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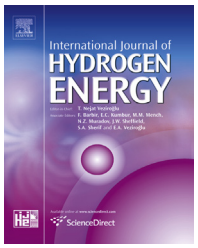

Study on tunable crosslinking anion exchange membranes fabrication and degradation mechanism

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ABSTRACT

A novel monomer who combined cross linker and functional groups together called 2,2'-(hexane-1,6-diyl)bis(2-methyl-2,3,3a,4,7,7a-hexahydro-1H-4,7-methanoisoindol-2-ium) iodide (HDHM-iodide) was synthesized and polymerized by Ring-opening Metathesis Polymerization (ROMP) to give a series of anion exchange membranes. The resulting monomers and polymers were characterized by ^{1}H and ^{13}C NMR, TGA. Directly cast from the polymerization solution on flat glass to form the clear, flexible anion exchange membrane. Swelling ratio and water uptake are only 6.2% and 28.04% at 60 °C for membrane with 2.32 mmol·g^{-1} ion exchange capacity (IEC). The conductivity of Poly (HDHM-Norbornene-hydroxide-12) and Poly(HDHM-Norbornene-chlorine-12) AEMs at room temperature up to 27 mS·cm^{-1} and 14 mS·cm^{-1} separately, and increased with temperature quickly. After 16 days immersed in 2 M NaOH solution, conductivity and IEC dropped at 60 °C in alkaline solution, 50% and 35% separately. The energy barrier of degradation pathways calculation reveled that Hofmann Elimination case 2 degradation pathway with the lowest energy barrier 12.181 kcal·mol^{-1} is most likely occurred when faced with hydroxide. Also, the energy barrier of Hofmann Elimination is lower than Nucleophilic Substitution degradation mechanism.

Introduction

With the development of society, energy shortage and environment pollution problems are becoming increasingly prominent. Fuel cells as a promising energy conversion device who can transform chemical energy to electricity and produce clean, no pollution product, have gained wide research and attention [1,2].

Membrane as the main part of fuel cell, not only stand as the separator of anode and cathode, also transport ions to keep

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the balance of cathode and anode. According to different kind of counterions, membrane were divided into proton exchange membranes (PEMs) and anion exchange membranes (AEMs) [3]. Nafion as the most famous and commercialized PEMs containing sulfonic acid as functional group, showed good mechanical properties, excellent chemical stability and quite high proton conductivity (80 $mS \cdot cm^{-1}$ 25 °C) [4,5]. However, Nafion is limited to acid working conditions and need thicker membrane to prevent uncontrollable membrane swelling and fuel cross over which would cause substantial performance losses [6]. Compared with proton exchange membrane fuel cells (PEMFCs), alkaline anion exchange membrane fuel cells (AEMFCs) can work under alkaline condition with much higher oxygen reduction kinetics [7,8], which can lead to use of non-precious metal as catalyst, and greatly reduce the cost of fuel cell device; Corrosion problems are less serious in alkaline than in acid environment [1,3,9]. Traditional alkaline fuel cells with aqueous solution of potassium hydroxide as electrolyte were greatly influenced by CO_2 from atmosphere, which can combine with hydroxide to produce bicarbonates salts and subsequently precipitated out of the solution. AEMFCs with hydroxide combined with quaternary ammonium cations and fixed in polymer backbones, which make it work in the presence of CO_2 without the precipitation problems [3,9].

While even with these strong points, AEMs were faced with alkaline stability and conductivity problems [3,9,10], both of them impede the wide usage of AEMFCs. Due to the existence of hydroxide counterions, quaternary ammonium cations follow two main degradation pathways: elimination [11] and nucleophilic substitution mechanism [12].

When a substituent in the β-position of the nitrogen atom bears at least one hydrogen atom, the alkalized quaternary ammonium group would be cleaved, called Hofmann Elimination [9,13,14], which lead to formation of an amine, an alkene and a water molecule.

The degradation of ammonium by a nucleophilic substitution corresponds to S_N2 reactions between an OH^- anion and a carbon atom in α-position of the ammonium group. Even though there would be different degradation pathways, the final products are alcohols and amine [9,15]. Different kind of polymer structure would result in different kind of degradation mechanism, and sometimes some of them would be combined to account for the real degradation process.

Bernd and coworkers [15] researched the degradation of benzyltrimethyl-ammonium cations under alkaline conditions. Due to the absence of β-H atoms, no elimination reaction can take place and four products were observed: benzyl alcohol, trimethylamine and benzyldimethylamine, methanol. Neagu and coworkers [16] studied the stability of pyridinium in aggressive media. At high pH the pyridinium group is chemically degraded by the hydroxyl ions. Komkova and coworkers [17] tested the stability of polyether sulfone membranes based on various aliphatic diamines used as a quaternized and cross-linked reagent. The membranes were exposed to 2 M NaOH solution at 40 °C and results showed that alkaline stability can be improved by changing the type and amount of diamines in the polymer. Even these membranes showed excellent electrochemical properties, the stability of the membrane in alkaline environment is not satisfied for fuel cells application. Get to know the most possible mechanism and find out the reason caused functional groups degradation under alkaline environment would help us design high alkaline stability AEMs for fuel cells application.

With properties of high reactivity, easy controllable and produce good mechanical property polymer Ring-Opening Metathesis Polymerization (ROMP) have been wildly researched [18–21]. With ROMP we can get functional polymers from quaternary ammonium functionalized monomers, whose conductivity and IEC can be improved by the number of functional groups in single monomer molecular, which is quite different from ways directly attach functional groups to polymer backbone [22–24]. Zha and coworkers [25] synthesized the first metal-cations based anion exchange membrane with ROMP. Anion conductivity and mechanical properties are comparable to traditional quaternary-ammonium-based AEMs as well as the alkaline stability. Clark and coworkers [26] copolymerized dicyclopentadiene (DCPD) and a tetraalkylammonium-functionalized norbornene with ROMP, this membrane exhibited conductivity at 18 $mS \cdot cm^{-1}$ that rose to 28 $mS \cdot cm^{-1}$ at 50 °C. Nicholas and coworkers [27] designed and synthesized a new cross-linked membrane material, conductivity of this membrane at room temperature (22 °C) as high as 68.7 $mS \cdot cm^{-1}$ and rose quickly with temperature increase. Even though these membranes showed excellent electrochemical and mechanical properties, the alkaline stability properties were not given. As the main consideration of AEMs apply for fuel cells, alkaline stability and degradation mechanism should be considered.

In this article, we have been developing a new structure called 2,2'-(hexane-1,6-diyl)bis(2-methyl-2,3,3a,4,7,7a-hexahydro-1H-4,7-methanoisoindol-2-ium) iodide (HDHM-iodide) derived from Cis-5-norbornene-endo-2,3-dicarboxylic anhydride. When norbornene derivatives were embedded with Grubbs catalyst [28,29], the high ring strain would be released and decrease entropy, then produced quaternary ammonium functionalized AEM directly [21].

Copolymerize HDHM-iodide and norbornene by ROMP with Grubbs 3rd generation as catalyst to build Poly(2,2'-(hexane-1,6-diyl)bis(2-methyl-2,3,3a,4,7,7a-hexahydro-1H-4,7-methanoisoindol-2-ium) iodide-norbornene) (Poly(HDHM-Norbornene)) AEMs. HDHM-iodide not only stand as cross linker, which can reduce the swelling of membrane and increase mechanical stability during fuel cells operation, also with two quaternary ammoniums as hydroxide transport sites. Three different ratio (1:2, 1:3 and 1:4) of HDHM-iodide and norbornene as monomer polymerized AEMs were synthesized. When the ratio of the two monomers smaller than 1:2, the polymer would be too brittle to make membrane. Also, the requirement of ion exchange capacity (IEC) make the ratio cannot be too high. The properties of the obtained membranes were evaluated in terms of ion exchange capacity (IEC), water uptake, swelling ratio, dimensional stability, ionic conductivity and alkaline stability. Li [30] and Wang [31] calculated the degradation mechanisms of guanidinium and imidazolium cations with density functional theory separately, and reveled the degradation mechanisms of cations under alkaline stability. After that, the energy barrier of different kind of degradation mechanism for Poly(HDHM-Norbornene) AEMs under alkaline environment were calculated by materials studio (MS) software with QMERA modules.