



Covalently incorporating a cationic charged layer onto Nafion membrane by radiation-induced graft copolymerization to reduce vanadium ion crossover

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ABSTRACT

Nafion membrane has been covalently functionalized with a cationic charged layer synthesized by radiation-induced graft copolymerization of *N,N*-dimethylaminoethylmethacrylate (DMAEMA) into Nafion substrate and subsequent protonation to reduce vanadium ion crossover for the application in vanadium redox flow battery (VRFB). The chemical composition and structure of the modified Nafion were characterized by microscopic Fourier transform infrared spectroscopy and thermogravimetric analysis. The grafting behavior was monitored by changing the experimental parameters including dose, dose rate and monomer concentration. The growth of cationic charged layer was studied by surface composition analysis of the membranes using X-ray photoelectron spectroscopy and atomic force microscope. The conductivity and permeability of vanadium ions of the obtained membranes with varying grafting yields were also measured. The functionalized Nafion membrane with a barrier layers displayed substantial resistance to permeability of vanadium ions accompanied by a relatively lower conductivity in comparison to that of the pristine Nafion membrane. The selectivity of the protonated Nafion-*g*-PDMAEMA membranes was higher than that of Nafion membrane, indicating the strategy is suitable for modifying Nafion membrane aiming at VRFB system. This work paves the way for the development of a new class of Nafion-based membranes for the application of VRFB.

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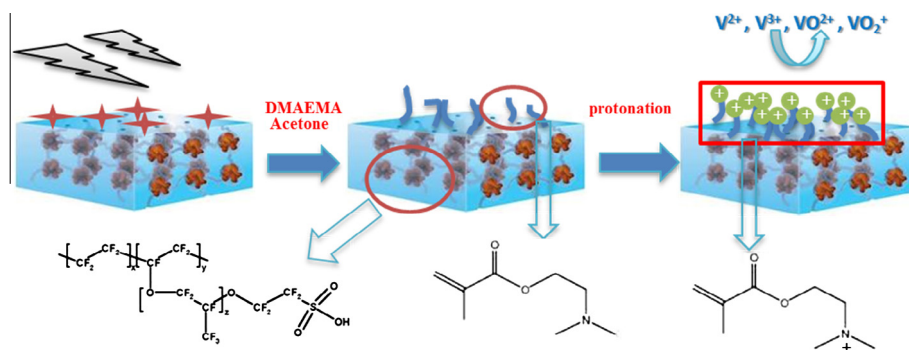
1. Introduction

Perfluorosulfonic acid membrane (i.e. Nafion[®]) to date has remained the most widely used commercial membrane for vanadium redox flow battery (VRFB) [1,2]. Its unique structure provides inherent high conductivity and excellent chemical stability which are as yet hard to repli-

cate in a material more suitable for VRFB applications [3]. However, Nafion membrane suffers from undesired transport of vanadium ions with different oxidation states across the membrane during the charge–discharge processes of VRFB, which results in electrochemical energy loss and energy efficiency reduction of the battery [4,5]. Hence improvements in the selective permeability characteristic of the membrane, facilitating the passage of water molecules and protons but restricting the permeability of vanadium ions, can produce significant gain in terms of device performance. Many efforts have been dedicated to modifying Nafion membrane through various methods to reduce the permeation of multivalent vanadium ions

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Scheme 1. Preparation route of Nafion-g-PDMAEMA and protonated Nafion-g-PDMAEMA.

through the membrane and improving the performance of VRFB [6]. These methods include surface modification with layer-by-layer self-assembly polyelectrolyte [7,8], in situ sol-gel reaction to incorporate inorganic oxide nanoparticles within the pores of Nafion [9,10], blending Nafion with other polymers [11,12], modification of Nafion through electrodeposition [13] and so on. These incorporated functional materials, such as inorganic oxide nanoparticles and polyelectrolyte, are combined with Nafion through intermolecular interactions such as van der Waals, hydrogen bonding or coulomb interactions, and these types of membranes can be classified as Nafion-based composite membranes. Unfortunately, to date, few methods have been developed to modify Nafion by incorporating functional polymer into the backbone through covalent linking at molecular level for VRFB application. Luo et al. [14] incorporated a cationic charged layer on the surface of Nafion117 by interfacial polymerization through the “grafting-to” reaction between polyethylenimine and chlorosulfonyl ($-\text{SO}_2\text{Cl}$) groups which were introduced as reactive groups onto the surface of Nafion membrane in advance. This process drastically reduced the permeation of vanadium ions across the membrane but the overall energy efficiency did not change significantly compared with that of Nafion because of a higher area resistance mainly caused by the transition of sulfonic acid groups.

Graft copolymerization is a process in which side chain grafts are covalently attached to a main chain of a polymer backbone to form branched polymer [15–18]. Previously, we provided a kind of amphoteric ion exchange membrane (AIEM) prepared by radiation grafting of styrene (St) and dimethylaminoethyl methacrylate (DMAEMA) into fluorinated film including poly(vinylidene fluoride) (PVDF) and poly(ethylene-co-tetrafluoroethylene) (ETFE), and subsequent sulfonation and protonation [19–21]. This approach relies on incorporating the unit of DMAEMA to prevent vanadium ion crossover due to the Donnan exclusion effect between $-\text{R}_3\text{NH}^+$ groups of protonated DMAEMA unit and vanadium ions, and the unit of St to transport the proton after subsequent sulfonation. It showed that the obtained AIEM exhibited higher conductivity, lower permeability of vanadium ions, as well as higher coulombic efficiency and energy efficiency than those of Nafion117 membrane when assembled and tested in VRFB system. For the purpose of long cycle life

of VRFB, the chemical stability of the ETFE-g-PDMAEMA was also evaluated in the vanadium (V) solution, which is used as the positive half cell electrolyte in VRFB [22]. It was found that the ETFE-g-PDMAEMA 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 ETFE-g-PDMAEMA was 41%, which was relatively lower than that of other commercial membranes. However, this process still has several obvious shortcomings in promoting the large-scale commercialization, for example, the complex production process, the structural influence of DMAEMA unit in AIEM during sulfonation reaction, and chemical instability of grafted polystyrenesulfonic acid group which degrades when attacked by oxidizing substances in running VRFB.

The object of this work is to provide a facile strategy to covalently modify Nafion membrane by radiation-induced graft copolymerization of DMAEMA into Nafion using γ -rays and subsequent protonation to reduce the permeability of vanadium ions for VRFB application. The preparation route is presented in Scheme 1. The grafting behavior was monitored by changing the reaction parameters, such as dose, monomer concentration and dose rate. The structure of modified Nafion membrane was characterized by microscopic Fourier transform infrared spectroscopy (Micro-FTIR), thermogravimetric (TG), X-ray photoelectron spectroscopy (XPS) and atomic force microscope (AFM) analysis. Moreover, the properties including conductivity and permeability of vanadium ions of the Nafion-g-DMAEMA were systematically investigated. It is expected that this work presents a new method for modification of Nafion membrane with improved properties.

2. Experimental

2.1. Materials

Nafion117 with thickness of 175 μm was purchased from DuPont. DMAEMA purchased from Acros with purity of more than 99% was used without further purification. Acetone (analytical reagent) was chosen as the reaction solvent. $\text{VOSO}_4 \cdot 5\text{H}_2\text{O}$ (analytical reagent) was supplied by Shanghai LvYuan Fine Chemical Plant.

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