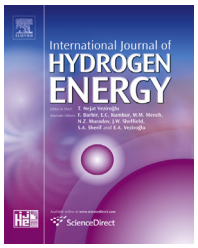
Available online at www.sciencedirect.com

ScienceDirect

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



Study on the effect of the degree of grafting on the performance of polyethylene-based anion exchange membrane for fuel cell application

Richard Espiritu [a,b,*], *Mohamed Mamlouk* [a], *Keith Scott* [a]

[a] *School of Chemical Engineering and Advanced Materials, Newcastle University, Merz Court, Newcastle upon Tyne, NE1 7RU, United Kingdom*

[b] *Department of Mining, Metallurgical and Materials Engineering, University of the Philippines Diliman, Quezon City 1101, Philippines*

ARTICLE INFO

Article history:
Received 15 July 2015
Received in revised form
25 September 2015
Accepted 24 October 2015
Available online 12 November 2015

Keywords:
Polyethylene
Degree of grafting
Anion exchange membrane
Radiation grafting
Alkaline fuel cell

ABSTRACT

Alkaline anion exchange membranes (AAEM) are fabricated using polyethylene as the base polymer offering a low cost AAEM. This study focuses on the synthesis and characterisation of AAEM with controlled degree of grafting (DOG) and ion-exchange capacity (IEC) with the following parameters investigated: LDPE film thickness 30–130 μm, gamma radiation dose and monomer concentration. The corresponding IEC, water uptake (WU) and degree of swelling (DS) are reported. The performance of 74.6% DOG membrane in a hydrogen fuel cell shows high OCV of 1.06 V with peak power density of 608 mW cm^{-2} at 50 °C under oxygen. The use of membrane with high DOG does not impact fuel cross-over significantly and provides improved fuel cell performance due to better conductivity, water transport and resilience to dehydration. The AAEM shows long term stability at 80 °C exhibiting a conductivity of ca. 0.11 S cm^{-1} over a period of 7 months under nitrogen. The membrane shows a degradation rate of 4 and 17 mS $month^{-1}$ under nitrogen and oxygen, respectively. The estimated life time of the membrane is 2 years under nitrogen and 5.5 months under oxygen operating at 80 °C.

Introduction

Renewed interest in the research and development of alkaline fuel cells has grown recently with the use of anion-exchange membrane (AEM) instead of liquid KOH as the electrolyte. An AEM is a solid polymer electrolyte membrane that contains positive ionic groups, typically containing quaternary ammonium groups: $-N^{+}CH_3$, and mobile negatively charged anions, usually OH^{-} [1]. The alkaline anion-exchange membrane fuel cell (AAEMFC) has been developed to address the challenges and limitations of the conventional AFCs. The AAEMFC offers the following advantages compared to proton-exchange membrane fuel cells (PEMFC), namely, (a) faster oxygen reduction reaction (ORR) kinetics under alkaline conditions, thus providing lower activation losses [2,3], (b)

* *Corresponding author*. School of Chemical Engineering and Advanced Materials, Newcastle University, Merz Court, Newcastle upon Tyne, NE1 7RU, United Kingdom.
E-mail address: r.espiritu@newcastle.ac.uk (R. Espiritu).

http://dx.doi.org/10.1016/j.ijhydene.2015.10.108

possibility of using non-noble metal catalysts [4–6], (c) osmotic drag associated with ion transport opposes the crossover of liquid fuels [4,7] and (d) lower membrane cost and cheaper cell components due to less corrosive environments [2,5,7].

The materials and methods required to produce AEMs are influenced by the desired properties of the resulting membrane in terms of performance, durability, stability and cost. The chemical and thermal stability greatly depend on the nature of the polymer backbone and on the functional group that enables the transfer of hydroxyl ions [8]. With these in mind, the major challenge is to synthesise AEM with a high OH^- ion conductivity using a stable polymer backbone with high ion exchange capacity but with controlled swelling and water uptake. One way to address this challenge is by employing polymer modification via grafting technique [9].

Radiation grafting is a widely used technique in industrial applications in order to improve the properties of the resulting polymer product [10] without altering their individual inherent properties [11]. In this method, active sites are formed on the polymer backbone using high energy radiation (gamma radiation, ultraviolet or electrons) and the irradiated base polymer is allowed to react with the monomer units which then propagate to form side chain grafts [9]. In fuel cell technology applications, in particular, radiation grafting is a cheaper way of producing ionomer membranes and offers a wealth of adjustable experimental parameters (e.g. radiation dose, temperature, film thickness) thus providing a large degree of tailorability [6]. Furthermore, reaction is completed in a fraction of a second, thus high product yield is obtained [12]. In terms of fuel cell performance, AEMs produced via radiation grafting can have high degree of grafting (DOG), low electrolytic resistivity, high IEC and high equilibrium water content [13].

The measure of the extent of polymerisation is often expressed in terms of the DOG. It is defined as the percentage mass of the grafted component with the copolymer matrix [14] and is an important parameter routinely studied due to its significant influence on the resulting properties of the AEM, namely, IEC, ionic conductivity, water uptake and swelling. In employing radiation to induce grafting of monomers, the type of radiation source, radiation dose and dose rate are important considerations that affect the resulting DOG of the membrane [15].

Polyethylene has been found to be a lucrative polymer backbone for AEMs due to its low cost, superior chemical stability, high crystallinity and hydrophobicity, good mechanical properties [16,17] and versatility to radiation grafting both for electrolyser and fuel cell applications [14,15,18]. Masson et al. [19] utilised gamma radiation source to graft low density polyethylene (LDPE) with acrylic acid followed by sulfonation while Faraj et al. [20] utilised UV-radiation source to graft LDPE with vinylbenzyl chloride (VBC) with subsequent amination to fabricate AEMs for water electrolysis. In terms of fuel cell application, Mamlouk et al. [21,22] successfully fabricated AEMs for alkaline fuel cells using LDPE and high density polyethylene (HDPE) as base polymer and employing VBC as the graft monomer. Aside from LDPE and HDPE based membranes for alkaline fuel cells, ultrahigh molecular weight polyethylene (UHMWPE) has also been used for radiation grafting but requires a melt pressing method to produce the membrane [23]. Shen et al. [24] on the other hand, performed methanol permeation studies on LDPE-based AEM for direct methanol fuel cells while Cheng et al. [25] evaluated the performance of LDPE-based AEM for direct borohydride fuel cell application.

Evolving research trend on polyethylene-based membranes involves grafting of polyethylene with another polymer in order to obtain the desired chemical and mechanical properties of the resulting copolymer backbone prior to functionalisation. Kim et al. [17] exploited the innate hydrophobicity of polyethylene and chemically grafted it with sulfonated poly(arylene ether sulfone) to produce membranes with high ion exchange capacity but with controlled swelling and water uptake. The work of Noonan et al. [26] showed the preparation of membranes with superb alkaline stability by chemically attaching phosphonium-based functional groups to polyethylene. Moreover, pore-filled composite membranes based on porous polyethylene exhibited high durability [27] and enhanced mechanical stability for high temperature fuel cell operation [28].

This particular study focuses on the facile synthesis and subsequent characterisation of AEM for alkaline fuel cells using LDPE alone as the base polymer thus offering an essentially cheaper alternative than commercially available AAEM. The effect of the DOG on the ionic conductivity and fuel cell performance, as influenced by gamma radiation dose and monomer concentration, is hereby investigated. Furthermore, this research examined the stability of the fabricated membranes in the vapour phase operating condition, which previous reports in literature have not included.

Experimental

Materials

Low-density polyethylene (melt index of 25 g/10 min) and linear low-density polyethylene (melt index of 1 g/10 min) pellets were procured from Sigma–Aldrich. Commercial polyethylene films were sourced from different suppliers, namely, British Polythene Industries plc (BPI) and VWR International (VWR). Microporous ultra-high molecular weight polyethylene (UHMWPE) films, with 40% porosity, were purchased from Entek Membrane LLC (ENTEK, USA). Vinylbenzyl chloride (mixture of 3– and 4–isomers, 97%) and trimethyl amine (in 45% solution in H_2O) were also procured from Sigma–Aldrich. Toluene solvent, potassium hydroxide pellets, acetone, methanol, sulphuric acid and sodium chloride were all analytical reagent grade and were used as received.

Anion exchange membrane preparation

Anion-exchange membranes (AEM) were synthesised using polyethylene as base polymer followed by radiation grafting with vinylbenzyl chloride (VBC) to form the copolymer. To obtain the AEM, trimethyl amine (TMA) was used to impart functionality to the copolymer. Aside from using commercial polyethylene films as base polymer, laboratory-produced polyethylene films were also prepared from commercial pellets and cast them into films.