



Study on the chemical stability of the anion exchange membrane of grafting dimethylaminoethyl methacrylate

Yu Wang, Jingyi Qiu, Jing Peng, Ling Xu, Jiuqiang Li, Maolin Zhai*

Beijing National Laboratory for Molecular Sciences, Department of Applied Chemistry and the Key Laboratory of Polymer Chemistry and Physics of the Ministry of Education, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, China

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ABSTRACT

A kind of anion exchange membrane (AEM) was prepared by radiation-induced grafting of dimethylaminoethyl methacrylate (DMAEMA) into ethylene-tetrafluoroethylene (ETFE) membrane and subsequent protonation. For the purpose of long cycle life of vanadium redox battery (VRB), the chemical stability of the resulting AEM was evaluated firstly in the vanadium (V) solution, which is used as the positive half cell electrolyte in VRB. It was found that the AEM had slight weight loss after soaking in 1.5 M vanadium (V) solution for 90 days and 0.1 M V(V) solution for 540 days. The increase of permeability of V(IV) ion after 540 days soaking in 0.1 M V(V) solution for the prepared AEM was 41% which was relatively lower than that of other commercial membranes. Further evaluation on the degradation mechanism of the resulting AEM was carried out in 3% H₂O₂ aqueous solution at 60 °C. Micro-FTIR, TGA and XPS analyses of the AEM before and after degradation in H₂O₂ aqueous solution confirmed the absence of –NH⁺(CH₃)₂ group in the degraded membrane. UV and ¹H NMR analyses of the degradation products proved that C–O bond of ester group in the poly(methacryloxyethyl dimethyl ammonium chloride) grafts of the AEM was vulnerable to be attacked by hydroxyl radicals in H₂O₂ aqueous solution.

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1. Introduction

In recent years, several studies have been performed on vanadium redox flow battery (VRB), which was first demonstrated by Skyllas-Kazacos et al. in 1984 [1–3]. Compared with other redox batteries [4], the VRB performs some advantages, such as higher energy efficiency, deeper discharge ability, longer operation life and lower cost. Especially, VRB system can be assembled for large-scale energy storage, which makes it potential applicable for voltage and frequency control, solar and wind energy storage and so on. Ion exchange membrane (IEM) is the key component of VRB, and it is used to prevent the crossover of vanadium ions of the positive and negative electrolytes and simultaneously allow the transport of ions to complete the current circuit. The ideal IEM should possess the following features: high ionic conductivity; low vanadium crossover; good chemical stability and low cost, etc.

For the purpose of high energy efficiency and long cycle life, the IEM designed for VRB should be stable over long periods of exposure to the vanadium electrolyte. However, the evaluation of some commercial membranes for VRB showed that most of them are unsuitable in view of their poor stability in the vanadium electrolyte [5]. Nonetheless, Nafion 112 (E.I. Du Pont, USA)

and AEM New Selemion (type 2) (Asahi Glass Co., Japan) showed relatively good stability in V(V) solution [5]. But the high cost of these membranes is still a limitation for practical application. Moreover, Nafion membrane suffered from the crossover of vanadium ions when assembled in VRB, which caused self-discharge and led to the decrease of energy efficiency of the VRB. Therefore, it is necessary to synthesize new IEMs that can possess good chemical stability, high performance and low cost for the VRB system. Recently, much research has been devoted to develop low-cost membranes for commercial use in VRB system [6–10]. Skyllas-Kazacos et al. [11] reported that V-fuel carried out a large screening programme and several new low-cost membranes were identified as potential candidates. Among them, VF11 membrane with a cost of less than one-third that of Nafion 112 showed excellent performance for use in most large-scale energy storage application.

Modification of low-cost membranes to prepare IEMs by grafting techniques is a kind of effective method to bring about cost reduction and has attracted much attention. Some researchers have studied the chemical stability of the prepared IEMs. For example, it was reported that a kind of cation exchange membrane (CEM) with aromatic sulfonic acid showed poor chemical stability and was found suffered decomposition after 48 h when it was tested in a 3% H₂O₂ solution at 50 °C [12]. This is because the tertiary hydrogen at the α-carbon of poly(styrene) branches was vulnerable to radical attack. Furthermore, some CEMs suffered from serious

* Corresponding author. Tel.: +86 10 62753794; fax: +86 10 62753794.
E-mail address: mlzhai@pku.edu.cn (M. Zhai).

crossover of vanadium ions through membranes when employed in a VRB [7,13]. On the contrary, anion exchange membranes (AEMs) could effectively suppress the crossover of vanadium ions due to the coulomb repulsion between the cation groups of AEMs and vanadium ions [14,15]. In our previous work, a kind of AEM poly(methacryloxyethyl dimethyl ammonium chloride) (PMAOEDMAC) has been prepared by radiation grafting of DMAEMA onto ethylene-tetrafluoroethylene (ETFE) membrane and subsequent protonation, and the performance of ETFE-g-PMAOEDMAC AEM in VRB has been investigated [15]. Comparing with Nafion 117 membrane, the prepared AEM with ca. 40% grafting yield (GY) possessed significantly lower permeability (P) of vanadium ions with different valences and P through the AEM is about 1/20 to 1/40 of that through Nafion 117 membrane. Moreover, our group further synthesized a kind of amphoteric ion exchange membrane (AIEM) ETFE-g-PSSA-co-PMAOEDMAC membrane containing DMAEMA grafting chains and the charge-discharge test was performed [16,17]. The results showed that the energy efficiency of VRB assembled with the prepared AIEM (75.1%) was higher than that with Nafion 117 membrane (72.6%). Furthermore, after 40 cell cycles testing of VRB fabricated by the AIEM, no efficiency decline was observed, which indicated that the AIEM containing DMAEMA component exhibited good stability in VRB. As a result, this kind of AIEM containing DMAEMA component will be an appropriate candidate membrane for the VRB. For the purpose of long cycle life of VRB and the optimization of the structure of the ion exchange membrane, the chemical stability of ETFE-g-PMAOEDMAC AEM and ETFE-g-PSSA-co-PMAOEDMAC AIEM should be studied thoroughly. However, up to now the investigation about the chemical stability of the AEM and AIEM has not been reported.

In this work, the chemical stability of ETFE-g-PMAOEDMAC AEM was evaluated firstly in V(V) solution which is fully charged of positive half-cell electrolyte in VRB. Considering the complexity of vanadium electrolyte, H_2O_2 aqueous solution was employed further to study the degradation mechanism of the AEM. By comparing ion exchange capacity (IEC), Micro-FTIR and XPS changes before and after the degradation process, as well as analysis of UV and 1H NMR of degradation solutions, the possible degradation mechanism was proposed. It was expected that the results would be helpful to design and optimize the IEM for the application in VRB.

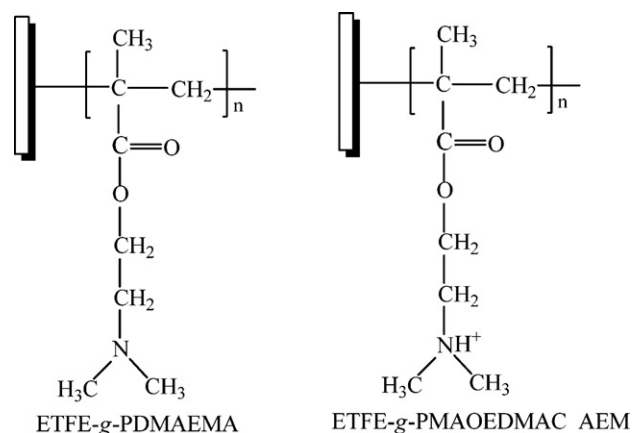
2. Experimental

2.1. Materials

ETFE membrane with a thickness of 50 μm was provided by Asahi Glass Co. (Japan). DMAEMA (99% purity) was purchased from Acros and was used without further purification. Acetone (analytical reagent) was supplied by Beijing Chemical Reagents Company. Hydrogen peroxide (30%) was purchased from Beijing Chemical Works. N,N-dimethylethanolamine was supplied by Sinopharm Chemical Reagent Beijing Co., Ltd. Deuterated chloroform was purchased from Cambridge Isotope Laboratories, Inc. $VOSO_4 \cdot 5H_2O$ (analytical reagent) was supplied by Shanghai LvYuan Fine Chemical Plant.

2.2. Preparation of the AEM

ETFE membrane was washed with acetone to remove the impurity on its surface before use. ETFE-g-PDMAEMA membrane with the grafting yield of ca. 40% and ETFE-g-PMAOEDMAC AEM (Scheme 1) were prepared according to the methods in our previous work [15]. The dose was 30 kGy at a dose rate of 30 Gy min^{-1} .



Scheme 1. The structure of ETFE-g-PDMAEMA membrane and ETFE-g-PMAOEDMAC AEM.

2.3. Chemical stability tests of the AEM

The chemical stability of the AEM was evaluated in 1.5 M and 0.1 M V(V) solution according to the methods reported by Mohammadi and Sukkar [5,18]. In our previous work, when VRB was assembled for charge-discharge test, 1.5 M V(II)/V(III) and V(IV)/V(V) in 2.5 M H_2SO_4 solution were used as the electrolytes in the positive and negative half cells, respectively [16]. In addition, it has been reported that the dilute 0.1 M V(V) electrolyte is able to enter the pores of the membranes easily and causes accelerated deterioration of the membranes [18]. Consequently, the chemical stability test of the AEM was performed in 1.5 M and 0.1 M V(V) solution. 1.5 M V(V) in 2.5 M H_2SO_4 solution was prepared by electrochemical oxidation of $VOSO_4$ in VRB system, and 0.1 M V(V) solution was prepared by dilution of 1.5 M V(V) solution with deionized water. The AEM was immersed into the V(V) solution and intermittently taken out of the solution. The weight and properties of the AEM before and after soaking in V(V) solution were determined. Weight change of the membrane was measured after wiping off the excess solution on the surface.

To study the degradation mechanism of the AEM, the membrane was immersed in a 3% H_2O_2 aqueous solution, which has been used to evaluate the chemical stability of the IEMs and kept at 60 °C for different time [12,19]. The change of weight and IEC of the AEM was investigated. The analysis of the AEM before and after degradation and the degradation products was studied.

2.4. Properties of the AEM

The ion exchange capacity (IEC) of the AEM was determined by acid-base titration. The AEM in 0.1 M V(V) solution and the H_2O_2 solution was periodically taken out, respectively, and dried to constant weight in vacuum after wiping off the excess surface water. Then the membrane with certain weight was immersed in 0.05 $mol L^{-1}$ HCl solution overnight at room temperature while occasionally stirred. Then the solution was back titrated with 0.05 $mol L^{-1}$ NaOH using an automatic titrator (Xianqu Weifeng ZDJ-2D) until titration endpoint was reached. According to the titration results, the IEC ($mmol g^{-1}$) was calculated as follows:

$$IEC = \frac{M_{0, HCl} - M_{E, HCl}}{W} \quad (1)$$

where $M_{0, HCl}$ and $M_{E, HCl}$ are moles of HCl before and after titration with NaOH, respectively, and W is the weight of the membrane.

The permeability of vanadium ions through the AEM was investigated according to the method prescribed by Llewellyn et al. [20]. The AEM was exposed to a solution of 1 M $VOSO_4$ in 2 M H_2SO_4 on

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