



Study of nitrile-containing proton exchange membranes prepared by radiation grafting: Performance and degradation in the polymer electrolyte fuel cell



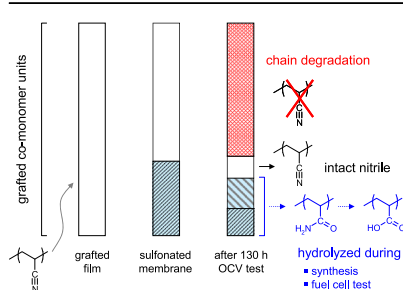
Zhuoxiang Zhang, Kaewta Jetsrisuparb, Alexander Wokaun, Lorenz Gubler*

Electrochemistry Laboratory, Paul Scherrer Institut, 5232 Villigen PSI, Switzerland

HIGHLIGHTS

- Radiation grafted membranes were prepared using styrene and nitrile co-monomers.
- Nitrile co-monomers used were acrylonitrile (AN) and methacrylonitrile (MAN).
- Nitrile containing membranes showed enhanced stability in the OCV hold tests.
- The improved stability is due to the enhanced gas barrier properties of the membranes.
- AN is susceptible to hydrolysis, which leads to a loss of the stabilizing property.

GRAPHICAL ABSTRACT



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ABSTRACT

The fuel cell performance and durability of three kinds of styrene based radiation grafted membranes are investigated and compared in the single cell. The styrene/methacrylonitrile (MAN) co-grafted membrane exhibits the best performance among the tested radiation grafted membranes. The accelerated tests under open circuit voltage (OCV) conditions and *post-mortem analysis* demonstrate that the nitrile-containing membranes exhibit significantly enhanced durability compared to the pure styrene grafted membrane, which is associated with the reduced gas crossover rates and attributed to the improved gases barrier properties due to the polarity of the nitrile group. To understand the influence of each functional group in the co-monomer units, both styrene/MAN and styrene/acrylonitrile (AN) co-grafted membranes are evaluated in a set of tests at OCV. The degrees of loss of the graft components are subsequently quantitatively analyzed based on FTIR spectra, showing a comparable decomposition rate of grafted styrene units, but more loss of nitrile in case of the styrene/AN co-grafted membrane. The styrene/AN co-grafted membrane, with AN lacking protection at the α -position in contrast to MAN, is found to be susceptible to significant hydrolysis, directly leading to an accelerated degradation in the late stages of the 130 h OCV test and inhomogeneous in-plane degradation.

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1. Introduction

The polymer electrolyte fuel cell (PEFC) is a promising candidate as an energy conversion device for many applications, such as electric vehicles, distributed power stations, consumer electronics

* Corresponding author. Paul Scherrer Institut, OVGA/103, CH-5232 Villigen PSI, Switzerland. Tel.: +41 56 310 2673; fax: +41 56 310 4416.

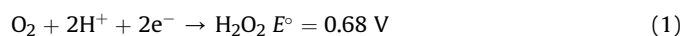
E-mail address: lorenz.gubler@psi.ch (L. Gubler).

etc. [1]. A thin organic proton exchange membrane is used in this kind of fuel cell, playing the dual role of electrolyte and separator for gases and electrons. The electron-beam or γ -ray induced radiation grafting provides a versatile tool to prepare proton exchange membranes owing to the wide choice of monomers available for grafting [2]. Moreover, radiation grafted poly(styrene sulfonic acid) (PSSA) membranes are potentially cost-effective alternatives to perfluoroalkylsulfonic acid (PFSA) membranes, such as the Nafion[®] series [3]. In essence, radiation grafting is a film modification technique, which consists of the addition of a second polymer, the “graft” component, into a preformed base polymer film to introduce a desired property, for instance proton conductivity [4]. In the process, the base polymer is exposed to ionizing radiation to create “active” sites, such as free radicals or peroxide groups. When the irradiated film is brought into contact with a solution containing monomers amenable to radical polymerization, the active sites initiate polymerization reactions, leading to the formation of grafted chains covalently attached to the base polymer. Often, further reactions are preformed after grafting, for instance sulfonation to introduce proton exchange sites. Radiation grafted membranes for fuel cells typically possess a chemically and mechanically robust base polymer, usually a fluoropolymer [5], e.g. poly(ethylene-co-tetrafluoroethylene) (ETFE), and hydrocarbon grafted chains composed of sulfonated polystyrene or its copolymers synthesized by co-grafting of styrene with selected co-monomers [2,6,7]. Unfortunately, due to the vulnerable α -hydrogen, the styrene based membrane is prone to degradation of the styrenesulfonic acid (SSA) units and thus the loss of proton conductivity under fuel cell conditions [8–11].

Advanced radiation grafted membranes with improved durability and performance have been investigated and developed through optimizing the properties of base films [12,13], replacing styrene with more stable combination of monomers [14,15] and introducing an optimized crosslinked network into the membranes [16]. In our previous research, methacrylonitrile (MAN) was used as co-monomer to promote the grafting of α -methylstyrene (AMS), and the obtained membranes displayed significantly higher durability in the fuel cell compared to pure styrene grafted membranes [17], and good fuel cell performance that was very close to that of Nafion[®] NR212 [18]. Furthermore, under constant current density (500 mA cm^{-2}) operation, a fuel cell assembled with styrene/MAN co-grafted membrane exhibited longer lifetime than a fuel cell using the membrane grafted with only styrene [19]. Recently, a 2'400 h durability test was performed in a 6-cell stack at 80°C under dynamic load conditions, and showed that the durability of optimized radiation grafted membranes comprising sulfonated α -methylstyrene as protogenic unit can even exceed that of state-of-the-art Nafion[®] XL-100 [20]. There is, however, considerable interest in further developing membranes based on grafted styrene, owing to its superior grafting kinetics compared to that of α -methylstyrene. Yet, the durability, especially chemical stability, of styrene based co-grafted membranes has not been comprehensively investigated and understood. In addition, the influence of co-monomers, such as MAN, on the deterioration of radiation grafted membranes still remains an open question and worthy of investigation for further discussing aging mechanisms and tailoring the properties of membranes. To answer this question and promote the understanding of the influence of each functional group in the MAN units, such as α -methyl and nitrile, we co-graft styrene with acrylonitrile (AN) for a comparison with styrene/MAN co-grafted membranes in terms of performance and durability.

It has been widely accepted that hydrogen peroxide (H_2O_2) and membrane-degrading species, such as $\text{HO}\cdot$, $\text{HOO}\cdot$, and $\text{H}\cdot$, are generated in the fuel cell due to the crossover of reactant gases through the membrane, which induce membrane chemical

degradation of both PFSA and PSSA based membranes [10,21–23]. Therefore, the gas crossover rate is critical for the chemical degradation mechanism of a polymer electrolyte membrane in the PEFC configuration. The chemical stability of radiation grafted membranes in this study is examined by accelerated stress tests in the presence of H_2 and O_2 and under conditions of OCV, which is often used as an accelerated stress protocol to assess chemical stability of the membranes [24]. Since there are no fuel and oxidant being consumed electrochemically at OCV, gas crossover through the membrane is potentially increased, leading to increased formation of peroxide and radicals that attack the membrane [25,26]. It is worth mentioning that the two-electron reduction of O_2 (cf. Equation (1)), which is another possible mechanism for generating the radical precursor H_2O_2 at the cathode independent of the gas crossover, does not play a significant role during OCV hold tests owing to, 1) the absence of faradaic current, and 2) the high cathode potential of $>0.9 \text{ V}$ [10]. However, the mechanism shown in Equation (1) is likely to occur at the anode, depending on O_2 permeation. Hence, with respect to the OCV durability test, gas barrier properties of proton exchange membranes are a significant factor for the formation of membrane-degrading species.



The hydrolysis of nitrile in the styrene/AN co-grafted membranes has been observed during the preparation of membranes [27]. However, the influence of hydrolysis on membrane durability has not been investigated yet. This is likely to be very interesting, because the hydrolysis process in the nitrile-containing membranes can convert the nitrile group to the carboxylic acid group, which is susceptible to attack by $\text{HO}\cdot$, as it has been reported in case of PFSA membranes with imperfections in the form of $-\text{COOH}$ end-groups [28]. To understand the influence of hydrolysis on membrane durability, it is thus important to quantify the fraction of nitrile groups converted to amide and carboxylic acid. We have developed a calculation method, based on integrating the characteristic IR-bands, to determine the degree of the nitrile hydrolysis after the fuel cell test (cf. supplementary data).

In this study, we investigate the effect of nitrile-containing co-monomers (MAN, AN) on fuel cell performance and membrane chemical degradation through testing styrene/MAN and styrene/AN co-grafted membranes in comparison to a pure styrene grafted membrane (Fig. 1) in the single fuel cell. The online measurement of cell voltage and membrane resistance as a function of run time over the OCV test period will be presented, and *post-mortem* tests are used to evaluate the durability of each kind of membrane. The gas permeation rates of the different radiation grafted membranes with and without nitrile units are measured, and their contribution for improving membrane stability will be elucidated. The degree of membrane degradation and the degree of nitrile hydrolysis are quantified to show the evolution of the decomposition of SSA units

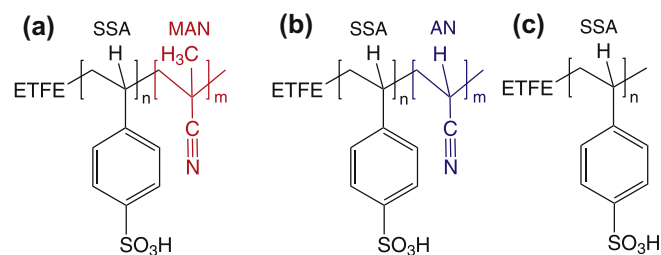


Fig. 1. Schematic of the chemical composition of the membranes used in this study. (a): styrene/MAN co-grafted membrane (grafted S-MAN); (b): styrene/AN co-grafted membrane (grafted S-AN); (c): pure styrene grafted membrane (grafted S).

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