



A facile synthesis of highly stable multiblock poly(arylene ether)s based alkaline membranes for fuel cells



Amaranadh Jasti ^{a, b}, Vinod K. Shahi ^{a, b, *}

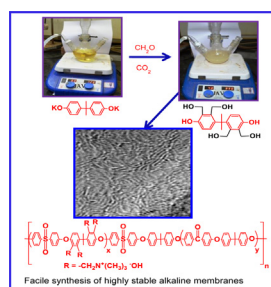
^a Academy of Scientific and Innovative Research, India

^b Electro-Membrane Processes Division, CSIR-Central Salt and Marine Chemicals Research Institute (CSIR-CSMCRI), G. B. Marg, Bhavnagar 364 002, Gujarat, India

HIGHLIGHTS

- Multiblock alkaline membranes are synthesized by a facile green method.
- Hydrophilic/hydrophobic phase separation causes for high conductivity.
- The presence of vicinal quaternary ammonium groups improves alkaline stability.
- Alkaline membrane for fuel cell applications.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 15 March 2014

Received in revised form

22 May 2014

Accepted 25 May 2014

Available online 4 June 2014

Keywords:

Aminated multiblock poly(arylene ether)s

Alkaline membrane

Hydrophilic/hydrophobic phase separation

Alkaline stability

Alkaline direct methanol fuel cell

ABSTRACT

Herein, we are disclosing simple route for the preparation of alkaline membranes (AMs) based on aminated multiblock poly(arylene ether)s (AMPes) synthesized by nucleophilic substitution-poly condensation followed by quaternization and alkalization reactions. In this procedure, four quaternary ammonium groups are successfully introduced without use of carcinogenic reagents such as chloromethylmethyl ether (CMME). Hydrophilic/hydrophobic phase separation is responsible for their high hydroxide conductivity ($\sim 150 \text{ mS cm}^{-1}$ at 80°C) due to development of interconnected ion transport pathway. AMs are exhibiting good alkaline stability due to the presence of two vicinal quaternary ammonium groups and avoid degradation such as Sommelet–Hauser rearrangement and Hofmann elimination. Vicinal quaternary ammonium groups also resist nucleophilic (OH^-) attack and suppress the Stevens rearrangement as well as $\text{S}_{\text{N}}2$ substitution reaction due to steric hindrance. Optimized AM (AMPE-M20N15 (55% DCM)) exhibits about 0.95 V open circuit voltage (OCV) and 48.8 mW cm^{-2} power density at 65°C in alkaline direct methanol fuel cell (ADMFC) operation. These results suggest promising begin for the preparation of stable and conductive AMs for ADMFC applications and useful for developing hydroxide conductive materials.

© 2014 Elsevier B.V. All rights reserved.

* Corresponding author. Electro-Membrane Processes Division, CSIR-Central Salt and Marine Chemicals Research Institute (CSIR-CSMCRI), G. B. Marg, Bhavnagar 364 002, Gujarat, India. Fax: +91 0278 2566970.

E-mail addresses: vkshahi@csmcri.org, vinodshahi1@yahoo.com (V.K. Shahi).

1. Introduction

Fuel cells are promising renewable energy sources for automotive, stationary and mobile applications because of their high efficiency and low pollution levels [1,2]. Proton exchange membrane fuel cells (PEMFCs) have attracted significant attention during the last few years but the obstacles like fuel crossover, conductivity loss

at elevated temperature, use of noble metal catalysts and their poisoning hampered their commercialization [2]. Alkaline direct methanol fuel cells (ADMFCs) have the potential to overcome the above problems due to good reaction kinetics, less fuel crossover (due to reverse electro-osmosis) in addition to avoid of noble metal catalysts results to high power output with low cost fuel cells [3–6]. To date, several types of AMs based on polystyrene [7], poly(phenylene oxide) [8], poly(ether-imide) [9], radiation-grafted fluorinated polymers [10,11], organic-inorganic hybrid composites [12–14], polybenzimidazole [15,16], or poly(arylene ether)s [17–23] have been reported. Although, these AMs displayed wide range of conductivity and suitability for ADMFC applications, the membrane stability in alkaline media at elevated temperatures is poor due to aforementioned possible degradation mechanisms of quaternary ammonium groups [18,24,25].

Researchers continued to explore alternatives to circumvent this obstacle by different way of quaternization techniques. Recently, Yan et al. [26] and Zhang et al. [21] synthesized AMs based on quaternary phosphonium and benzyl quaternary guanidinium respectively with high conductivity and good alkaline stability. Further, Hickner et al. [27] reported quaternized poly(2,6-dimethyl phenylene oxide) containing long alkyl side chain pendant to the central nitrogen based AMs in order to resist nucleophilic attack but there is a possibility of ammonium groups degradation via Hofmann elimination due to presence of β -hydrogen atom on quaternary ammonium group. However, the above reported AMs have only single cationic group and can carry only one anion. On the other hand, presence of four quaternary ammonium groups has the potential to increase the ion exchange capacity and hydroxide conductivity of the membranes. Watanabe and Miyatake et al. group reported AMs based on anion conductive poly(arylene ether)s [18] and successfully introduced four cationic groups by Fridel-Crafts chloromethylation reaction using CMME but the reagent was carcinogenic and potentially harmful to human health [28–31]. Recently, Hickner et al. [32] reported quaternary ammonium functionalized benzylmethyl containing poly(arylene ether ketone)s having six quaternary ammonium groups with Br^- as counter anion. But these AMs are quite sensitive in alkaline conditions and easily undergo Sommelet–Hauser rearrangement, Stevens rearrangement and $\text{S}_{\text{N}}2$ substitution reaction due to the presence of more ortho-hydrogen and α -H atoms which causes to functional group degradation. Thus, the development of highly stable and conducting AMs by a facile green method is still an interesting challenge [33,34].

We have reported a series of AMs with well-controlled composition and structure which shows high hydroxide ion conductivity, excellent alkaline stability for ADMFCs applications by introducing four cationic groups via pre-chloromethylation of bisphenol monomer in a facile green manner. The introduction of two vicinal quaternary ammonium groups in the membrane matrix is the key part of the reported method. This imparts the membrane alkaline stability and avoids the degradations such as Sommelet–Hauser rearrangement owing to the absence of ortho hydrogen adjacent to quaternary ammonium groups. Further, Hofmann elimination was also rule out due to absence of β -hydrogen atoms. Even though the developed AMs have more α -H atoms, Stevens rearrangement and $\text{S}_{\text{N}}2$ substitution reaction has been also suppressed due to the steric hindrance of vicinal quaternary ammonium groups. A detailed investigation on membrane properties such as water affinity, swelling ratio (%), hydroxide ion conductivity, mechanical, alkaline stability and long term durability, on membrane composition was carried out to assess the suitability of these AMs for ADMFC application.

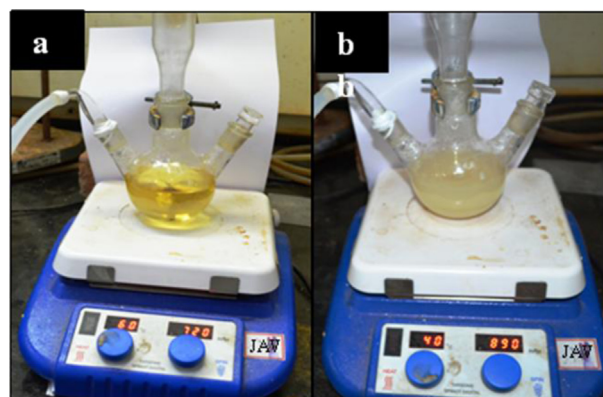
2. Experimental section

2.1. Materials and methods

4,4'-Difluorophenyl sulfone (FPS), 4,4'-difluorobenzophenone (DFBP), and bisphenol A (BPA) were obtained from Aldrich, and crystallized in toluene/ethanol. Formaldehyde, potassium carbonate, calcium carbonate, thionyl chloride, *N,N'*-dimethylacetamide, toluene, methanol, 1,1,2,2-tetrachloroethane (TCE) and trimethylamine aqueous solution (35wt %) were purchased from Spectrochem, India and used as received. Chloroform, sodium hydroxide, ethanol, and acetone were (AR grade; SD Fine Chemicals, India) used as received. Nitrogen and argon gases were purchased from Ultra-Pure Gases (I) PVT. LTD., India.

2.1.1. Synthesis of 2,2',3,3'-tetrakis(chloromethyl)bisphenol (TCMBP) monomer

A 300 mL round-bottomed flask was charged with bisphenol-A (40 mmol), K_2CO_3 (100 mmol) and water (200 mL) containing 37% formaldehyde (740 mmol) under constant stirring in an inert atmosphere at 60 °C for 4 h. CO_2 was bubbled through yellow coloured solution at 30 °C until it turned to cloudy (as shown in the photograph). The reaction mixture was extracted with ethyl acetate and dried in MgSO_4 followed by removal of solvent under reduced pressure. The obtained 2,2',3,3'-tetrakis(hydroxymethyl)bisphenol (THMBP) monomer was diluted with CHCl_3 followed by drop-wise addition of SOCl_2 (120 mmol) solution in CHCl_3 (100 mL) over 30 min. Above solution was stirred for 1 h and washed with saturated aqueous NaHCO_3 to remove excess of SOCl_2 . Now the organic layer was dried (MgSO_4) and solvent was removed under reduced pressure. 55% yield of 2,2',3,3'-tetrakis(chloromethyl)bisphenol (TCMBP) monomer was obtained. The structure of obtained monomers was confirmed by ^1H NMR spectra. (a) THMBP (40% yield): δ 4.76 (br, 4H), 4.93 (br, 4H), 1.70 (s, 6H), 7.17 (d, 2H), 7.24 (d, 2H) and (b) TCMBP(55% yield): δ 4.61 (s, 4H), 4.74 (s, 4H), 1.53 (s, 6H), 7.00 (d, 2H), 7.06 (d, 2H).



(a) Before and (b) after the gas purging

Here SOCl_2 is not an innocuous material; causes skin burning and eye damage. In contact with water it liberates toxic gas so it's necessary to avoid moisture in the reaction. This reagent can be handled easily with proper safety protocol.

2.1.2. Synthesis of aminated poly(arylene ether)s (AMPES) based alkaline membranes

AMs are synthesised by nucleophilic substitution-poly condensation of TCMBP, FPS and DFBP monomers. Detailed Synthesis of aminated poly(arylene ether)s (AMPES) based alkaline

Download English Version:

<https://daneshyari.com/en/article/1286594>

Download Persian Version:

<https://daneshyari.com/article/1286594>

[Daneshyari.com](https://daneshyari.com)