European Polymer Journal 53 (2014) 75–89

Contents lists available at ScienceDirect

European Polymer Journal

journal homepage: www.elsevier.com/locate/europolj

Proton conducting membranes prepared by radiation grafting of styrene and various comonomers

Kaewta Jetsrisuparb [a,b], Sandor Balog [c], Corine Bas [d], Lara Perrin [d], Alexander Wokaun [b], Lorenz Gubler [a,b,*]

[a] *Electrochemistry Laboratory, Paul Scherrer Institut, CH-5232 Villigen PSI, Switzerland*
[b] *Research Department General Energy, Paul Scherrer Institut, CH-5232 Villigen PSI, Switzerland*
[c] *Adolphe Merkle Institute, University of Fribourg, CH-1723 Marly 1, Switzerland*
[d] *LEPMI, UMR 5279, CNRS, Grenoble INP, Université de Savoie, Université J. Fourier, LMOPS, INES, Bât. Hélios, Campus de Savoie Technolac, F-73376 Le Bourget du Lac Cedex, France*

ARTICLE INFO

Article history:
Received 26 August 2013
Received in revised form 22 November 2013
Accepted 14 January 2014
Available online 22 January 2014

Keywords:
Comonomer
Polymer electrolyte fuel cell
Proton exchange membrane
Graft copolymers
NMR
SAXS

ABSTRACT

Proton conducting membranes are synthesized by radiation grafting a fluoropolymer matrix, poly(ethylene-alt-tetrafluoroethylene) (ETFE), with styrene and various non-crosslinking comonomers: methacrylonitrile (MAN), acrylonitrile (AN), methyl methacrylate (MMA), and methacrylic acid (MAA). During sulfonation, hydrolysis of nitrile and ester groups takes place to different extents. Solid-state NMR spectroscopy confirms the cyclic ketone structure formed in styrene/MAA co-grafted membranes. The comonomer influence on the membrane properties is studied by characterizing the ion exchange capacity (IEC), water uptake, proton conductivity, and the nano-scale morphology via small-angle X-ray scattering (SAXS). In water swollen state, the proton conductivities of grafted membranes with similar IEC are comparable, while at reduced relative humidity (<80%) the co-grafted membranes exhibit lower proton conductivity compared to the styrene grafted membrane, regardless of the type of comonomer. It is proposed, based on the SAXS analysis, that this is a consequence of an increased average distance between the acid groups in co-grafted membranes.

1. Introduction

One of the major challenges in the energy sector nowadays is unquestionably the large-scale introduction of clean energy. In view or the need for clean energy conversion, the fuel cell is one of the promising technologies. Fuel cells are reaching commercialization especially in the field of portable energy sources and remote electricity generation [1].

A critical aspect in the development of proton conducting membranes for fuel cell applications is to reach a compromise between membrane cost, performance and durability. The state of the art membranes are perfluorosulfonic acid (PFSA) ionomers, such as Nafion. Under favorable conditions, Nafion can achieve a lifetime of 60,000 h [2,3]. Under application-relevant conditions, the lifetime is much lower due to the use of thin membranes and dynamic operating conditions [4,5]. In addition, the high cost is a major shortcoming of PFSA ionomers [6].

Radiation grafted membranes have attracted interest in recent years because of their simple synthesis and encouraging membrane properties endowed by the combination of base film and grafted monomer properties [7,8]. Among different fluoropolymers, ETFE is considered a suitable base film, owing to its relatively good resistance to radiation induced damage and superior mechanical properties [9–11]. Extensive studies on potential base films for the

---

[*] Corresponding author at: Electrochemistry Laboratory, Paul Scherrer Institut, CH-5232 Villigen PSI, Switzerland. Tel.: +41 56 310 2673; fax: +41 56 310 4416.

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

http://dx.doi.org/10.1016/j.eurpolymj.2014.01.021

synthesis of radiation grafted fuel cell membranes have been reported, to which the reader is referred for more detail [9–11].

Styrene and its derivatives are the most widely used monomers for the preparation of radiation grafted proton conducting membranes [7,10,12,13]. Attention was given to styrene owing to its low cost, amenability to radical polymerization, and easy sulfonation. Yet, styrene based membranes are prone to chemical degradation under fuel cell conditions due to the presence of weak α-H [14–16]. Styrene derivatives with a protected alpha-position [3,17], such as α,β,β-trifluorostyrene (TFS) [18,19] or α-methylstyrene (AMS) [20], increase membrane durability but suffer from a low grafting rate [20–23].

To circumvent these limitations, comonomers of styrene and styrene derivatives are introduced to improve membrane stability. Crosslinking monomers, such as divinylbenzene (DVB) and diisopropylbenzene (DIPB), are used to improve chemical and mechanical stability of the membranes [24–26]. Although a crosslinker may improve the lifetime, it also lowers proton conductivity and increases brittleness [27]. A non-crosslinking monomer, methacrylonitrile (MAN), has shown to significantly promote the grafting kinetics of α-methylstyrene [28] and also improve the fuel cell durability of styrene/MAN co-grafted membranes compared to a pure styrene grafted membrane [29].

In the study reported here, a number of radiation grafted membranes was prepared by grafting of styrene with different comonomers to investigate the potential influence of the nature of the comonomer on the structure and properties, such as proton conductivity as a function of relative humidity (RH), of the resulting membranes. Four comonomers with different functional groups, namely MAN, acrylonitrile (AN), methyl methacrylate (MMA), and methacrylic acid (MAA), were grafted with styrene into ETFE base film followed by sulfonation to form proton conducting membranes. Both MAN and AN have shown to improve the stability of styrene based radiation grafted membranes against chemical degradation, yet AN hydrolyzes more readily under fuel cell operating conditions, owing to the absence of the methyl group at the α-position of the monomer [30]. Based on these findings, the question arose whether other comonomers, when co-grafted with styrene, could have beneficial effects on the characteristics of radiation grafted membranes, be it on the conductivity, water uptake or other fuel cell relevant properties, or the durability under fuel cell operating conditions. MMA was chosen as a potentially suitable co-monomer because it is chemically similar to MAN. The comparison between MAN and MMA containing membranes can provide an understanding of the role of the functional group (nitrile or ester). In addition, MAA was chosen as a fourth comonomer. In case that grafted MAN and MMA units hydrolyze during fuel cell operation, the nitrile and methyl ester, respectively, are converted to carboxylic acid. Therefore, MAA as comonomer can serve as a model compound to study the effect of hydrolysis on membrane properties. In addition, with MMA being a rather hydrophobic comonomer and MAA being a hydrophilic one, which, in addition, can participate in the formation of a hydrogen bond network, the effect of the hydrophilicity of the comonomer can be studied.

Favorable copolymerization kinetics with styrene was another requirement for the comonomer choice. In preliminary experiments, it was established that the four comonomers chosen exhibit a tendency towards alternating copolymerization with styrene, which allows it to adjust the composition of the grafts in straightforward manner. Details regarding the co-grafting kinetics of styrene/MAN and styrene/AN onto ETFE film can be found in a recent publication [31]. In principle, the list of potential comonomers could be easily extended to many other compounds to introduce specific functionalities, which, however, is beyond the scope of this study.

In this study, the first series of results (Section 3.1) is devoted to the preparation and characterization of the various co-grafted films and membranes. The composition and structure are determined to identify the various intermediates and end products. Fuel cell relevant properties, i.e., ion exchange capacity, water uptake, and conductivity, are subsequently measured for the different co-grafted membranes and compared to those of a pure styrene grafted membrane and Nafion 212 as a commercial standard. Samples of co-grafted membranes are selected that have a molar ratio of styrene to comonomer of around 1:1 to maximize the likelihood of alternating sequence of comonomer units. In a final section, the analysis of the nano-scale morphology of the various membranes in dry state based on small-angle X-ray scattering (SAXS) experiments is presented, which can be used to interpret conductivity data at low relative humidity and thus establish structure–property relationships in this class of polymers.

2. Experimental

The chemicals used during membrane preparation included styrene (99%, Aldrich), methacrylonitrile (MAN) (99%, Aldrich), acrylonitrile (AN) (99.5%, Fluka), methyl methacrylate (MMA) (99%, Aldrich), methacrylic acid (99%, Aldrich) and chlorosulfonic acid (98%, Fluka). The ETFE base film (TEFZEL® 100LZ, 25 μm, purchased from DuPont, Circleville, USA) was electron beam irradiated in air at Leoni Studer AG in ambient atmosphere (Däniken, Switzerland), into which the grafted chains were grown from the activated sites known as the "grafting-from" approach [32]. A dose of 1.5 kGy was applied to the base films to graft styrene, styrene/MAN and styrene/MMA. For reasonable grafting time, a dose of 3 and 15 kGy were applied to the base film for grafting of styrene/AN and styrene/MAA, respectively. The grafting solution contained 20% (v/v) mixture of styrene and comonomer and 80% (v/v) solvent, comprising of a 1:7 (v/v) ratio of water to isopropanol. For styrene/MAA, pure ethanol was used as solvent.

The grafting reaction was carried out at 60 °C under nitrogen atmosphere. After a given reaction period, the grafted films were removed from the reactor and washed thoroughly overnight and dried under vacuum at 80 °C. Toluene was used as a solvent to wash grafted films containing MAN, AN and MMA. In case of styrene/MAA, the