Journal of Membrane Science 488 (2015) 194–202

Contents lists available at ScienceDirect

Journal of Membrane Science

journal homepage: www.elsevier.com/locate/memsci

Application and degradation mechanism of polyoxadiazole based membrane for vanadium flow batteries

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ARTICLE INFO

Article history:
Received 29 March 2015
Received in revised form
10 April 2015
Accepted 13 April 2015
Available online 30 April 2015

Keywords:
Polyoxadiazole
Vanadium flow battery
Degradation mechanism
Membrane

ABSTRACT

A new type of membrane composed of poly (4,4′-diphenylether-1,3,4-oxadiazole) (POD) was prepared and first investigated in a vanadium flow battery (VFB). In contrast to traditional hydrocarbon ion exchange membranes, the proton transport of POD was driven by the interaction between the acid in the electrolytes and the heterocyclic atoms in the POD backbone. A VFB single cell assembled with a POD membrane exhibits higher columbic efficiency (96.87%) and energy efficiency (83.29%) than does a Nafion 115 membrane (CE 94.6%, EE 82.1%) under the same operating conditions. However, the cell performance of the assembled POD membrane suddenly drops after continuously running for 60 cycles. The degradation mechanism of POD under strongly acidic and oxidized medium was investigated by UV–vis spectrometry, nuclear magnetic resonance (NMR) and attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR). The chemical structure of the degradation product was clarified, and the degradation mechanism was proposed, indicating that the oxadiazole ring in POD membrane becomes a strong electrophilic center due to the protonated ethereal oxygen atom and highly electronegative nitrogen atoms under strong acidic conditions. Next, the electrophilic center was attacked by the lone electron pair of the vanadium oxygen species. This work will provide valuable information to further improve the stability of polyoxadiazole under VFB conditions.

1. Introduction

There is an urgent need for large-scale energy storage systems to stabilize the fluctuations of electricity generated by renewable energy sources, such as solar and wind power. A vanadium flow battery (VFB) is one of the most suitable candidates for large-scale energy storage due to its attractive features, such as flexible design, long cycle life, high efficiency and high safety [1,2]. A VFB normally consists of two electrolyte tanks filled with the electrolytes of V(II)/V(III) and V(IV)/V(V) in sulfuric acid solutions, pumps and a battery stack. As a key component of a VFB, the function of the membrane is to prevent cross mixing of the positive and negative electrolytes, while still allowing the transport of ions to complete the circuit during the passage of current [3–13]. The membrane of a VFB should exhibit low vanadium ion permeability, high ionic conductivity, good chemical stability and low cost. Currently, the membranes used in VFBs are composed of perfluorosulfonic acid polymers (e.g., Dupont Nafion [14,15]). However, in addition to their poor ion selectivity, these membranes are also highly expensive [16]. Therefore, considerable effort has been made to develop new chemically stable ion exchange membranes because a high quality and cost-effective membrane is vital to achieve VFB commercialization. Several types of hydrocarbon membranes have already been investigated for VFB applications, such as sulfonated or quaternary ammoniated aromatic polymers [17–22]. Although these membranes showed very high selectivity on the vanadium ions, their oxidation stability still needs to be further improved [4]. Although the degradation mechanism of these types of membranes is not very clear [23], the ion exchange groups exert great influence on their chemical stability. Fujimoto et al. investigated the oxidation stability of sulfonated Diels Alder poly (phenylene) (SDAPP) with different ion exchange capacities (IECs), showing that the oxidation stability decreased with increasing content of ion exchange groups [24]. Hickner et al. proposed a degradation mechanism for sulfonated poly (sulfone) (S-Radel) using VFB medium. These researchers hypothesized that the vanadium (V) oxygen species first attack the S-Radel by incorporating hydroxyl groups into the polymer backbone and later oxidize the groups into quinine [23]. Zhai et al. evaluated the chemical stability of a dimethylamino ethylmethacrylate (DMAEMA)

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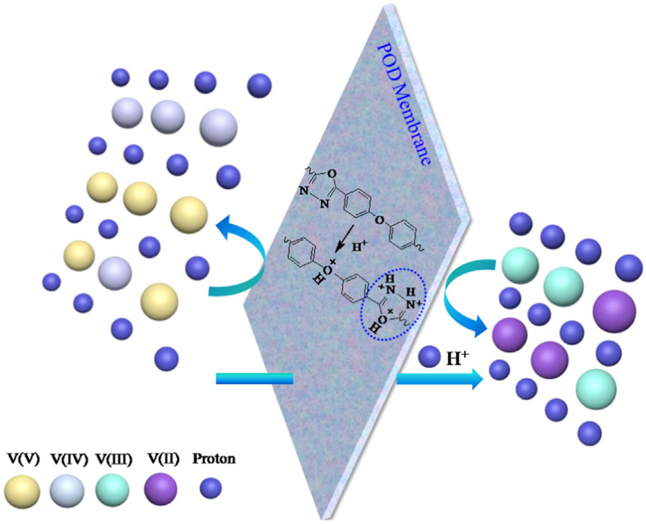
http://dx.doi.org/10.1016/j.memsci.2015.04.019
0376-7388/

grafted ethylene-tetrafluoroethylene (ETFE) membrane by immersing the polymer in 3% H_2O_2 aqueous solutions at 60 °C, demonstrating that the C–O bond can be attacked by hydroxyl radicals in H_2O_2 aqueous solution [25].

As one type of aromatic polymers, polyoxadiazoles (PODs) have received wide attention due to their outstanding mechanical, thermal, chemical and electrical properties [26]. Their usages in membrane fields have been reported earlier for gas separations [27]. Recently, some new applications have also been promoted in connection with the presence of basic heterocyclic rings. This basicity in a conjugated structure enables the use of polyoxadiazoles as well as other polymers, such as poly(benzoxazole) and poly(pyridine), for high temperature fuel cells [28–30].

As acid sensors, PODs are widely applied to polymer electrolyte fuel cells, due to their ability to transport protons or OH^- under acidic or basic medium [31]. Mai et al. was the first to report on a solid electrolyte membrane based on alkali-doped poly (4,4′-diphenylether-1,3,4-oxadiazole) and its application in direct borohydride fuel cells, exhibiting both high chemical stability and ion conductivity [32]. Nunes et al. performed much work on these types of polymers, such as benzimidazole sulfonic acid doped sulfonated poly (oxadiazole–triazole) copolymer, sulfonated polyoxadiazoles, polyoxadiazolena nanocomposites and fluorinated polyoxadiazole (e.g.) and investigated their applications in fuel cells [29,30,33,34]. They found that the benzimidazole sulfonic acid doped sulfonated poly (oxadiazole–triazole) membranes showed very high proton conductivities (up to 4×10^{-3} S cm^{-1}) at high temperature (120 °C) and low relative humidity (5 and 10%) [33]. Specifically, Nunes et al. reported a type of fluorinated polyoxadiazole membrane doped with phosphoric acid for the application of high temperature fuel cells, showing remarkable chemical stability [34]. In fuel cells application, the oxygen and nitrogen in the POD ring could be easily protonated under acidic medium conditions, thus providing the membrane with ion conductivity. Considering the strong acidic environment of VFBs, POD could be very promising for their applications in VFBs due to the interaction between the acid and the nitrogen groups. Different from traditional anion exchange membranes, the cation exchange functional groups in POD are bound directly on the backbone, which could prove beneficial for improving their chemical stability. However, the repulsion between the positively charged basic heterocyclic groups and the vanadium ions will be beneficial for the improving ion selectivity of the membrane (Scheme 1).



Scheme 1. Schematic of the POD membrane utilized in a VFB.

In this work, POD membranes were first proposed and reported for VFB applications due to their good mechanical and chemical stability. The membranes' performance, as well as their degradation mechanism, in VFBs were studied in detail.

2. Experimental section

2.1. Materials

4,4′-diphenyl–etherdicarboxylic acid (DPE) was obtained from TCI Shanghai. Hydrazine sulfate (HS) and poly(phosphoric acid) (PPA) were purchased from Aldrich. V(V) electrolyte consisting of 1.5 M VO_2^+ + 3.0 M H_2SO_4 was prepared by electron-oxidation of 1.5 M VO^{2+} in 3.0 M H_2SO_4 and the 0.15 M VO_2^+ in 3.0 M total sulfate solution was prepared by diluting the 1.5 M VO_2^+ in 3.0 M total sulfate solution with sulfuric acid according to the literature [35]. All of the other reagents were used as received.

2.2. Polymer synthesis

The POD was prepared according the procedure as reported previously, where the POD can be obtained by the polymerization of a dicarboxylic acid and a salt of hydrazine in solution or by the solid state cyclodehydration of polyhydrazides [26]. In this paper, the direct polymerization of 4,4′-diphenyl-etherdicarboxylic acid (DPE) and hydrazine sulfate (HS) in solutions of poly(phosphoric acid) (PPA) was selected to synthesize POD. The polymerization was performed in a 250 mL three-necked flask equipped with a mechanical stirrer. Dry nitrogen was continuously fed into the flask to keep the reaction atmosphere free of oxygen and water. Initially, 42.6213 g PPA was added to the flask and heated up to 100 °C, and then 1.5621 g HS was added to the flask under vigorous stirring. Afterwards, the mixture was heated to 160 °C, and then 3.1734 g DPE was added to the flask. After 3 h, the reaction mixture was quenched by adding a 5% NaOH solution. The polymer was thoroughly rinsed with water, filtered and dried. The molar dilution rate (PPA/HS) and the molar monomer rate (HS/DPE) were kept at 1.0 and 1.2, respectively.

2.3. Membrane preparation

The POD membrane was prepared by the solution cast method. The POD polymer was dissolved in N-methyl-2-pyrrolidone (NMP) to form a 3 wt% solution. The solution was cast onto a glass plate and dried at 50 °C for 48 h. The membrane was peeled off from the substrate and then immersed in deionized water. The thickness of membranes was measured by using a spiral-micrometer, whereas each result was the average value of at least three parallel experiments.

2.4. Membrane characterization

2.4.1. TGA measurement

TGA measurements were conducted on a PerkinElmer Pyris Diamond TG/DTA instrument, at a heating rate of 10 °C min^{-1} under nitrogen flow.

2.4.2. ATR-FTIR

The ATR-FTIR, measured by a JASCO FTIR 4100 spectrometer, was used to determine the chemical structure of the membrane. Each spectrum was recorded at the average rate of 48 scans with a resolution of 4 cm^{-1} collected from 600 to 4000 cm^{-1} in reflection mode.