Solid State Ionics 277 (2015) 38–43

Contents lists available at ScienceDirect

Solid State Ionics

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

Reduction of the monomer quantities required for the preparation of radiation-grafted alkaline anion-exchange membranes

Simon D. Poynton *, John R. Varcoe

Department of Chemistry, University of Surrey, Guildford, Surrey GU2 7XH, UK

ARTICLE INFO

Article history:
Received 28 August 2014
Received in revised form 8 March 2015
Accepted 25 April 2015
Available online 14 May 2015

Keywords:
Poly(ethylene-co-tetrafluoroethylene)
Vinylbenzyl chloride
Radiation–grafting
Alkaline polymer electrolyte fuel cell (APEFC)
Alkaline anion-exchange membrane (AAEM)

ABSTRACT

Alkaline anion-exchange membranes (AAEM) for alkaline polymer electrolyte fuel cells (APEFC) were successfully prepared using electron beam irradiated poly(ethylene-co-tetrafluoroethylene) precursor films grafted with vinylbenzyl chloride (VBC) monomer. The resulting chloromethyl groups were subsequently reacted with trimethylamine to form quaternary ammonium anion-exchange functional head-groups. The concentration of toxic and expensive VBC, that is required to achieve an optimal level of grafting, was reduced from 100%*v*/*v* (undiluted) to 20%*v*/*v* by dilution with propan-2-ol and the inclusion of a surfactant. Fuel cell tests using hydrogen and oxygen gave the same peak power densities (164 ± 3 mW cm^{-2}) for the AAEMs prepared with both 100%*v*/*v* VBC and 20%*v*/*v* VBC. This highlights the (desirable) lack of any detrimental effect on performance of the resulting APEFC with the reduction in grafting monomer concentration used for the synthesis of the component AAEM.

1. Introduction

Proton exchange membrane fuel cells (PEMFCs) have received a large amount of interest as power sources for both stationary and mobile applications. However, they commonly involve the incorporation of expensive commercial perfluorinated proton-exchange membranes (such as Nafion® by Du Pont) as the solid electrolyte and platinum-based electrocatalysts [1]. More recently, alkaline anion-exchange membranes (AAEM) have been developed as an alternative electrolyte for use in low temperature fuel cells: such alkaline polymer electrolyte fuel cells (APEFCs) have been shown to exhibit lower fuel permeability, across the AAEM (compared to proton exchange membranes) when used in direct alcohol mode [2], and the ability to utilise cheaper and more abundant non-precious-metal electrocatalysts (especially at the cathode due to a more facile oxygen reduction reaction at high pH) [3–5]. AAEMs consist of covalently bound positive functional head-groups, typically quaternary-ammonium-type ($-N^+R_3$), and mobile anions (*i.e.* cationic polymers with anion conduction). Having polymer-bound cationic groups, instead of the mobile metal cations found in traditional liquid electrolyte alkaline fuel cells, gives the APEFCs an enhanced resistance to the undesirable accumulation of metal carbonate precipitates [6].

AAEMs produced from the radiation-induced grafting of monomers onto preformed fluorinated, partially fluorinated, and non-fluorinated polymer films have been extensively studied and reported [7–10]. Generally, precursor polymer films are modified using either a simultaneous grafting method [11] or a pre-irradiation method [8,12] with either gamma-(γ-)ray or electron-(e-)beam irradiation. Simultaneous radiation–grafting is where the precursor polymers are irradiated whilst submerged in the grafting monomer solution of choice and pre-irradiation–grafting is where the polymer precursors are initially irradiated (commonly in air) and then subsequently treated with the grafting monomer solution. The AAEMs produced at the University of Surrey are based on the e-beam pre-irradiation–grafting of poly(ethylene-co-tetrafluoroethylene) (ETFE) with vinylbenzyl chloride (VBC) monomer (previously used in large quantities and undiluted) before subsequent quaternisation with a tertiary amine of choice [12–14]. VBC is both expensive and hazardous when used in large quantities (potential mutagen, acutely toxic on skin adsorption and ingestion, and very toxic to aquatic life): it is therefore vital to significantly reduce the quantity required during the grafting step. This has widely been reported for other monomers, such as styrene (used to synthesise radiation-grafted proton-exchange membranes), by dilution with appropriate solvents [15–17].

The reaction between monomer and the radiation induced reaction sites (peroxides and radicals) of the polymer is governed by the diffusion properties of the monomer and lifetimes of the reaction sites. Without solvents, grafting typically follows the grafting front mechanism [18,19]: this is where the grafting initially occurs at the surfaces of the polymer films (and particles), and more monomer molecules can then penetrate deeper, when the grafted layers subsequently swell. The introduction of a suitable additional solvent leads to enhanced swelling within the polymer substrate and increased monomer accessibility to the internal substrate layers, resulting in a higher (more uniform) level of grafting [20]. This is especially important for ion-exchange membranes, as

---

* Corresponding author. Tel. +44 1483 682616; fax: +44 1483 683010.
E-mail address: simon.poynton@surrey.ac.uk (S.D. Poynton).

http://dx.doi.org/10.1016/j.ssi.2015.04.013
0167-2738/

homogeneous grafting throughout the entire membrane thickness is vital for effective ion conductivity. Nasef *et al.* measured the effect of several pure solvents on pristine ETFE films at ambient temperature and observed that the polymer film decreasingly swelled in the order; toluene > dimethylformamide > > propan-2-ol > ethanol > methanol. However, for the alcohol systems, the degree of swelling was substantially increased when ETFE was submerged in an alcohol–monomer mixture (*ca.* 50:50 *v*/*v*) compared to when submerged in only alcohol [16]. The dilution of the monomer can also affect the overall grafting as a result of concentration, and thus viscosity, effects. Elmidaoui *et al.* proposed that by decreasing the monomer concentration, the viscosity is lowered, and this leads to a higher diffusivity of monomer into the membrane thickness and allows facilitated access to the deeper grafting sites; however, this will also lead to a simultaneous decrease in local monomer concentration and a reduction in the diffusion via the graft front mechanism [21]. This situation becomes further complicated when the solubility of the monomer in the solvent is taken into account. It is well known that solvents with similar solubility parameters to the monomer improve the overall degree of grafting, whereas large differences in solubility parameters hinder the reaction [22]. The differences between the monomer–solvent solubility parameters are, however, reduced by the inclusion of an appropriate surfactant [23]. Thus a balance needs to be struck regarding the influence the solvent has over both the membrane and monomer; making the correct choice of solvent to use essential. The most commonly encountered solvents are methanol [16,17], toluene [8,16,17,24], propan-2-ol [16,25,26] or combinations of these with water [27,28].

The ultimate aim is to use water as a VBC dispersion: Waring *et al.*, described a post-irradiation emulsion technique where VBC was diluted with water along with an emulsifier and chain transfer agent [29]. However, ETFE based AAEMs (with quaternary amine (TMA) functionality produced using this method) evaluated in collaboration with Mamlouk *et al.*, exhibited extremely low through-plane conductivity with high anisotropy, resulting in them being labelled "*unsuitable for fuel cell tests*". This was attributed to the poor distribution of the VBC monomer through the profile of the membrane, due to the lack of polymer swelling in water and the low solubility of the VBC in water (the emulsion technique used a only 3%*v*/*v* VBC) [30]. The severe immiscibility of VBC in water (even within an emulsion based system) is proving difficult for the production of highly ionic conductive AAEMs with the pre-irradiation grafting method (that is more useful when the radiation source is not on site). Instead, this paper details the successful production of *m^2-batch-sizes* of radiation-grafted trimethylammonium-type AAEMs using e-beam pre-irradiated ETFE film where a significant reduction in VBC concentration was achieved by dilution in propan-2-ol. The solubility of VBC in propan-2-ol was further enhanced on addition of a surfactant. This formulation promoted successful grafting with monomer concentrations as low as 20%*v*/*v*; the resultant AAEM had comparable properties to the benchmark produced using 100%*v*/*v* (*i.e.* undiluted) VBC.

2. Experimental procedures

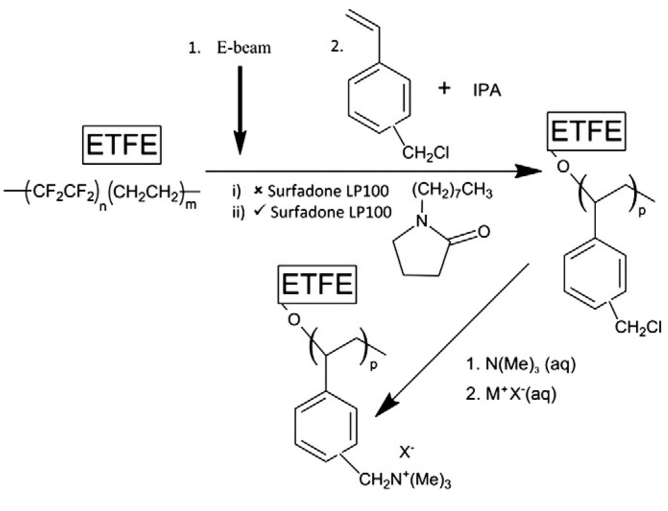
2.1. Chemicals and materials

Poly(ethylene-co-tetrafluoroethylene) film, (ETFE, 50 μm thick, Nowoflon ET-film) was supplied by Nowofol Kunstoffprodukte GmbH (Germany). Vinylbenzyl chloride monomer (VBC, mixture of 3- and 4-isomers; used without removal of inhibitor) was purchased from Dow Chemicals (Germany). Surfadone LP-100 (1-octyl-2-pyrrolidone) was obtained from ISPcorp (USA). Propan-2-ol, toluene, poly(vinylbenzyl chloride) were of reagent grade and supplied from Sigma-Aldrich (UK) whilst *N,N,N′,N′*-tetramethylhexane-1,6-diamine (TMHDA) and trimethylamine (TMA, 50%wt in water) were supplied from Acros Organics (UK). Pt/C electrocatalyst (Johnson Matthey Hispec 3000, 20%mass Pt on Vulcan carbon) was purchased from Alfa Aesar (UK). The carbon cloth electrodes used for conductivity determination contained a micro-porous layer (MPL) on one side consisting of carbon powder (1 mg cm^{-2}) and 20%wt PTFE as a binder and were supplied by CeTech (Taiwan). The carbon paper electrodes used for fuel cell testing contained a MPL on one side of a wet proofed (20%wt PTFE) carbon paper gas diffusion layer [GDL] and was purchased from Hesen (China): the MPL consisting of 1 mg cm^{-2} of carbon powder with 20%wt PTFE as binder. All chemicals were used as received and the water used has a resistivity of 18.2 MΩ cm.

2.2. Membrane preparation

The AAEMs were prepared from pre-formed ETFE films using the method previously reported [9] with modifications to the grafting step as detailed below and as summarised in scheme 1. The ETFE films were subjected to electron-beam irradiation in air to a total dose of 70 kGy (using a 4.5 MeV Dynamatron Continuous DC Electron Beam Unit Synergy Health, South Marston, UK). After irradiation, the films were transported back to the laboratory (University of Surrey) in dry ice, then stored at −36 ± 2 °C and used within 12 months of irradiation. The effect of extensive cold storage on electron-beamed ETFE for up to 16 months has been shown not to produce a statistically significant reduction in the ion-exchange capacities of the resulting membranes allowing flexibility in producing multiple grafted batches from a single electron-beam treatment [31].

For the grafting step, the irradiated ETFE films (twenty A4 sheets—the size of grafting was only limited by the size of the reaction vessel) were loosely wound in single ply tissue paper (in a *Swiss-roll* formation to separate the films and facilitate access of monomer solution to all surface areas) and immersed in propan-2-ol solutions of VBC at various concentrations (5 to 100%*v*/*v* VBC) in sealed vessels both with and without addition of surfactant (1%*v*/*v* Surfadone LP-100 (1-octyl-2-pyrrolidone)). Undiluted VBC was used to manufacture the benchmark membranes. Full details of the VBC dilutions used for each membrane are summarised in Table 1. The solutions were then purged with N_2 for 1 h before the vessels were sealed and heated at 60 °C for 3 d. After the reaction period, the films were removed from the solutions, washed in toluene and then heated in toluene at 70 °C for 5 h; this process is employed to remove excess unreacted VBC and any VBC homopolymer (polymerised VBC that is not grafted to the ETFE) that may be present. The resulting intermediate ETFE-g-poly(VBC) films were subsequently dried at 70 °C for 5 h in a vacuum oven to remove all traces of solvent. The degree of grafting was not recorded for any of the membrane samples. This was to reduce the period between the



Scheme 1. The synthesis of the trimethylammonium AEMs via the radiation–grafting of VBC onto ETFE both (i) without surfactant and (ii) with surfactant. IPA = propan-2-ol.