

# Stability and Degradation Mechanisms of Radiation-Grafted Polymer Electrolyte Membranes for Water Electrolysis

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## S Supporting Information

**ABSTRACT:** Radiation-grafted membranes are a promising alternative to commercial membranes for water electrolyzers, since they exhibit lower hydrogen crossover and area resistance, better mechanical properties, and are of potentially lower cost than perfluoroalkylsulfonic acid membranes, such as Nafion. Stability is an important factor in view of the expected lifetime of 40 000 h or more of an electrolyzer. In this study, combinations of styrene (St),  $\alpha$ -methylstyrene (AMS), acrylonitrile (AN), and 1,3-diisopropenylbenzene (DiPB) are grafted into 50  $\mu\text{m}$  preirradiated poly(ethylene-co-tetrafluoroethylene) (ETFE) base film, followed by sulfonation to produce radiation-grafted membranes. The stability of the membranes with different monomer combinations is compared under an accelerated stress test (AST), and the degradation mechanisms are investigated. To mimic the conditions in an electrolyzer, in which the membrane is always in contact with liquid water at elevated temperature, the membranes are immersed in water for 5 days at 90 °C, so-called thermal stress test (TST). In addition to testing in air atmosphere tests are also carried out under argon to investigate the effect of the absence of oxygen. The water is analyzed with UV–vis spectroscopy and ion chromatography. The ion exchange capacity (IEC), swelling degree, and Fourier transform infrared (FTIR) spectra of the membranes are compared before and after the test. Furthermore, energy-dispersive X-ray (EDX) spectroscopic analysis of the membrane cross-section is performed. Finally, the influence of the TST to the membrane area resistance and hydrogen crossover is measured. The stability increases along the sequence St/AN, St/AN/DiPB, AMS/AN, and AMS/AN/DiPB grafted membrane. The degradation at the weak-link, oxygen-induced degradation, and hydrothermal degradation are proposed in addition to the “swelling-induced detachment” reported in the literature. By mitigating the possible paths of degradation, the AMS/AN/DiPB grafted membrane is shown to be the most stable membrane and, therefore, it is a promising candidate for a membrane to be used in a water electrolyzer.

**KEYWORDS:** radiation-grafted membranes, polymer electrolyte, stability, degradation, electrolyzer, fuel cell, hydrogen crossover, resistance

## 1. INTRODUCTION

A water electrolyzer is a device to produce hydrogen by splitting water electrochemically using electrical energy.<sup>1–3</sup> One of the common types of water electrolyzers is the polymer electrolyte water electrolyzer (PEWE).<sup>3–5</sup> The PEWE has a proton conducting membrane as its electrolyte. It comprises usually thick perfluorosulfonic acid (PFSA) membranes, such as Nafion N115 (~125  $\mu\text{m}$ ) and N117 (~175  $\mu\text{m}$ ).<sup>5–8</sup> These thick membranes are relatively stable, and have acceptable gas barrier and mechanical properties. However, the area resistance of thick PFSA membranes leads to considerable efficiency losses at current densities of 2 A/cm<sup>2</sup> or higher.<sup>9</sup> In addition, a lower cost of the membrane electrolyte would be desirable.<sup>1,10,11</sup>

Many alternatives to PFSA membranes have been investigated for electrolyzer application. Hydrocarbon membranes, such as poly(ether sulfones) (PES), poly(ether ether ketones) (PEEK), sulfonated polyphenyl quinoxaline (SPPQ), and

polybenzimidazoles (PBI) have been considered, since they are of potentially lower cost than PFSA membranes.<sup>12–16</sup> Ion conducting membranes prepared by radiation grafting are another option. The advantages of this method are its versatility and a potentially low cost fabrication.<sup>17</sup> The membrane properties can be readily modified by varying the composition and architecture of the graft copolymer.<sup>18</sup>

Masson et al.<sup>19</sup> prepared a membrane for water electrolyzer by radiation-induced grafting of styrene onto a polyethylene (PE) matrix, and Scherer et al.<sup>6</sup> grafted  $\alpha,\beta$ -trifluorostyrene onto poly(ethylene-co-tetrafluoroethylene) (ETFE) and styrene onto poly(tetrafluoroethylene) (PTFE), followed by sulfonation of the aromatic ring. In our previous study, we reported on radiation-grafted membranes for water electrolyzer application

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based on styrene (St), acrylonitrile (AN) and 1,3-diisopropenylbenzene (DiPB) grafted onto ETFE, and showed that these membranes have lower gas crossover, area resistance, and better mechanical properties than commercial Nafion membranes.<sup>20</sup>

The stability of the polymer electrolyte membrane is an important factor for the lifetime of an electrolyzer. Some accelerated stress tests, such as open circuit voltage hold test, cyclic variation of operating conditions (relative humidity, temperature, potential, start–stop), chemical stability test in Fenton reagent, etc., have been developed to investigate membrane stability for fuel cell application.<sup>21–30</sup> However, to the best of our knowledge, there is still no established accelerated stress test protocol for membranes for the water electrolyzer.

Although the chemistry of membranes for fuel cell and water electrolyzer are similar, the degradation process is somewhat different in the two devices. In the fuel cell, the degradation caused by radical attack of reactive oxygen species is one of the key mechanisms.<sup>23,31</sup> The emission of fluoride as a result of chemical degradation of PFSA membranes is also reported for electrolyzers.<sup>32</sup> However, membranes for water electrolysis generally exhibit less chemical degradation than polymer electrolyte fuel cells.<sup>33</sup> Since the cell interior of an electrolyzer is flooded with water, reactive intermediates created in the membrane electrode assembly are effectively diluted, unlike in a fuel cell operating with subsaturated reactants.

In the context of the development of alternative, non-perfluorinated membranes and the operating conditions of an electrolyzer, involving an acidic environment at elevated temperature, with the presence of hydrogen and oxygen, one has to consider that in certain classes of polymers specific degradation mechanisms may be prevalent. A study related to fuel cell application that can be relevant to radiation-grafted membranes in an electrolyzer was performed by General Electric. Hodgdon et al. investigated the degradation of poly(styrenesulfonic acid) (PSSA) as ion exchange compounds. The PSSA was degraded under following conditions: electrolysis above 1.1 V at 80 °F (26.7 °C), under combined action of H<sub>2</sub> and O<sub>2</sub> on Pt catalyst, auto-oxidation under O<sub>2</sub> with or without the presence of Pt. The degradation was suggested to be triggered by “weak bonds”, such as a peroxide bond, whereby oxygen was found to promote the degradation with or without the presence of Pt.<sup>34</sup> Although the PSSA was not incorporated into a membrane, the suggested mechanisms have to be considered for radiation-grafted membranes.

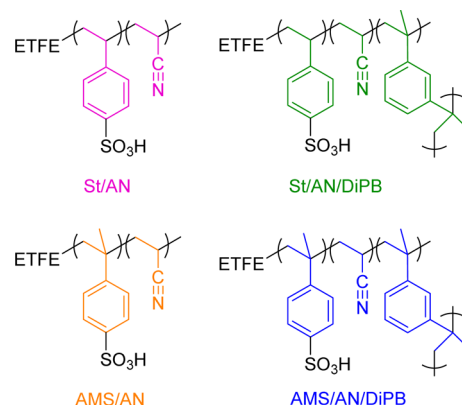
Another investigation of the degradation signature of a radiation-grafted membrane, which is intended for fuel cell application, performed by Enomoto et al. can also be relevant for the electrolyzer application. They showed that PSSA grafted onto cross-linked poly(tetrafluoroethylene) (cPTFE), poly(ethylene-co-tetrafluoroethylene) (ETFE), and poly(ether ether ketone) (PEEK) undergoes swelling-induced detachment of grafts in water at elevated temperature.<sup>35</sup> The degradation mechanism is believed to be based on the interfacial stress between the hydrophobic backbone polymer and hydrophilic polyelectrolyte chains. Although this experiment is intended to simulate the conditions in an operating fuel cell at high water content, it can be relevant to the water electrolyzer application, since the membranes are constantly in contact with liquid water at elevated temperature in the operating electrolyzer. According to their study, one may suspect that radiation-grafted membranes, which have hydrophobic backbone and hydrophilic

chains, will generally undergo swelling-induced detachment and may not be suitable for electrolyzer application.

In this study, the stability and degradation mechanisms of radiation-grafted membranes in hot water are investigated based on different monomer combinations and ETFE as base film. In an approach similar to that of Enomoto et al. the membranes are immersed in water for 5 days at 90 °C, which is referred to as thermal stress test (TST).

Styrene (St),  $\alpha$ -methylstyrene (AMS), acrylonitrile (AN), and 1,3-diisopropenylbenzene (DiPB) monomer combinations are cografted into preirradiated 50  $\mu$ m thick ETFE base film, followed by sulfonation and hydrolysis to produce the radiation-grafted membranes (Scheme 1). These combinations

**Scheme 1. Investigated Range of Monomer Combinations in Radiation-Grafted Membrane**



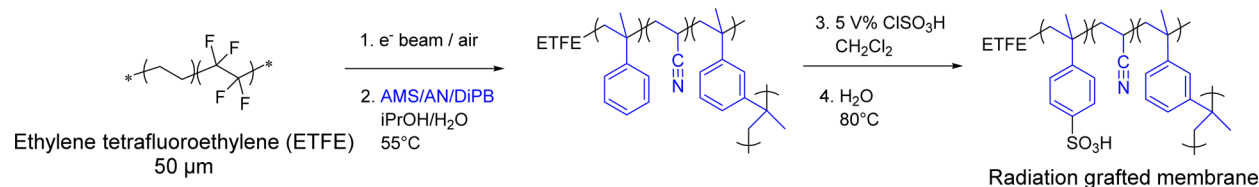
are chosen owing to the superior properties of these membranes in terms of hydrogen crossover, area resistance, and mechanical properties to those of commercial Nafion membranes.<sup>20</sup>

ETFE was selected as base film because it demonstrates low mechanical degradation upon electron beam irradiation, unlike PTFE.<sup>36</sup> St and AMS are chosen to investigate the effect of the substituent at the  $\alpha$ -position on the stability of the membranes. It is known that the  $\alpha$ -hydrogen of St is the weak site in the context of radical attack and oxidative degradation.<sup>37</sup> By substituting St for AMS, the oxidative stability of the membrane under fuel cell operating conditions could be increased.<sup>38</sup> However, such comparison has not been performed in the context of the electrolyzer.

AN is used as comonomer to promote the polymerization of AMS. Moreover, AN improves the gas barrier properties when incorporated into polymer materials.<sup>39–41</sup> Unfortunately, methacrylonitrile (MAN) is not commercially available any more in Europe and could not be shipped to Europe during this study for regulatory reasons. Therefore, the investigation of the effect of the  $\alpha$ -position in the nitrile monomers could not be conducted. Incorporation of a cross-linker, such as 1,3-diisopropenylbenzene (DiPB), is known to effectively improve the stability of the membrane in the fuel cell.<sup>18</sup> Moreover, unlike the more common divinylbenzene (DVB), DiPB has the advantage to yield a more homogeneous cross-linker distribution in the grafted film.<sup>42</sup> DiPB is chosen to investigate the effect of a cross-linker on the stability of membranes in hot water.

After 5 days of thermal stress test, the water in which the membrane was immersed is analyzed with UV–vis spectroscopy

Scheme 2. Reaction Scheme for Preparing AMS/AN/DiPB Radiation-Grafted Membranes



py and ion chromatography to identify degradation products of the membrane in water. The membrane is analyzed using Fourier transform infrared (FTIR) spectroscopy to identify changes in the functional groups after the test. The ion exchange capacity (IEC) of the membrane is measured before and after the test to quantify the amount of sulfonic acid functional groups. Correlation of swelling degree of the membrane and extent of degradation is investigated. Energy-dispersive X-ray (EDX) spectroscopic analysis of the membrane cross-sections is performed in the scanning electron microscope (SEM) to detect possible gradients in degradation across the thickness of the membrane. In addition, the thermal stress test is performed in argon atmosphere to study the influence of oxygen on the degradation behavior. Finally, the area resistance and hydrogen crossover values of the membranes, key properties for water electrolyzer application, are measured and compared before and after the test. By understanding the possible degradation mechanisms, the stability of radiation-grafted membranes can be improved and optimized for application in a water electrolyzer.

## 2. MATERIALS AND METHODS

**2.1. Chemicals.** DuPont Tefzel ETFE 200 LZ (50  $\mu$ m thickness) was used as base film for the preparation of radiation-grafted membranes. The chemicals for the membrane preparation were styrene ( $\geq 99\%$ , Sigma-Aldrich),  $\alpha$ -methylstyrene (99%, Sigma-Aldrich), acrylonitrile ( $\geq 99\%$ , Aldrich), 1,3-diisopropenylbenzene (97%, Aldrich), 2-propanol ( $\geq 99.7\%$ , VWR), acetone ( $\geq 99.8\%$ , VWR), dichloromethane ( $\geq 98\%$ , VWR), and chlorosulfonic acid (98%, Fluka).

Poly(4-styrenesulfonic acid) solution (18 wt % in H<sub>2</sub>O, Aldrich), 4-styrenesulfonic acid sodium salt hydrate (Aldrich), p-toluenesulfonic acid monohydrate ( $\geq 98\%$ , Sigma-Aldrich), 4-hydroxybenzenesulfonic acid solution (65 wt % in H<sub>2</sub>O, Aldrich), isobutyronitrile ( $\geq 98\%$ , Merck), acetonitrile ( $> 99.5\%$ , VWR), and acrylonitrile ( $\geq 99\%$ , Aldrich) were diluted in deionized water and used as comparative compounds to identify the possible products of degradation in water after the TST.

Potassium chloride ( $\geq 99\%$ , VWR) and potassium hydroxide solution for 1000 mL,  $c(\text{KOH}) = 0.1$  mol/L (Titrisol, Merck) were used for the measurement of the ion exchange capacity. The potassium hydroxide solution is diluted prior use to obtain a concentration of 0.05 mol/L. Deionized water with a resistivity of 18.2 M $\Omega$ -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 mgPt/cm<sup>2</sup> were used for the 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 a purity of at least 99.995% were used as received.

**2.2. Instruments.** The thermal stress test was carried out in two identical closed 250 mL three-neck round-bottom flasks

with reflux condenser. The temperature was controlled with a magnetic stirrer with heating from IKA RH digital white and an IKA ETS-DS electronic contact thermometer.

UV-vis measurement was performed with a Cary UV-vis Spectrophotometer Varian 4000 with Cary Varian UV Scan Version 3.00 software. The liquid sample was contained in a High Precision Cell Quartz Suprasil cuvette with a light path of 10 mm from Hellma Analytics. Ion chromatography was performed with Metrohm 882 Compact IC plus and 863 Compact Autosampler with MagIC Net Version 2.4 software. As the calibration solution, Dionex Combined Five Anion Standard from Thermo Fischer Scientific (fluoride, chloride, nitrate, phosphate, sulfate) was used.

Acid-base titrations for IEC determination of the membranes were performed using a Metrohm SM Titrino 702. FTIR spectra were recorded in absorbance mode with a Bruker Vertex 70 V with OPUS software, version 7.0. Sixty-four scans were recorded at a resolution of 4 cm<sup>-1</sup> for each sample analyzed. EDX analysis was performed in a Carl Zeiss Ultra 55 scanning electron microscope (SEM) using EDAX TSL, AMETEK, with EDAX Genesis Version 6.02 software. A Leica EM SCD500 high vacuum sputter coater with Cr target was used for the EDX sample preparation.

The experimental setup for the hydrogen crossover and area resistance measurements is described elsewhere.<sup>20</sup>

## 3. EXPERIMENTAL SECTION

**3.1. Membrane Preparation.** The base film treatment and the detailed synthesis of St/AN and St/AN/DiPB radiation-grafted membranes are described elsewhere.<sup>20</sup> The AMS/AN and AMS/AN/DiPB membranes were prepared in a similar way (Scheme 2). However, the ETFE films were weighed prior to irradiation to reduce the time to insert the films into the reactor during membrane preparation. In addition, the following composition of the reaction mixture was used: water (15 vol %), isopropanol (55 vol %) and monomer (30 vol %). The monomer volume ratio was 83/17 for AMS/AN and 79/17/4 for AMS/AN/DiPB. The reaction temperature was 55 °C, and the reaction time 28.5 h for AMS/AN and 20 h for AMS/AN/DiPB in order to obtain the desired graft level of 40% with a 5 kGy preirradiated base film. The grafted film was sulfonated by immersing the film into a solution of 5 vol % chlorosulfonic acid and 95 vol % dichloromethane at room temperature for 6 h. Afterward, the membrane was placed in a water bath at 80 °C for 16 h for hydrolysis of the sulfonyl chloride to the sulfonic acid. Finally, the membranes were dried under ambient condition and stored until further use.

**3.2. Thermal Stress Test.** The thermal stress test was performed by introducing a 5.4 cm  $\times$  5.4 cm sized piece of membrane in 100 mL deionized water at 90 °C for 5 days under stirring. The test was conducted at least twice per membrane type. The experiment under argon atmosphere was performed by immersing the membrane in argon saturated deionized water and applying a continuous flow of argon gas to prevent oxygen from entering the flask.

The experimental water was analyzed using UV-vis spectroscopy every 24 h and ion chromatography after 5 days. For the UV-vis measurement, 3 mL of the solution was removed and returned afterward to maintain the same volume of water in the flask. Deionized



water is used as the baseline. For ion chromatography, 5 mL of the solution was used.

IEC, swelling degree and weight loss of the membranes were measured before and after the test. FTIR and EDX analysis were also performed before and after the test. The detailed experimental procedure for the determination of the IEC is described elsewhere.<sup>20</sup> The weight loss is calculated from the weight difference of the membrane in their dry protonated form before and after the test. FTIR spectra of the radiation-grafted membranes were taken in the K<sup>+</sup> form. EDX analysis of the membranes was performed for sulfur and nitrogen detection.

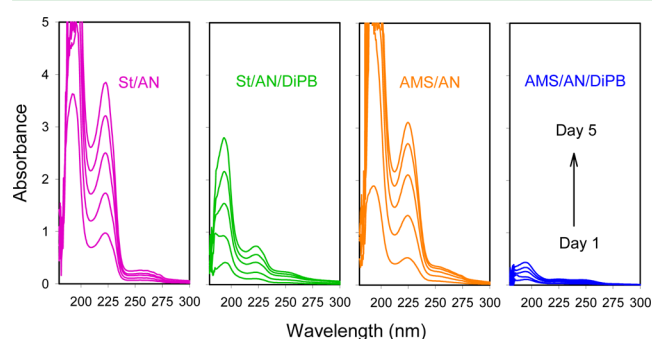
The hydrogen crossover and area resistance values of the membranes were also measured before and after the test. Experimental details of hydrogen crossover and area resistance measurements is described elsewhere.<sup>20</sup>

## 4. RESULTS

### 4.1. Analysis of Soaking Water–UV–vis Spectroscopy.

The water used in the thermal stress test (TST) was analyzed using UV–vis spectroscopy. UV–vis spectroscopy provides information about the type of degraded species of the radiation-grafted membranes and their qualitative amount in the soaking water.

Figure 1 shows the UV–vis spectra over 5 days of TST. The signals gradually increase from day to day, which indicates that



**Figure 1.** UV–vis spectra of the soaking water during 5 days of thermal stress test.

degradation occurs steadily with time. Absorbance peaks after the TST are generally observed for all membranes at 193–194 and 225–226 nm. These peaks are compared to the spectra of model compounds in aqueous solution to identify the possible degradation products (cf., [Supporting Information](#)).

The spectra of the degradation products of the radiation-grafted membranes are most similar to that of poly(4-styrenesulfonic acid) solution, which indicates that the observed degraded species are in form of polymer chain fragments, and not monomer units, which is in agreement with the results of Enomoto et al.<sup>35</sup> The nitrile signals around 190 nm are most probably overlapping with the signals of aromatic compounds and therefore could not be distinguished.

The observed UV–vis signal of grafted chain fragments can however result from washed-out occluded polymer chains, since entangled polymer chains can be relatively immobile inside the polymer networks and may remain in the membrane after preparation.<sup>43</sup> The thermal stress test experiment under air atmosphere was therefore extended to 7 days to test this hypothesis. The absorbance signature of the decomposition products in the water continued to increase in apparent linear manner. This indicates that the signals originate mainly from

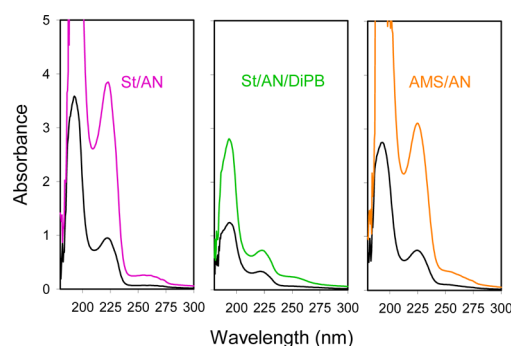
degradation products and only to a small extent from occluded polymer.

The radiation-grafted membranes that contain cross-linker, St/AN/DiPB and AMS/AN/DiPB grafted membranes, show a lower amount of degraded grafted polymer chains than the membranes without cross-linker, St/AN and AMS/AN grafted membranes. It seems that the cross-linker reduces the degradation effect.

Furthermore, the AMS based membranes show lower degradation than the St based membranes. The methyl group at the  $\alpha$ -position instead of hydrogen seems to increase the stability of the membranes in water. This proves that the  $\alpha$ -position is not only relevant for the stability of radiation-grafted membranes during radical attack occurring in a fuel cell, but also for the stability of the membrane in water for electrolyzer application.

The AMS/AN/DiPB membrane with both DiPB cross-linker and AMS incorporated into the membrane exhibits the lowest degradation rate, showing additive influence of the two features. The stabilizing effect of a cross-linker and  $\alpha$ -methyl position was not subject of the study of Enomoto et al., since St was used as only grafting monomer.<sup>35</sup>

In a second set of experiments, the thermal stress test is performed under argon atmosphere to investigate the effect of the absence of oxygen. Figure 2 shows UV–vis spectra of the



**Figure 2.** UV–vis spectra of the thermal stress test solution after 5 days under air (in color) and argon atmosphere (in black), respectively.

solution after 5 days of TST under air (colored curves) and argon atmosphere (black curves), respectively. This test was not performed in case of the AMS/AN/DiPB grafted membrane, since it has already a low UV–vis signature under air atmosphere. In the absence of oxygen, the UV–vis signals are lower. This indicates that oxygen is an important factor in the degradation process.

For comparison, the commercial Nafion membranes N115 and N117 are also subjected to the TST. Since Nafion membranes do not have any chemical constituents that absorb UV–vis light, there is no signal observed in the soaking water.

### 4.2. Analysis of Soaking Water–Ion Chromatography.

Ion chromatography provides information about possibly generated and released ions from the membrane during the TST. Table 1 shows the result of the ion chromatography measurements after 5 days thermal stress test under air and argon atmosphere, respectively. The amount of sulfate in the soaking water in case of the radiation-grafted membranes is higher than in case of the Nafion membranes. However, a concentration of 0–4 ppm only corresponds to a loss of up to 3% of the membranes' IEC. This indicates that desulfonation

**Table 1. Results of Ion Chromatography of Soaking Water after 5 Days Thermal Stress Test, in ppm (Equivalent to mg/L)**

sample	SO <sub>4</sub> <sup>2-</sup>	F <sup>-</sup>
blank test	0.02	
St/AN	1.02	0.06
	0.27	0.03
(argon)	(0.17)	(0.03)
St/AN/DiPB	3.64	0.14
	2.02	0.05
(argon)	(0.64)	(0.05)
AMS/AN	0.64	0.09
	0.71	0.07
(argon)	(0.16)	(0.04)
AMS/AN/DiPB	1.20	0.02
	1.62	0.05
N115	0.11	0.03
N117	0.14	0.04

takes place to a very low extent in radiation-grafted membranes and that the sulfate ion is not the main degradation product during the exposure to hot water over 5 days. This is similar to the finding in the exhaust water of a fuel cell with PSSA grafted membrane after an accelerated stress test.<sup>44</sup> In argon atmosphere, desulfonation is almost unnoticeable. The amount of fluoride released from the membranes is also low, indicating that the ETFE base polymer does not undergo degradation.

**4.3. Membrane Analysis—Ion Exchange Capacity.** The ion exchange capacity (IEC) and swelling degree of the radiation-grafted membranes before and after the test are shown in Table 2. The IEC quantifies the number of sulfonic acid functional groups available in the membrane.

After the TST, the St based membranes, that is, St/AN and St/AN/DiPB, lose 35–45% of their IEC, which indicates that these membranes are less stable than the AMS-based membranes, which only lose 10% and 4% IEC in case of the AMS/AN and AMS/AN/DiPB cogenerated membrane, respectively. This is in agreement with the UV–vis result in that the AMS-based membranes are more stable than the St-based membranes.

Interestingly, the presence of the cross-linker does not lead to a decrease of the IEC loss in case of the St/AN/DiPB grafted membrane, although its UV–vis response is lower than that of the un-cross-linked St/AN grafted membrane. This suggests that there is a degradation mechanism that causes the loss of sulfonic acid functional groups from the polymer chains without any chain scission occurring.

The change of the experimental condition to the argon atmosphere does not affect the IEC loss of St-based radiation-grafted membranes, St/AN and St/AN/DiPB. This is another result in disaccord with the result of UV–vis measurements. The latter indicates that less polymer chain fragments are formed under argon atmosphere. This indicates the existence of another degradation mechanism in the absence of oxygen, which is active only in case of the St-based membranes.

The swelling degree shows interesting results, since according to Enomoto et al., the higher the swelling, the higher the extent of degradation caused by swelling-induced detachment should be. However, the results presented in Table 2 show that the degree of swelling does not correlate directly with the extent of degradation.

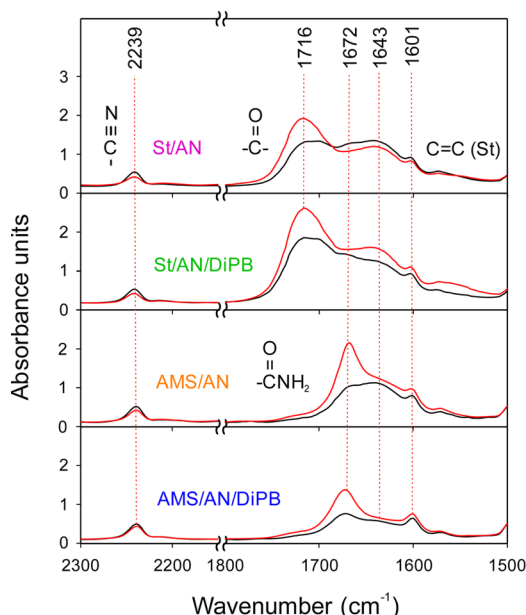
The St/AN grafted membrane shows a lower IEC loss than the St/AN/DiPB grafted membrane, although the St/AN grafted membrane has a higher swelling degree. In addition, the IEC loss of AMS/AN and AMS/AN/DiPB cogenerated membranes is less pronounced, although they exhibit a swelling degree similar to that of St/AN and St/AN/DiPB cogenerated membranes. This suggests that the chemical structure influences the stability of radiation-grafted membrane more than the interfacial stress between the hydrophobic (base film) and hydrophilic (grafted polymer) constituents of the membrane as described by the swelling-induced detachment mechanism.

The weight loss shows a similar trend to the IEC and UV–vis results, which indicate the St-based membranes are less stable than the AMS based membranes. For the St-based membranes, the expected weight loss is however less than the corresponding IEC loss. 40% of IEC loss should result in 6–8% weight loss for St-based membranes, but only 3–4% weight loss is observed. This finding supports the notion of a degradation mechanism that causes the loss of sulfonic acid functional groups from the polymer chains without any chain scission occurring in the St-based membranes. This is not the case for the AMS based membranes, since the 10% of IEC loss contributes to 2–3% weight loss for the AMS based membranes, and the measured weight loss is in agreement with the IEC loss within the uncertainty of the measurement.

**4.4. Membrane Analysis—FTIR Spectra.** Figure 3 shows the FTIR spectra of the membranes before and after the test. Before the test, intensity related to the C=O stretch vibration of carbonyl is already observed, which is a result of partial hydrolysis of nitrile groups during membrane synthesis.<sup>45</sup> The nitrile peak is smaller after the thermal stress test and the carbonyl peak is higher for all the membranes. This indicates that the nitrile group is further hydrolyzed during the TST. Interestingly, the position of the carbonyl peak in case of the St-

**Table 2. Ion Exchange Capacity, Swelling Degree, and Weight Loss of the Membranes before and after 5 Days Thermal Stress test**

membranes	ion exchange capacity (mmol/g)			swelling degree (wt %)		weight loss (wt %)
	before	after	% loss	before	after	% loss
St/AN	1.24 ± 0.01	0.82 ± 0.06	34.1 ± 4.7	66.6 ± 0.9	54.4 ± 3.0	3.3 ± 1.6
(argon)	(1.25 ± 0.02)	(0.82 ± 0.01)	(34.4 ± 1.7)	(67.8 ± 2.4)	(63.2 ± 1.6)	(0.4 ± 0.3)
St/AN/DiPB	1.20 ± 0.00	0.67 ± 0.01	44.2 ± 0.8	35.1 ± 3.2	40.9 ± 3.5	4.4 ± 2.7
(argon)	(1.11 ± 0.02)	(0.57 ± 0.06)	(49.1 ± 5.9)	(34.9 ± 1.5)	(31.7 ± 6.3)	(0.9 ± 0.1)
AMS/AN	1.65 ± 0.03	1.48 ± 0.00	10.3 ± 0.0	56.5 ± 0.5	60.0 ± 0.5	1.9 ± 2.2
(argon)	(1.65 ± 0.01)	(1.59 ± 0.03)	(3.19 ± 2.0)	(53.0 ± 1.3)	(58.5 ± 1.3)	(~0)
AMS/AN/DiPB	1.58 ± 0.00	1.52 ± 0.01	4.2 ± 0.5	31.7 ± 0.6	-	~ 0



**Figure 3.** FTIR spectra of membranes before (in black) and after (in red) 5 days of the thermal stress test under air.

based membranes is different than in case of the AMS based membranes. The peak observed at  $1716\text{ cm}^{-1}$  in the St-based membranes could be associated with the carbonyl peak of ketone or carboxylic acid. The peak at  $1672\text{ cm}^{-1}$  in the St and AMS-based membranes could be assigned to an amide (amide-I peak). Also, the rather broad peak of the H–O–H bending vibration of water is found in the region around  $1640\text{ cm}^{-1}$ . In both cases, AN is possibly hydrolyzed only to amide. The additional ketone or carboxylic acid peak in case of St-based membranes could be indicative of an additional functional group formed upon degradation in water.

The FTIR peaks associated with aromatic sulfonic acid in the range  $1000\text{--}1050\text{ cm}^{-1}$  are not shown due to excessive ETFE-

backbone related absorption in this region, rendering quantification impossible. The FTIR spectra of the membranes treated under argon atmosphere are similar to the ones shown in Figure 3, hence they are not shown.

#### 4.5. Membrane Analysis–EDX Elemental Mapping.

The EDX analysis of membrane cross-sections (cf., Supporting Information) shows that the distribution of sulfur and nitrogen atoms in the AMS-based grafted membranes is more homogeneous than in case of the St-based grafted membranes. This is a result of the lower grafting kinetics of AMS based membranes, which prevents the formation of pronounced grafting fronts.<sup>46</sup> The EDX elemental maps before and after the test indicates that there is no localized degradation of the membranes in hot water.

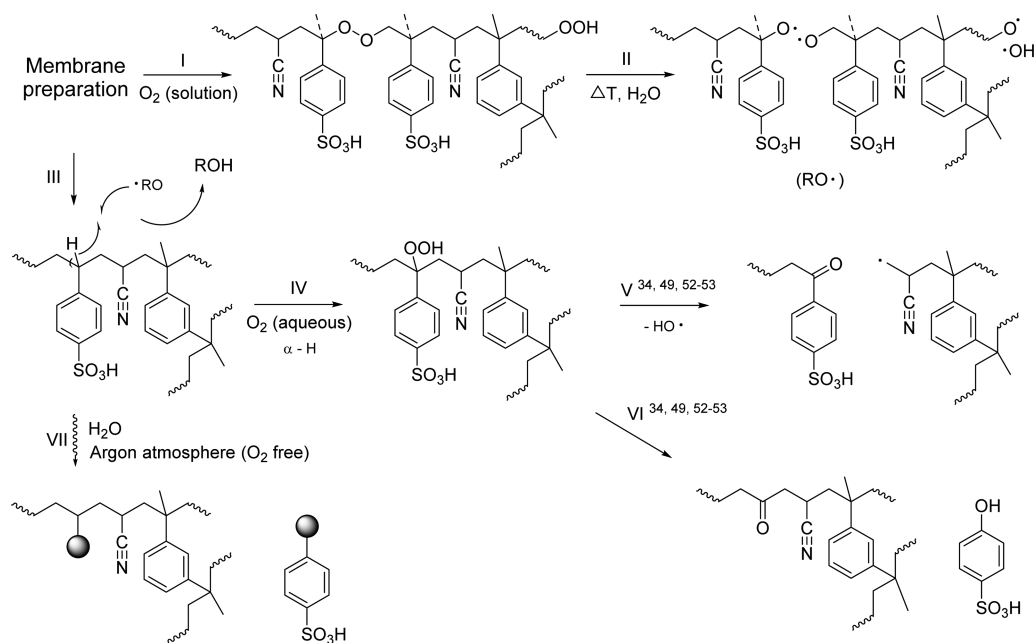
### 5. DISCUSSION

On the basis of the water (UV–vis, IC) and membrane analysis (IEC, FTIR, EDX) of the thermal stress test under air and argon atmosphere, and the effect of varying the monomer combinations and adding cross-linker, 3 degradation mechanisms of radiation-grafted membranes in hot water are proposed (Scheme 3) in addition to the “swelling induced detachment” described in the literature:<sup>35</sup> degradation at the weak-link, oxygen-induced degradation, and hydrothermal degradation.

**5.1. Degradation at the Weak Link.** Degradation at the weak-link is the degradation caused by the scission of a weak chemical bond that leads to the scission of grafted polymer chains. This mechanism is supported by the fact that some degradation products are in the form of polymer chains as indicated by the UV–vis spectra and the weight loss of the membranes.

According to the work of Hodgdon et al. on the oxidative degradation of PSSA, this polymer contains “weak-links”, possibly peroxide bonds, O–O, which originate from oxygen that is incorporated into the growing polymer chain during the radical polymerization process.<sup>34,47</sup> It is conceivable that such peroxide bonds may also exist in the grafted polymer chains at

**Scheme 3.** Proposed Degradation Mechanisms of Radiation-Grafted Membranes in Hot Water



the focus of this study, since the small residual amount of oxygen in the grafting monomer solution can be involved during the propagation of the polymer chain reaction and incorporated into the grafting polymers. Moreover, peroxide is usually also formed in the film during the irradiation in air even in the presence of small amounts of oxygen.<sup>48</sup> In addition, oxygen may react with chain-end radicals to form peroxy radicals or peroxides at the end of the grafting reaction when the film is removed from the reaction solution and exposed to air (step I).

This peroxide bond is susceptible to heat induced cleavage, which results in the formation of radical species (step II). This degradation sequence can be avoided if the membrane is prepared in the complete absence of oxygen, which is practically difficult. However, the fact that the membranes with cross-linker are more stable than the membranes without cross-linker means that the presence of a cross-linker can reduce the effect caused by this degradation mechanism. It is most likely a consequence of the multiple connectivity of grafted polymer chains in a cross-linked network structure. This degradation mechanism is present in all radiation-grafted membranes which are prepared in the presence of trace amounts of oxygen.

**5.2. Oxygen-Induced Degradation.** The oxygen-induced degradation is supported by the fact that the degradation is less pronounced under argon atmosphere according to the UV-vis spectra. The weak site is possibly the  $\alpha$ -position of a monomer unit, since the IEC loss data indicate that St based membranes are less stable than AMS based membranes.

This reaction is initiated by the abstraction of hydrogen at the  $\alpha$ -position of a monomer unit by the radical formed after the scission of a weak-link (step III). This mechanism applies only to St based membranes, that is, St/AN and St/AN/DiPB grafted membranes, since the hydrogen at the  $\alpha$ -position of St is prone to abstraction.<sup>49</sup> The hydrogen at the  $\alpha$ -position of the AN may undergo a similar reaction, since the bond dissociation energy of  $\alpha$ -H of AN is only slightly higher than that of St. The bond energy of  $\alpha$  C–H of cumene (2-phenylpropane) is 350–365 kJ/mol and that of isobutyronitrile (2-methylpropanenitrile) is 360–385 kJ/mol.<sup>50</sup> Cumene and isobutyronitrile represent St and AN monomer units, respectively, in the grafted chain.

The radical formed at the  $\alpha$ -position can then easily add oxygen dissolved in water and form a peroxy radical, which can again abstract hydrogen from a nearby  $\alpha$ -position to form a hydrogen peroxide group (step IV).<sup>51</sup> The hydrogen peroxide group at the  $\alpha$ -position can lead to the scission of the polymer chain (step V), or to the splitting off of the St unit and formation of a ketone functional group as suggested by FTIR (step VI).<sup>34,49,52,53</sup> The splitting of the St unit in step VI is supported by the observation that the weight loss of the membranes is less than the corresponding IEC loss. The splitting of only St units without polymer chain scissions does not contribute to the weight loss significantly, only to IEC loss.

This degradation mechanism can be mitigated by changing the susceptible hydrogen at the  $\alpha$ -position into, for example, a methyl group. Therefore, AMS-based membranes are more stable than the St-based membranes. Since the mechanism also leads to the scission of polymer chains, the presence of cross-links minimizes the effect of the degradation as in the first mechanism described above.

**5.3. Hydrothermal Degradation.** Hydrothermal degradation leads to the removal of molecules containing sulfonic acid,

which is possibly also caused by the weak site at the  $\alpha$ -position of St. This mechanism is supported by the observation that under argon atmosphere, although the UV-signal and the weight loss indicate a lower extent of degradation than in the presence of oxygen, the IEC loss of the St based membranes, that is, St/AN and St/AN/DiPB cogenerated membranes, does not change.

The IEC loss is caused by the removal of a molecule with a moiety containing sulfonic acid, and not of sulfate ions (desulfonation), since ion chromatography only showed a small amount of released sulfate ions. The species in question is not in the form of polymer fragments, since the UV-vis signal and weight loss related to St-based membranes are lower in the absence of oxygen. However, the exact mechanism and the products of the degradation reaction are still unknown. Likewise, this degradation mechanism can be mitigated by changing the hydrogen at the  $\alpha$ -position into, for example, a methyl group, since AMS-based membranes show both a lower UV-signature and less IEC loss under argon atmosphere.

**5.4. Influence of Composition of Grafts.** The St/AN grafted membrane undergoes all 3 degradation mechanisms and therefore is the least stable membrane in this study. The St/AN/DiPB grafted membrane also undergoes all 3 degradation mechanisms, yet the cross-linker effectively reduces the loss of chain fragments.

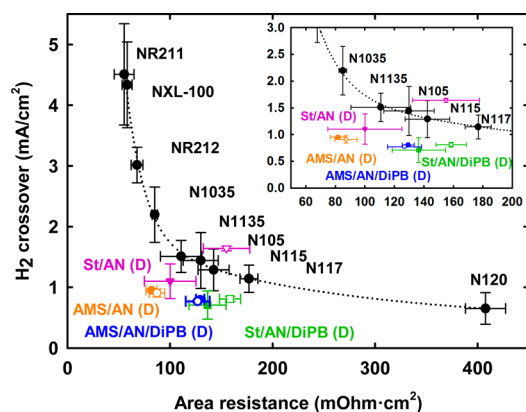
The AMS/AN grafted membrane undergoes “degradation at the weak-link” and probably “oxygen-induced degradation at the  $\alpha$ -position of AN”, which leads to polymer chain scission. “Oxygen-induced degradation at the  $\alpha$ -position of AMS” and “hydrothermal degradation” are absent. Therefore, the AMS/AN grafted membrane is more stable than the St/AN/DiPB grafted membrane. Similar to the AMS/AN grafted membrane, the AMS/AN/DiPB grafted membrane undergoes degradation at the weak-link and probably oxygen-induced degradation at the  $\alpha$ -position of AN. However, owing to the presence of cross-links, the AMS/AN/DiPB grafted membrane is the most stable membrane in the series, since all degradation paths in hot water are mitigated.

## 6. GAS CROSSOVER VERSUS AREA RESISTANCE

The property map provides information about the hydrogen crossover and area resistance values of Nafion and radiation-grafted membranes.<sup>20</sup> In addition to our previous work, the property map includes two additional membranes, namely AMS/AN and AMS/AN/DiPB grafted membranes. The hydrogen crossover and area resistance values of all radiation-grafted membranes before and after the thermal stress test are shown in Figure 4. Before the thermal stress test, the AMS/AN and AMS/AN/DiPB grafted membranes show similar hydrogen crossover and area resistance to those of the St/AN and St/AN/DiPB grafted membranes, which are better than the state-of-the-art membranes for water electrolysis, N115 and N117. After the thermal stress test, it can be observed that the membrane with a higher extent of degradation shows a more pronounced increase of hydrogen crossover and area resistance.

According to the changes of the hydrogen crossover and area resistance values, the stability of radiation-grafted membranes increases in the series St/AN (least stable) < St/AN/DiPB < AMS/AN < AMS/AN/DiPB (most stable). The results are in agreement with the soaking water and membrane analysis in the thermal stress test, which shows the same stability trend of the radiation-grafted membranes. The AMS/AN/DiPB grafted membrane is considered as the most suitable candidate for use





**Figure 4.** Property map of radiation-grafted membranes before (filled symbols) and after (empty symbols) 5 days thermal stress test, compared to the Nafion series of membranes.

in a water electrolyzer among all radiation-grafted membranes tested in this study, since it shows the highest stability in the series and has a more favorable combination of hydrogen crossover and area resistance than the Nafion membranes series.

## 7. CONCLUSIONS

The stability of radiation-grafted membranes for water electrolyzer application is investigated by immersing the membranes in water at 90 °C for 5 days under air and argon atmosphere (thermal stress test, TST). UV–vis spectra indicate that some degradation products are in the form of polymer fragments. Ion chromatography indicates that desulfonation occurs only to a minor extent. The measurement of ion exchange capacity before and after the test reveals that the St based membranes lose more sulfonic acid functional groups than the AMS based membranes. In contrast to the swelling-induced detachment mechanism reported in the literature, the swelling degree of a given membranes does not correlate with its extent of degradation. The weight loss measurements indicate that some degradation occur without polymer chain scissions in the St based membranes. The FTIR spectra show that the AN group is hydrolyzed to amide, and a ketone functional group is formed during the degradation of St based membranes. The experiment under argon atmosphere indicates that oxygen promotes the degradation.

In addition to the swelling-induced detachment, 3 additional degradation mechanisms of radiation-grafted membranes in hot water are proposed: degradation at the weak-link, oxygen-induced degradation, and hydrothermal degradation. A stable membrane can be obtained by removing oxygen completely during the membrane preparation to avoid the formation of weak-links, or using monomers with a protected  $\alpha$ -position and cross-linker to mitigate degradation.

The radiation-grafted membranes have lower hydrogen crossover and area resistance than the commercial Nafion membranes, N115 and N117, before the TST. After the TST, the increase of hydrogen crossover and area resistance of radiation-grafted membranes reflects the degree of membrane degradation. The stability increases along the series St/AN, St/AN/DiPB, AMS/AN, and AMS/AN/DiPB grafted membrane and is in agreement with the water and membrane analysis during the TST. Combination of low hydrogen crossover, low area resistance, and encouraging stability in hot water makes

the AMS/AN/DiPB grafted membrane a promising alternative membrane for the water electrolyzer application.

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.6b03050.

UV–vis of model compounds and EDX analysis (PDF)

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### Notes

The authors declare no competing financial interest.

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## ■ ABBREVIATIONS

AMS,  $\alpha$ -methylstyrene  
 AN, acrylonitrile  
 cPTE, cross-linked poly(tetrafluoroethylene)  
 DiPB, 1,3-diisopropenylbenzene  
 DVB, divinylbenzene  
 EDX, energy-dispersive X-ray spectroscopy  
 ETFE, ethylene tetrafluoroethylene  
 FTIR, Fourier transform infrared  
 IC, ion chromatography  
 IEC, ion exchange capacity  
 MAN, methacrylonitrile  
 PBI, polybenzimidazole  
 PE, polyethylene  
 PEWE, polymer electrolyte water electrolyzer  
 PEEK, poly(ether ether ketone)  
 PES, poly(ether sulfone)  
 PFSA, perfluoroalkylsulfonic acid  
 PSSA, poly(styrenesulfonic acid)  
 PTFE, poly(tetrafluoroethylene)  
 SEM, scanning electron microscopy  
 St, styrene  
 SPPQ, sulfonated polyphenyl quinoxaline  
 TST, thermal stress test  
 UV–vis, ultraviolet–visible

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