



Novel ETFE based radiation grafted poly(styrene sulfonic acid-co-methacrylonitrile) proton conducting membranes with increased stability

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ABSTRACT

Styrene radiation grafted ETFE based proton conducting membranes are subject to degradation under fuel cell operating conditions and show a poor stability. Lifetimes exceeding 250 h can only be achieved with crosslinked membranes. In this study, a novel approach based on the increase of the intrinsic oxidative stability of uncrosslinked membranes is reported. Hence, the co-grafting of styrene with methacrylonitrile (MAN), which possesses a protected α -position and strong dipolar pendant nitrile group, onto 25 μm ETFE base film was investigated. Styrene/MAN co-grafted membranes were compared to a styrene based membrane in durability tests in single H_2/O_2 fuel cells. It is shown that the incorporation of MAN considerably improves the chemical stability, yielding fuel cell lifetimes exceeding 1000 h. The membrane preparation based on the co-grafting of styrene and MAN offers the prospect of tuning the MAN content and introduction of a crosslinker to enhance the oxidative stability of the resulting fuel cell membranes.

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1. Introduction

The stability and reliability of the proton exchange membrane in fuel cells is one of the crucial issues to bring this technology from the prototype to the commercial level. Likewise, the development of cost effective proton exchange membranes to replace the state-of-the-art and expensive perfluorinated membranes (e.g., Nafion[®]) is another main challenge. The radiation induced grafting technique in combination with low cost materials, either fluorinated or partially fluorinated base polymers, offers several advantages [1]. Radiation induced grafting is a versatile technique which allows the functionalization of the base material for the introduction of a desired property (proton conductivity). The attractiveness of this technique is based on the possibility to easily tune and control key membrane parameters, such as ion exchange capacity and water uptake, in a wide range to obtain desired properties.

Our working group is devoted to the development of low cost polymer electrolyte membranes prepared by radiation grafting, and extensive work to improve the mechanical and chemical stability has been carried out. Lifetimes exceeding 4000 h at a temper-

ature of 80 °C and steady state conditions were achieved with radiation grafted crosslinked membranes based on styrene/divinylbenzene (DVB: crosslinker) grafted onto poly (tetrafluoroethylene-co-hexafluoropropylene) (FEP) [1,2]. The crosslinking and graft level (GL) were pointed out to be the key parameters which can be tuned to find a balance between the conductivity and mechanical as well as chemical stability in radiation grafted membranes. Therefore, FEP based membranes were optimized with respect to their performance and durability [3].

In order to increase the intrinsic properties of the base polymer, partially fluorinated poly(ethylene-*alt*-tetrafluoroethylene) (ETFE) has been chosen as base film [4]. Several advantages over FEP base film were identified, such as superior mechanical properties [5], higher grafting kinetics owing to higher monomer solubility [6], and less radiation-induced damage [7]. Hence, a detailed study on the influence of grafting parameters and reaction kinetics was performed for the grafting of styrene onto ETFE [8]. Moreover, the influence of crosslinker concentration was investigated and correlations between the content of DVB and the *ex situ* and *in situ* relevant properties for fuel cells were established [9,10].

It is well known that the styrene sulfonic acid group in the grafted membrane suffers from the weakness of the α -hydrogen position, which is prone to radical attack under fuel cell conditions [11]. Substantial work is devoted to improve the stability of radiation grafted membranes by the use of new monomer combinations

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with low cost impact. Several authors reported on the use of styrene/acrylonitrile [12,13], α -methylstyrene/styrene [14] and *p*-methylstyrene/*tert*-butyl styrene [15] as grafting monomers. So far, no fuel cell experiments were shown and only *ex situ* chemical stability in H₂O₂ was reported. However, the membrane degradation mechanism under fuel cell operating conditions is complex (hydration/dehydration, mechanical stress, aggressive species (HO \cdot ; HOO \cdot)) and single cell tests are needed to evaluate the membranes. Recently, alternative monomers and monomer combinations were reported and tested, such as α,β,β -trifluorostyrene derivatives [16] and α -methylstyrene/methacrylonitrile [17], which show better stability but suffer from slow grafting kinetics.

A novel approach for the preparation of radiation grafted membranes with increased stability via co-grafting of styrene and MAN is presented here. Selected membranes prepared at the same conditions were characterized for their *ex situ* relevant fuel cell properties (ion exchange capacity, water uptake, conductivity), and the fuel cell performance and durability of the membrane electrode assemblies (MEAs) were evaluated and compared against those of styrene based membranes. As far as we are aware, this is the first combination of these two monomers in proton exchange membranes for fuel cell application.

2. Experimental

ETFE (Tefzel[®] 100LZ) films of 25 μ m thickness, purchased from DuPont (Circleville, USA), were used as base polymer. ETFE films were washed in ethanol and dried in vacuum at 60 $^{\circ}$ C. The films were electron beam irradiated with a dose of 1.5 kGy at Leoni Studer AG (Däniken, Switzerland) [9]. Subsequently, the films were stored at -80° C until used. Grafting reactions were carried out in a glass reactor under a nitrogen atmosphere. The grafting solution consisted of 20% (v/v) monomer (mixture of styrene/MAN #1 and #2: 1/1 and 1/4 (mol/mol), respectively), 70% (v/v) isopropanol and 10% (v/v) water. The grafting reaction and the sulfonation reactions were performed as described elsewhere [6].

The graft level (GL) of each film was determined from the weight of the irradiated film (W_i) and the grafted film (W_g):

$$GL \% = \frac{W_g - W_i}{W_i} \times 100\% \quad (1)$$

The composition of the grafted films was determined via FTIR spectroscopy using a Perkin Elmer FTIR System 2000 spectrometer. Using pure styrene and MAN grafted films, respectively, calibration curves based on the vibrational bands appearing at 1494 cm^{-1} (C=C) for styrene and at 2234 cm^{-1} (C \equiv N) for MAN were obtained. The peak-fitting was performed using GRAMS/386 software (version 3.02) from Galactic Industries.

The *ex situ* membrane properties, i.e., ion exchange capacity (IEC), proton conductivity, water uptake and hydration number in fully swollen state at room temperature, were determined using in-house developed procedures [4]. The dimensional stability of the membranes was obtained by measuring the area change between wet and dry state (membranes dried *in vacuo* for 2 h at 80 $^{\circ}$ C).

The ETFE based membranes were hotpressed (110 $^{\circ}$ C/5 MPa/180 s) together with ELAT[®] electrodes (type LT140EWSI, E-TEK/BASF Fuel Cell, Inc.) with a platinum loading of 0.5 mg cm^{-2} . The electrochemical characterization (polarization curves, impedance spectroscopy, H₂ permeation) and the description of the used procedure are reported in detail elsewhere [10]. After completion of the test and disassembling the membrane from the MEA, it was exchanged into salt form (K⁺) and then dried over night at 60 $^{\circ}$ C. A *post mortem* analysis by FTIR was performed in the active area of the tested membrane by the use of a metallic slit mask (rectangular aperture 0.5 $\text{cm} \times 1.9 \text{ cm}$).

3. Results and discussion

Styrene/MAN grafting into ETFE films was carried out for 6 and 8 h reaction time, under the same conditions as reported earlier [9]. In order to determine the molar ratio of MAN to styrene in the membranes, the infrared vibration bands appearing at 1494 cm^{-1} (C=C) and at 2234 cm^{-1} (C \equiv N) were exploited to determine the ratio of the styrene and MAN moieties (Fig. 1). The FTIR spectra show clearly that the nitrile group is not affected by the sulfonation step during the membrane preparation.

Selected membranes were characterized for their *ex situ* fuel cell relevant properties (Table 1). The graft level of the styrene/MAN membranes is higher ($\sim 27\%$) compared to the styrene ($\sim 21\%$) based membrane to compensate for the presence of MAN, which does not contribute to the proton density. The ion exchange capacity (IEC) of styrene/MAN membrane #1 is therefore similar to that of the styrene grafted membrane, the IEC of styrene/MAN membrane #2 is, however, somewhat lower owing to the higher MAN content and concomitant lower density of styrene sulfonic acid groups. The water uptake is only slightly affected, yet the hydration number increases with the incorporation of MAN.

The conductivity of the styrene/MAN based membrane with a molar ratio of styrene to MAN in the copolymer of 0.26 was higher compared to that of a pure styrene grafted membrane, despite the slightly lower IEC value. It is assumed that the hydrophilicity of the nitrile group and its ability to form hydrogen bonds with water influences proton mobility in a favourable way [18].

Both styrene/MAN grafted membranes and the styrene grafted membrane were assembled into fuel cells and operated at a constant current density of 500 mA cm^{-2} (Fig. 2). Current pulse, H₂ permeation and electrochemical impedance measurements were performed intermittently over the testing period to characterize the cell *in situ*, as described previously [10] (Table 2). The Nafion[®]112 based MEA exhibits a lower polarization resistance in comparison to the MEAs with grafted ETFE membranes. The poorer membrane electrode interfacial properties (high polarization resistance) in the case of the radiation grafted membranes is a consequence of the lower compatibility of these grafted membranes to the Nafion[®] ionomer used in the catalyst layer [4].

The single cell test of the pure styrene grafted membrane had to be stopped after 241 h due to high gas crossover and pinhole formation in the active area. The styrene/MAN co-grafted membranes

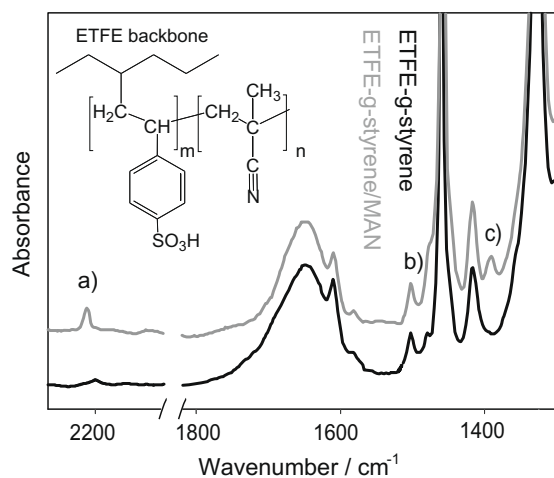


Fig. 1. FTIR spectrum of sulfonated styrene/MAN co-grafted and pure styrene grafted membranes based on ETFE. The large band 1000–1350 cm^{-1} is an ETFE backbone signal. Graft component relevant peaks: (a) C \equiv N stretch vibration at 2234 cm^{-1} , (b) C=C aromatic skeleton stretch vibration at 1494 cm^{-1} and (c) C-H deformation vibration in α -methyl at 1388 cm^{-1} .

Table 1

Ex situ properties of ETFE based styrene/MAN co-grafted and pure styrene grafted membranes, compared against Nafion®112. Membrane #1 was prepared with a styrene to MAN molar ratio in the grafting solution of 1:1, membrane #2 with a ratio of 1:4.

| Membrane | Graft level (%) | Molar ratio MAN/styrene | Thickness (μm) | Ion exchange capacity (mmol g^{-1}) | Conductivity ^a (mS cm^{-1}) | Water uptake ^a (%wt) | Hydration number ($n(\text{H}_2\text{O})/n(\text{SO}_3\text{H})$) |
|------------------|-----------------|-------------------------|-----------------------------|--|---|---------------------------------|---|
| g-Styrene/MAN #1 | 27.4 | 0.26 ± 0.04 | 40 ± 0.6 | 1.35 ± 0.07 | 69 ± 3 | 26.8 ± 1.5 | 10.6 ± 0.8 |
| g-Styrene/MAN #2 | 27.1 | 0.41 ± 0.04 | 36 ± 0.3 | 1.14 ± 0.02 | 42 ± 2 | 25.5 ± 0.4 | 12.8 ± 0.8 |
| g-Styrene | 20.8 | – | 35 ± 0.5 | 1.46 ± 0.06 | 49 ± 2 | 25.6 ± 3.1 | 9.7 ± 0.7 |
| Nafion®112 [4] | – | – | 58 ± 3.0 | 0.91 | 82 ± 6 | 33.5 ± 1.8 | 18.0 ± 0.9 |

^a Measurements were performed in fully swollen state at room temperature.

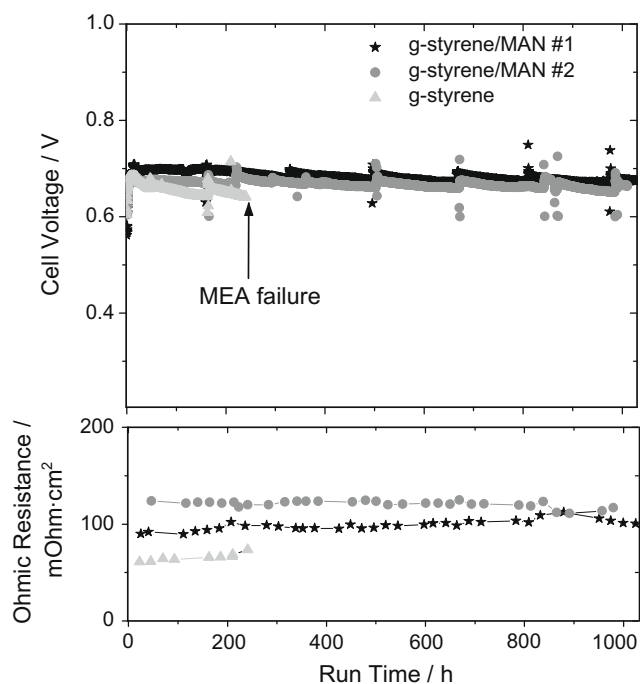


Fig. 2. Single cell durability test using radiation grafted membranes based on ETFE at 500 mA cm^{-2} , cell temperature 80°C ; H_2/O_2 at a stoichiometry of 1.5/1.5, atmospheric gas pressure, full humidification at 80°C .

were operated for 1000 h without failure before the tests were discontinued. Membrane failure in H_2/O_2 fuel cells can be due to both chemical or mechanical degradation. Mechanical failure is often caused by mechanical stress induced by hydration and dehydration processes. In our case, this failure mode is unlikely to play a role as the experiments were conducted at constant current density. In addition, the dimensional stability of the styrene/MAN and styrene membrane with similar IEC is almost identical (Table 2).

The chemical degradation of fuel cell membranes is believed to be caused by aggressive species formed as a consequence of the interaction of H_2 and O_2 , interdiffusing through the membrane, on the noble metal catalyst surface [19]. The rate of reactant crossover is therefore expected to govern the rate of membrane degra-

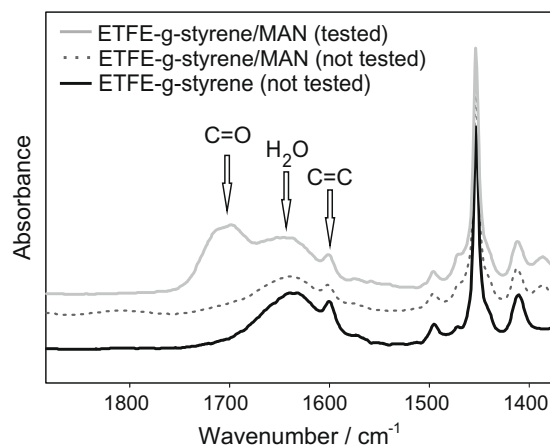


Fig. 3. FTIR spectra of pristine membranes and a tested styrene/MAN (#2) co-grafted membrane.

ation. In this context, the significantly lower *in situ* measured H_2 permeation rates through the styrene/MAN grafted membranes compared to the pure styrene grafted membrane (Table 2) could explain the improved durability in the fuel cell. The effect has to be an intrinsic property, since the thicknesses of all the grafted membranes are similar (Table 1) and the density of the styrene membrane even somewhat higher (Table 2). The lower permeability observed for styrene/MAN membranes is possibly a result of the chain interaction between the polar nitrile groups to create a physical network by hydrogen bond formation. Indeed, a shift in the nitrile infrared band position to higher wavenumbers was observed with increasing MAN content, indicating a ‘stiffening’ of the bonding state. More investigations on the state-of-water in styrene/MAN grafted membranes are needed to understand the differences to pure styrene grafted membranes.

Post mortem analysis of the tested membranes reveals the existence of a new broad peak appearing at $\sim 1700 \text{ cm}^{-1}$ in case of the styrene/MAN co-grafted membranes, which is assigned to C=O vibration (Fig. 3). The observed C=O group is considered to appear as a result of nitrile group hydrolysis under fuel cell operating conditions, yielding carboxylic acid. The sulfonation reaction during membrane preparation does not affect the nitrile group and no

Table 2

Membrane and MEA performance characteristics from fuel cell test data of styrene/MAN co-grafted and pure styrene grafted membranes and Nafion®112 after 165 h of operating time. Dimensional stability of the membranes is determined by measuring the difference in area between wet and dry state.

| Membrane | Time on test (h) | Density (wet state) (g cm^{-3}) | Wet \rightarrow dry area shrinkage (%) | Ohmic resistance ($\text{m}\Omega \text{ cm}^2$) | Polarization resistance ($\text{m}\Omega \text{ cm}^2$) | H_2 permeation (mA cm^{-2}) |
|------------------|-------------------|--|--|--|---|---|
| g-Styrene/MAN #1 | 1032 ^a | 1.31 | 25.9 | 108 | 153 | 0.31 |
| g-Styrene/MAN #2 | 1009 ^a | 1.29 | 17.7 | 132 | 188 | 0.35 |
| g-Styrene | 241 ^b | 1.39 | 24.2 | 80 | 216 | 0.53 |
| Nafion®112 | 600 ^a | 1.77 | 25.9 | 83 | 138 | 0.90 |

^a No failure.

^b Crossover leak $>10 \text{ ml min}^{-1}$.

hydrolysis of this group was observed in the as-prepared membrane. Therefore, the intensity of the nitrile (2234 cm^{-1}) and α -methyl (1388 cm^{-1}) vibrational bands of MAN in the tested and pristine membrane was employed to establish that the extent of degradation and hydrolysis in membrane #1 at the end of test were 36% and 13%, respectively, and mostly located near the O_2 inlet. Hydrolysis of the nitrile group is not necessarily detrimental, since the grafted chain remains intact.

4. Conclusion

Novel radiation grafted membranes using $25\text{ }\mu\text{m}$ ETFE base film were successfully prepared via co-grafting of commercially available inexpensive styrene and MAN monomers. The grafting rate of this system is much faster compared to that of the α -methylstyrene/MAN system [17]. The obtained membranes have exploitable conductivities over 50 mS cm^{-1} with lower hydration numbers in comparison to Nafion[®]112, and the water uptake shows a dependency on the content of MAN in the graft component. Single fuel cell tests showed a notable improvement in the lifetime of the co-grafted styrene/MAN over the styrene based membranes. The H_2 crossover in MAN containing membranes was found to be markedly lower. The *post mortem* analysis reveals the existence of carboxylic acid, which is attributed to the hydrolysis of a fraction of the nitrile groups. In further work, the role of the nitrile group on stability and proton transport will be investigated. The optimization of the MAN concentration and extent of crosslinking is the next step to optimize the stability of these membranes.

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