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Degradation of guanidinium-functionalized anion exchange membrane during alkaline environment

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ABSTRACT

A guanidinium-functionalized anion exchange membrane (AEM) was prepared and characterized. The AEM stability in an alkaline environment and transition structures during the degradation process were studied with DFT (density functional theory)/B3LYP method, 6-31 + G (d) basis set. Experimental results and theoretical analysis showed that the second step (Step 2') of degradation reaction was the control procedure; guanidinium cation was unstable under alkaline condition. It had lower energy barriers, which decided it was easier for the degradation reaction to occur in high pH environment. The ionic conductivity of AEM was $2.4 \times 10^{-2} \text{ S cm}^{-1}$ at 80 °C. However, the AEM soaked in 1 M NaOH solution, fragments were found after 10 days. The FTIR analysis showed that the structure of the membrane had been changed due to the attack of hydroxide ion. A new substance, tetramethylurea, had produced.

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Introduction

Compared with proton exchange membrane fuel cells, alkaline anion exchange membrane fuel cells with non-noble metal catalysts such as Co and Ni, and cheaper material are better performing due to the facile kinetics at the cathode as well as at the anode [1–3]. Anion exchange membranes (AEMs) can help to reduce the methanol crossover and simplify the water management system [4]. However, these membranes have several major defects such as low ionic conductivity and poor membrane stability [5–7]. In order to improve the anion conductivity and stability of AEMs, a lot of

improvements have conducted up to now. These methods include using more stable polymer main chain, adding ionic liquid [8], cross-linked composite [9,10], and radiation grafting [11,12] and so on. Kim prepared a phenyl guanidinium-functionalized polymer which exhibited highly efficient anion conductivity and promising stability in high pH conditions [13]. However, the membrane was immersed in 0.5 M NaOH solution at 80 °C after 380 h, the conductivity dropped rapidly. Zhang studied the stability of guanidinium grafted poly (aryl ether sulfone) in 2 M NaOH solution for 24 h. It was found that the conductivity of the membrane decreased from 0.024 to 0.021 S cm⁻¹ at 80 °C [14]. In the above researches, guanidinium is chosen as functional group. Guanidine has a

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Abbreviations

AEM	anion exchange membrane
DFT	density functional theory
TMU	tetramethylurea
FPAEO	fluorinated poly(aryl ether oxadiazole)s
TM-BPA	2, 2-bis (4-hydroxy-3, 5-dimethylphenyl) propane
FPOx	2, 5-bis(2,3,4,5,6-pentafluorophenyl)-1,3,4-oxadiazole
FPAEO-TM	fluorinated poly(aryl ether oxadiazole)s based on 2, 2-bis (4-hydroxy-3, 5-dimethylphenyl) propane
DMAC	dimethylacetamide
NBS	N-bromosuccinimide
BPO	benzoyl peroxide
FPAEO-G	guanidinium-functionalized fluorinated poly(aryl ether oxadiazole)s
FPAEO-xBrTM	bromide methylated poly (aryl ether oxadiazole)s
DMF	N,N-dimethylformamide
PMG	pentamethylguanidine
EIS	electrochemical impedance spectrum
FTIR	Fourier Transform Infrared Spectroscopy
TS	transition state
FPAEO-G-OH	the membrane after soaking
PMBG ⁺	1, 1, 2, 3, 3-pentamethyl-2-benzylguanidinium
PMPG ⁺	1, 1, 2, 3, 3-pentamethyl-2-phenylguanidinium
HMG ⁺	1, 1, 2, 2, 3, 3-hexamethylguanidinium
HOMO	highest occupied molecular orbital
LUMO	lowest unoccupied molecular orbital

high alkaline, which is conducive to improve the ionic conductivity of the AEMs [15]. In its molecular structure, the positive charge is uniformly distributed on the central carbon atom and three nitrogen atoms, resulting in having good thermal and mechanical stability [16]. In an alkaline solution, hydroxide ions attack the central carbon atom of the guanidinium to generate a cationic intermediate, and then further degradation reactions proceeds from this intermediate. The reaction would generate the end products-tetramethylurea (TMU) and a secondary amine. Guanidine decomposition reaction eventually led to the loss of ionic conductivity. Currently, a variety of guanidinium-functionalized AEMs have synthesized, but their research on stability theory and degradation mechanism in an alkaline environment is relatively small.

Pentamethylguanidine as a function of reagent is expected to obtain a high chemical stability and mechanical properties of the main chain, which is a fluorinated poly(aryl ether oxadiazole)s (FPAEO) anion exchange membrane. Because of the oxadiazole structure formed in FPAEO, the structure has a high electron-deficient group. This should help to improve the mechanical stability of the AEM. At the same time, the incorporation of fluorine atoms into polymer chains leads to the improved thermal stability and hydrophobic of polymers [17,18]. The FPAEO as a main chain prepared guanidinium-based AEM, imidazole-based AEM and quaternary

ammonium AEM have synthesized in our team. The AEMs not only can be used in alkaline fuel cells, but also can be applied to all vanadium redox flow battery. They showed good selectivity in vanadium redox flow battery. The vanadium ion permeability was of $2.1 \times 10^{-8} \text{ cm}^2 \text{ min}^{-1}$ [19–21].

In this study, a guanidinium-functionalized AEM prepared by polycondensation, brominated and guanidinylation based on the previous studies. The degradation mechanism of guanidinium cation under alkaline environment was investigated using density functional theory (DFT). The minimum energy change and the energy changes were calculated on the basis of experiment data. On the basis of the mechanism, the effects of alkaline solution concentration and different substituents on the degradation were respectively studied.

Material and methods

Materials

All the reagents used in this work such as 2, 3, 4, 5, 6-Pentafluoro benzoic acid, 2, 2-bis (4-hydroxy-3, 5-dimethylphenyl) propane (TM-BPA), tetramethylurea (TMU), and oxalylchloride were purchased from common commercial suppliers without further purification.

Preparation and membrane casting of poly(aryl ether oxadiazole)s containing pendant guanidinium (FPAEO-G)

Synthesis of 2,5-bis(2,3,4,5,6-pentafluorophenyl)-1,3,4-oxadiazole (FPOx) [22]

Pentafluorobenzoic acid (21.2 g, 0.1 mol) and hydrazine sulfate (8.6 g, 0.066 mol) were added into polyphosphoric acid (150 ml) in a round-bottom flask. The mixture was slowly heated to 150 °C under nitrogen atmosphere and maintained at this temperature until no more gas release was observed. The reaction solution was then cooled to 50 °C and poured into distilled water with stirring. The obtained white precipitate was washed with hot water until the filtrate was neutral. The crude product was dried and recrystallized to provide pure FPOx white crystal.

Synthesis of FPAEO based on TM-BPA (FPAEO-TM)

FPOx (2.43 g, 6.0 mmol), TM-BPA (1.70 g, 6.0 mmol) and K_2CO_3 (2.48 g, 18 mmol) were added to dimethylacetamide (DMAC, 30 ml) in a round-bottom flask. The mixture was stirred at 20 °C for several hours until the viscosity increased observably. Under stirring, the filtered solution was then dropped into deionized water to precipitate the copolymer, which was further washed with deionized water three times and dried to produce FPAEO-TM.

Bromination of FPAEO-TM (FPAEO-xBrTM)

The typical procedure for preparing FPAEO-4BrTM was described as follows: FPAEO-TM (3.34 g, 5 mmol) was dissolved in 1, 2-dichloroethane (80 ml) in a flask at magnetic stirring. N-bromosuccinimide (NBS, 3.56 g, 20 mmol) and benzoyl peroxide (BPO, 34.5 mg) were added to the solution. Then the solution was heated to reflux at 85 °C. After 5 h, the solution was cooled to room temperature and poured into 400 ml

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