranes. In order to get the desired graft level of 40%, reaction times under the conditions used of 6.4 h for St/AN (D), 7.1 h for St/AN (SG), 9.2 h for St/AN/DiPB (D), and 11.1 h for St/AN/DiPB (SG) are required. According to the reaction time, which is indirectly related to the production time, DuPont ETFE base film is preferred over Saint-Gobain ETFE for membrane preparation from an economical point of view.

Successful preparation of radiation-grafted membranes is proven by EDX analysis of the membrane cross-section. Figure 2 shows the SEM image and EDX mappings of nitrogen and sulfur of the (cross-linked) St/AN/DiPB (D) membrane cross-section. The nitrogen distribution is relatively homogeneous with a concentration in the center of about 70−80% of the concentration near the surface. This means acrylonitrile is largely uniformly distributed. The presence of sulfur proved the successful grafting of styrene and its sulfonation. However, there is a pronounced sulfur gradient. The concentration in the center of the membrane is only about half the concentration

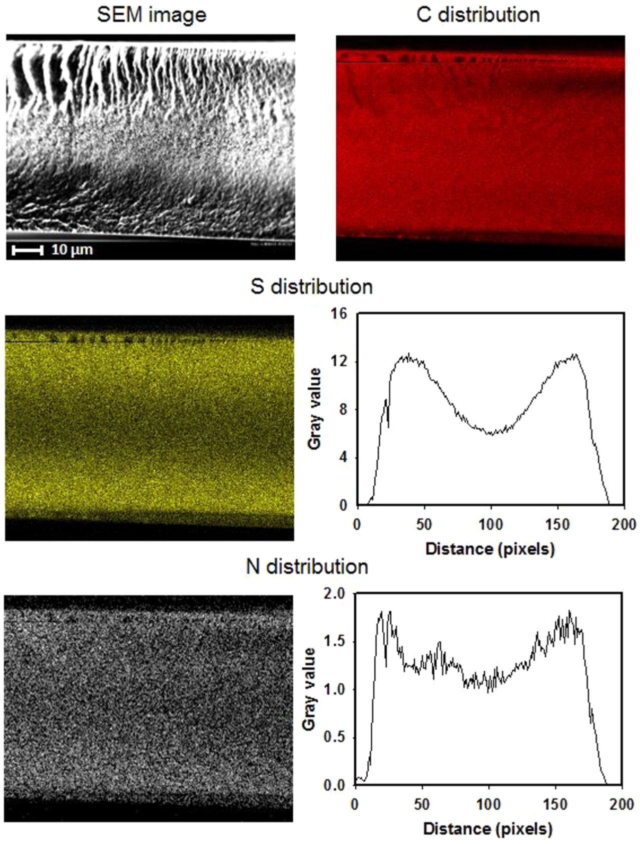


Figure 2. SEM image and EDX mappings of a cross-section of St/AN/DiPB (D) membrane with a graft level of 42%.

near the surface. The inhomogeneous sulfur distribution may cause a higher membrane area resistance compared to a membrane with homogeneous sulfur distribution. The calculated degree of sulfonation is 89% for St/AN (D) and 94% for St/AN (SG). The calculation is based on the estimated ratio of St/AN in the membrane according to Jetsrisuparb et al.[45] In case of cross-linked membranes containing DiPB, the exact composition of the grafts is not known, hence the degree of sulfonation cannot be estimated. The inhomogeneous sulfur distribution could be a result of the grafting procedure or of incomplete sulfonation in the center of the membrane, in view of the sulfonation degree. Further work is needed to optimize the membrane preparation, for example, by using another grafting condition (different irradiation dose, temperature, or solvent or combinations thereof) or sulfonation procedure (e.g., swelling the grafted films in an appropriate solvent before sulfonation or using higher chlorosulfonic acid concentration).

Table 1 shows relevant ex situ properties of Nafion and radiation-grafted membranes. IEC values of radiation-grafted membranes with a graft level of 40% are slightly higher than those of Nafion membranes. Water uptake and hydration level of cross-linked radiation-grafted membranes are comparable to those of Nafion membranes and higher than those of un-cross-linked membranes.

3.2. Gas Crossover versus Area Resistance. The results of gas crossover and area resistance measurements are represented in a property map (Figure 3). It appears that all the Nafion membranes, regardless of whether they are extruded or solvent-cast or mechanically reinforced (NXL-100), follow a general trend, indicated by the dotted line. Their position in the diagram is governed by the respective membrane thickness. Thicker membranes, such as N115 and N117, have lower hydrogen crossover but higher area resistance. Because of their gas barrier properties, they are preferred for electrolyzer application over thin membranes like NXL-100 and NR212, which are typically used for fuel cell applications. It is understandable to favor the membranes with lower gas crossover, since in the electrolyzer the purity of the produced gases is an important quality feature, and an explosive mixture of H_2 and O_2 needs to be avoided under any circumstance.

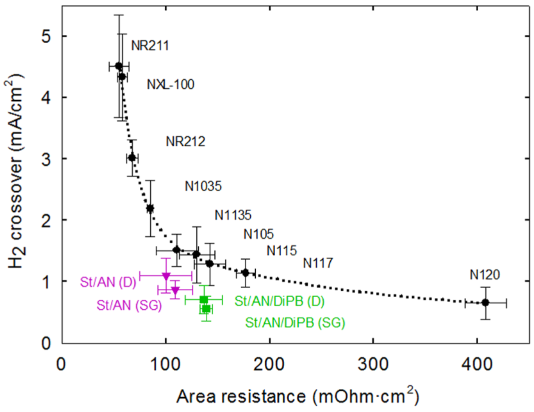


Figure 3. Property map showing hydrogen crossover vs area resistance values of various membranes.

Table 1. IEC, Water Uptake, and Hydration Values of Membranes

membrane	graft level (%)	wet thickness (μm)	IEC (mmol/g)	water uptake (wt %)	hydration (H_2O/SO_3H)
St/AN (D)	41	86.0 ± 1.0	1.25 ± 0.02	67.8 ± 2.4	30.1 ± 0.9
St/AN (SG)	40	95.3 ± 1.1	1.29 ± 0.02	68.6 ± 1.7	29.6 ± 0.3
St/AN/DiPB (D)	41	79.5 ± 0.7	1.20 ± 0.00	33.1 ± 1.0	15.3 ± 0.5
St/AN/DiPB (SG)	39	79.5 ± 0.5	1.15 ± 0.02	34.4 ± 1.9	16.6 ± 1.1
NR211		30.5 ± 0.0	1.22 ± 0.01	28.1 ± 13.6	12.7 ± 6.1
NXL-100		37.3 ± 0.3	1.01 ± 0.04	29.3 ± 4.7	16.1 ± 2.1
NR212		61.7 ± 1.3	1.16 ± 0.01	38.6 ± 6.8	18.6 ± 3.3
N1035		114.2 ± 3.8	1.15 ± 0.00	46.1 ± 3.8	22.3 ± 1.9
N1135		103.8 ± 1.5	1.05 ± 0.02	39.3 ± 2.4	20.8 ± 1.0
N105		152.3 ± 1.5	1.10 ± 0.00	47.9 ± 0.3	24.1 ± 0.1
N115		153.0 ± 1.0	1.04 ± 0.02	39.9 ± 2.9	21.2 ± 1.2
N117		202.7 ± 1.0	1.04 ± 0.00	39.9 ± 0.1	21.4 ± 0.0
N120		293.0 ± 8.2	0.83 ± 0.00	27.2 ± 0.3	18.3 ± 0.2

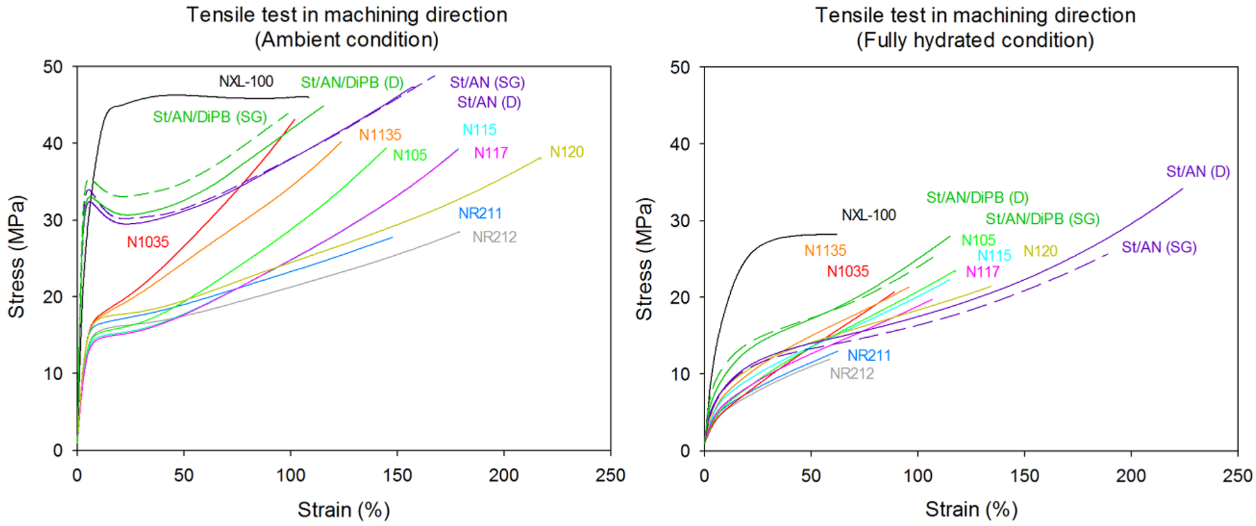


Figure 4. Results of tensile tests of membranes in the machining direction under (left) ambient and (right) fully hydrated conditions.

Moreover, high differential pressure, such as 165 bar, is used in some electrolyzer system designs.[20]

The property map can be utilized as a benchmark for evaluating alternative membranes, such as radiation-grafted membranes. The development target is a membrane with lower hydrogen crossover and lower area resistance than Nafion membranes. St/AN and St/AN/DiPB radiation-grafted membranes have lower area resistance and hydrogen crossover than N115 and N117, which makes them promising as alternative electrolyzer membranes.

Here the effect of using different base film suppliers on the properties of the resulting radiation-grafted membranes can be observed. In addition to faster grafting kinetics, radiation-grafted membranes from the DuPont base film have lower resistance but higher hydrogen crossover than membranes from the Saint-Gobain base film. This could be caused by different processing parameters used by DuPont and Saint-Gobain, which influence the microstructure of ETFE and eventually the grafting reaction.[54] The cross-linker in the St/AN/DiPB membrane results in a membrane with lower gas crossover but higher area resistance than the un-cross-linked membrane, St/AN, since the water uptake of cross-linked membranes is also reduced.

Radiation-grafted membranes, in particular the cross-linked versions, compare favorably with N115 and N117, membranes typically used in water electrolyzers, in that they offer similar or lower area resistance with considerably improved gas barrier properties. There is room for improvement to reduce the area resistance of radiation-grafted membranes by optimizing membrane preparation, increasing the graft level, or improving the homogeneity of sulfonic acid group distribution through the membrane. Moreover, the membrane resistance can be lowered by minimizing the loss of surface or near-surface radicals at different stages of film processing (irradiation, storage, and grafting), as the amount of grafted polymer on the surface depends on the concentration of surface radicals and it influences the proton conductivity of the membrane.[38]

3.3. Mechanical Properties. Tensile tests were performed at room temperature for Nafion and radiation-grafted membranes under ambient and fully hydrated conditions, in the machining and transverse directions (MD and TD). Ambient refers to the humidity during cell assembly, and fully hydrated refers to the hydration state of the membrane during operation of the electrolyzer. The trend in MD and TD turned out to be rather similar; therefore, only the results for MD are shown in Figure 4.

All Nafion membranes, except NXL-100, have similar yield stress under ambient humidity conditions. NXL-100 is the only membrane with expanded PTFE reinforcement, which explains the high yield stress and low elongation at break. Thicker Nafion membranes, such as N115 and N117, have higher elongation at break values than the thinner membranes.

The elongation at break of all Nafion membranes is much lower and their yield stress becomes indistinct under fully hydrated conditions, especially for thin Nafion membranes such as NR211, NXL-100, and NR212. In addition to high gas crossover values, this is another reason why NXL-100 and NR212, as typical representatives of fuel cell membranes, are unsuitable for electrolyzer applications. Although they have a low area resistance, the low elongation at break of these membranes is unfavorable for electrolyzer operation under fully hydrated and differential pressure conditions.

Under ambient humidity conditions, radiation-grafted membranes have a characteristic upper and lower yield point, which are higher than the yield stress of N115 and N117. St/AN membranes have an elongation at break value similar to that of the N115 and N117 membranes. St/AN/DiPB membranes, which contain cross-linker, have a lower elongation at break than the un-cross-linked membranes.

Under fully hydrated conditions, radiation-grafted membranes still have higher yield stress than N115 and N117. Interestingly, the elongation at break of St/AN membranes increases under fully hydrated conditions, whereas for St/AN/DiPB membranes the value is about the same as that under dry conditions. The results show that the mechanical properties of radiation-grafted membranes are superior to those of Nafion membranes, especially under wet conditions. Mechanical properties of the final obtained membranes seem to be independent of the ETFE supplier.

Toughness or tensile energy to break, U_T, which indicates the required energy to break the membrane, can be obtained from the area under the stress−strain curve.[55] N120, the thickest Nafion membrane with an equivalent weight of 1200 g/mol, exhibits the highest toughness compared to other Nafion membranes (Table 2). The (un-cross-linked) St/AN membranes show higher toughness than any of the Nafion membranes under ambient as well as fully hydrated conditions. St/AN/DiPB membranes show values similar to those of Nafion membranes under ambient conditions and slightly higher values under fully hydrated conditions.

Table 2. Toughness or Tensile Energy to Break for Membranes under Ambient and Fully Hydrated Conditions

	U_T (MJ/m^3)			
	ambient conditions		fully hydrated consitions	
membrane	MD	TD	MD	TD
St/AN (D)	55 ± 5	61 ± 6	46 ± 4	40 ± 5
St/AN (SG)	62 ± 6	60 ± 4	33 ± 8	36 ± 13
St/AN/DiPB (D)	40 ± 3	39 ± 1	22 ± 3	17 ± 5
St/AN/DiPB (SG)	35 ± 1	33 ± 3	19 ± 5	17 ± 4
NR211	31 ± 1	31 ± 2	6 ± 2	7 ± 3
NXL-100	46 ± 6	41 ± 3	14 ± 8	18 ± 5
NR212	37 ± 2	40 ± 4	8 ± 7	7 ± 5
N1035	27 ± 2	36 ± 2	10 ± 3	12 ± 3
N1135	33 ± 4	43 ± 3	13 ± 2	14 ± 3
N105	35 ± 3	41 ± 2	17 ± 2	16 ± 2
N115	43 ± 1	45 ± 3	16 ± 2	14 ± 4
N117	41 ± 4	45 ± 3	13 ± 4	14 ± 5
N120	57 ± 2	57 ± 4	21 ± 5	24 ± 1

3.4. Figure of Merit.

By combination of the hydrogen crossover, area resistance, and toughness values, a figure of merit of the membranes for electrolyzer application is established. Average toughness values (machine and transverse directions) under fully hydrated conditions are taken for the figure of merit calculation. Normally, a thicker membrane has lower gas crossover and better mechanical properties but higher area resistance, while the opposite is observed for a thinner membrane. With the figure of merit, the most favorable combination of these three properties in a membrane can be determined. The figure of merit (FOM) is defined as

$$\text{FOM} = \frac{U_T}{R_\Omega i_x}$$

where U_T is the tensile energy to break/toughness (megajoules per cubic meter, MJ/m^3, or megapascals, MPa), R_Ω is the area resistance of the membrane (ohm square centimeter, $\Omega \cdot$cm^2) and i_x is the hydrogen crossover current density (amperes per square centimeter, A/cm^2). The figure of merit therefore has the unit megapascals per volt, MPa/V. The obtained data are presented in Figure 5.

Radiation-grafted membranes, which have lower gas crossover, lower resistance, and better mechanical properties than N115 and N117, consequently have a markedly higher figure of merit. Radiation-grafted membranes based on ETFE from Saint-Gobain have a higher figure of merit and therefore are preferred from that point of view over membranes based on ETFE from DuPont. However, if the reaction time is considered (Figure 1), radiation-grafted membranes based on DuPont's ETFE are preferred, since the difference in figure of merit between membranes based on different base films is small. St/AN grafted membranes show a higher figure of merit than St/AN/DiPB grafted membranes, since they have lower resistance and higher tensile energy to break. The DiPB content and level of cross-linking is expected to have an influence on the stability and lifetime of the membrane in the electrolyzer. Radiation-grafted membranes are therefore promising alternatives to Nafion membranes for electrolyzer applications. Ultimately, optimization of the membrane composition and architecture will be based on performance as well as stability attributes of the material.

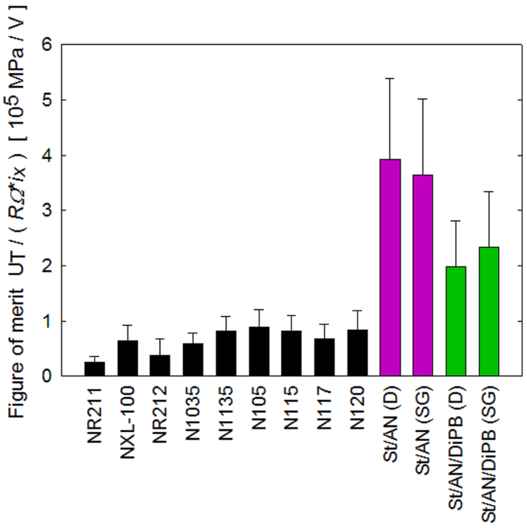


Figure 5. Figures of merit for various membranes, calculated from mechanical toughness (U_T), ohmic resistance (R_Ω), and hydrogen crossover (i_x).

3.5. Electrolyzer Test.

A preliminary electrolyzer test was performed in this study, using the MEA based on St/AN/DiPB (SG) radiation-grafted membrane and a commercial MEA. The obtained result is shown in Figure 6. The polarization curve taken with the St/AN/DiPB (SG)-based MEA shows a slightly better performance at low current densities compared to the commercial MEA; for example, St/AN/DiPB (SG) shows 20 mV lower overpotential at 0.2 A/cm^2. However, at higher current densities, the performance of St/AN/DiPB (SG) significantly decreases. The polarization curve of St/AN/DiPB (SG) appears to be limited by mass transport. It shows 110 mV higher overpotential compared to the commercial MEA at 0.7 A/cm^2. The exact reason for this behavior is unclear at the moment. It could be due to limited water transport in the electrode, limited ionic transport in the electrode or at the

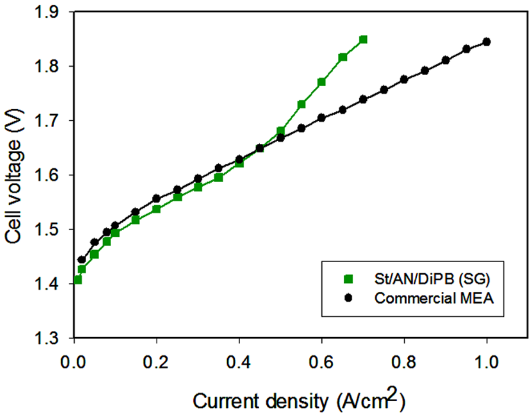


Figure 6. Polarization curve of MEA based on St/AN/DiPB (SG) radiation-grafted membrane with a graft level of 39% and commercial MEA.

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membrane/electrode interface, inhomogeneous sulfur distribution through the membrane, or a combination of these. Studies are ongoing to investigate performance characteristics and loss terms in cells with radiation-grafted membranes.

4. CONCLUSIONS

Radiation-grafted membranes based on cografted styrene (St) and acrylonitrile (AN) were successfully synthesized from electron-beam-preirradiated 50 μm ETFE base films. Cross-linked membranes were prepared by addition of a cross-linking agent, 1,3-diisopropenylbenzene (DiPB). ETFE from DuPont yielded faster grafting kinetics than ETFE from Saint-Gobain. SEM/EDX elemental mappings proved the successful incorporation of both monomers. Inhomogeneous sulfur distribution across the membrane thickness could be caused by an incomplete sulfonation process in the center. IEC values of radiation-grafted membranes with graft level of 40% are slightly higher than those of Nafion membranes. Water uptake and hydration values of cross-linked membranes are comparable to those of Nafion membranes and higher ithan those of un-cross-linked membranes.

Evaluation of the membranes for electrolyzer applications is focused on three key properties: gas crossover, area resistance, and mechanical properties. A property map, comprising hydrogen crossover and area resistance values, indicates that Nafion membranes follow a general trend. The diagram can be used as a benchmark for evaluating alternative membranes, such as radiation-grafted membranes. St/AN and St/AN/DiPB radiation-grafted membranes show lower gas crossover and lower area resistance compared to N115 and N117. Cross-linked membranes have lower crossover but higher area resistance than un-cross-linked membranes. Tensile tests showed that all radiation-grafted membranes have better mechanical properties than Nafion membranes under ambient and especially fully hydrated conditions.

The three key membrane properties can be combined into a figure of merit. Radiation-grafted membranes showed a higher figure of merit compared to various Nafion membranes. The figure of merit of radiation-grafted membranes based on Saint-Gobain base film are higher than those based on DuPont base film. However, if grafting kinetics are considered, the membranes based on DuPont base film are preferred.

An electrolysis cell test of an MEA based on St/AN/DiPB (SG) and a commercial MEA showed that this radiation-grafted membrane had a better performance at low current density. At higher current density, the overpotential of St/AN/DiPB (SG) became higher than that of the commercial MEA, which could be a result of water transport limitations or inhomogeneous sulfur distribution through the membrane.

Further work is aimed at electrolysis cell tests and improving (i.e., reducing) area resistance of radiation-grafted membranes, for example, by optimizing membrane preparation, increasing the graft level, and achieving a homogeneous sulfonic acid group distribution through the membrane. When the potentially lower cost is considered, radiation-grafted membranes are a promising alternative to N115 and N117 for electrolyzer applications.

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Notes

The authors declare no competing financial interest.

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■ ABBREVIATIONS

AN, acrylonitrile
DiPB, 1,3-diisopropenylbenzene
EDX, energy-dispersive X-ray spectroscopy
ETFE, ethylene tetrafluoroethylene
FOM, figure of merit
IEC, ion-exchange capacity
MEA, membrane electrode assembly
PBI, polybenzimidazoles
PE, polyethylene
PEEC, polymer electrolyte electrolysis cell
PEEK, poly(ether ether ketones)
PEFC, polymer electrolyte fuel cell
PES, poly(ether sulfones)
PFSA, perfluorosulfonic acid
PTFE, poly(tetrafluoroethylene)
St, styrene
SEM, scanning electron microscopy
SOEC, solid oxide electrolysis cell
SPPQ, sulfonated polyphenyl quinoxaline

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