

# Synthesis and properties of chemically cross-linked poly(vinyl alcohol)–poly (acrylamide-co-diallyldimethylammonium chloride) (PVA–PAADDA) for anion-exchange membranes

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## ABSTRACT

Alkaline anion-exchange membranes were prepared from poly(vinyl alcohol) and poly(acrylamide-co-diallyldimethylammonium chloride) by blending, then chemical cross-linking using glutaraldehyde as the cross-linking agent (PVA–PAADDA–GA). Membranes were characterized by Fourier-transform infrared (FT-IR) spectroscopy, thermogravimetric analysis (TGA) and scanning electron microscopy (SEM). OH<sup>−</sup> conductivities in the range of  $7.7 \times 10^{-4}$ – $3.03 \times 10^{-3}$  S cm<sup>−1</sup> were obtained for PVA–PAADDA–GA membranes at room temperature ( $23 \pm 2$  °C) along with the IEC values changed from 0.91 to 1.63 mequiv g<sup>−1</sup>. The temperature dependences of OH<sup>−</sup> conductivities followed the Arrhenius relationship at a temperature range from 20 to 90 °C. The apparent activation energy for OH<sup>−</sup> conduction was in the range of 15–19 kJ mol<sup>−1</sup> depending on PAADDA content in the polymer. High alkaline stability of PVA–PAADDA–GA membranes was retained after conditioning in 6.0 M KOH at 80 °C for 24 h. Also, the membranes showed excellent dimensional stability in both hot water and hot methanol solutions at 90 °C. Although a relatively high water uptake (more than 2-fold of Nafion 115), the PVA–PAADDA–GA membranes showed excellent methanol resistance with the methanol permeability ranged from  $2.85$  to  $4.16 \times 10^{-7}$  cm<sup>2</sup> s<sup>−1</sup>, which were 5–6 times lower than that of the Nafion 115.

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## 1. Introduction

Polymer electrolyte fuel cells (PEFCs) have been considered to be promising for powering stationary and residential applications [1]. Among which most efforts have been devoted to the development of proton exchange membrane fuel cells using acidic electrolytes based on sulfonated polymers, i.e., Nafion® (developed by DuPont). However, it has become clear that the commercialization of these fuel cells is hindered by the high cost and low durability of important components, such as the polyelectrolytes, the noble metal electrocatalysts and the graphite bipolar plates [2]. The downsides can be improved by switching from an acidic medium to a basic one [3], that is, using anion-exchange membranes (AEMs) for alkaline fuel cells. In a basic environment, the catalyst activity toward oxygen reduction reaction is much higher, leading to reduced Pt loading and extended choices for suitable Pt alternatives [4]. Furthermore, the alcohol 'crossover' problem can be effectively reduced due to the hydroxide ion transport from cathode to anode, thus offering the fuel flexibility [5].

To date, much effort has been undertaken to develop various types of AEMs based on quaternized polymers such as polysiloxane [6], poly(oxyethylene) methacrylates [7], polysulfone [8], polyethersulfone cardo [9], poly(phthalazinone ether sulfone ketone) [10], poly(ether-imide) [11] and radiation-grafted PVDF and FEP [12].

One of the most significant problems for AEMs is the stability of quaternary ammonium groups, which are likely to decompose in concentrated alkali solutions, especially at elevated temperatures (above 60 °C) via either an E2 Hofmann elimination or by an SN2 substitution reaction [13–16]. Another challenge is to find the high soluble quaternary ammonium hydroxide containing polymers in low-boiling-point solvents such as water and ethanol because these solvents are easy and safe to handle and remove during the membranes preparation [17]. But as of now, very few AEMs reported could fulfill all the aforementioned requirements and the development of AEMs with desirable properties is still a key issue [18–20].

In this article, new type of alkaline anion-exchange membranes based on glutaraldehyde cross-linked poly(vinyl alcohol) and poly(acrylamide-co-diallyldimethylammonium chloride) composite (PVA–PAADDA–GA) is proposed aiming at the cost-effective, easier preparation and alkaline stability. PVA is a polyhydroxy polymer that is very commonly used in practical applications because of its

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easy preparation and biodegradability [21]. Also, PVA has film-forming capacity, hydrophilic properties, and a high density of reactive chemical functions that are favorable for cross-linking by irradiation, chemical, or thermal treatments [22]. Furthermore, it shows superior methanol barriers to Nafion®[23]. PAADDA, a water soluble quaternized copolymer, can offer anions as charge carriers conducting hydroxide ( $\text{OH}^-$ ). The membranes were prepared by a blending technique, followed by chemical cross-linking modifications using GA as a cross-linking agent, so that the highly water-soluble property of PVA and PAADDA is effectively improved. PVA–PAADDA–GA membranes are thus designed to possess all the required properties of an anion-exchange membrane including moderate swelling, good mechanical strength and flexibility along with the good ionic conductivity due to “trapped” PAADDA chains in the PVA network. The membrane properties are characterized based on such points of view as AC impedance technique, FT-IR spectra, SEM images, TG profiles, water uptake, the ion-exchange capacity (IEC) and the methanol permeability. The dimensional stability of the membranes is also evaluated both in water and methanol in a temperature range from 25 to 90 °C.

## 2. Experimental

### 2.1. Materials and membrane preparation

The membrane was prepared by a simple solution-casting method. A stock PVA (99% hydrolyzed, average molecular weight  $M_w = 86,000$ – $89,000$ , Aldrich) aqueous solution was prepared by dissolving PVA (50 g) in deionized water (500 ml) and then heating at 90 °C with continuous stirring until a transparent solution was obtained. Appropriate amounts of PAADDA (10% water solution, average  $M_w = 423 \text{ g mol}^{-1}$ , Aldrich) was then mixed with the aforementioned PVA solution in selected blend ratios, followed by addition of GA (25 wt.% glutaraldehyde solution in water, SCRC) in acetone to react at 30 °C for 20 min. Cross-linking proceeded between the  $-\text{OH}$  of PVA and the  $-\text{CHO}$  of GA in the polymer due to an acid-catalyzed reaction upon addition of a small amount of HCl to the solution. The resulting solution was poured into plastic petri dishes, and the water was evaporated under ambient conditions. When visually dry, the chemically cross-linked membranes were peeled from the plastic substrate with the thickness of about 80–100  $\mu\text{m}$ . The membranes obtained are thus designated as PVA- $x$ -GA, where  $x$  indicates the mass content of PAADDA and ranged from 0.25 to 1.0. On this condition, the content of PVA is 1, and the content of GA is 0.3 by mass, respectively. The chemical structure of PVA and PAADDA used in this work is shown in Fig. 1.

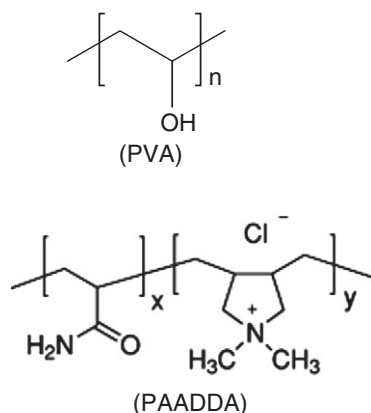


Fig. 1. Chemical structure of PVA and PAADDA used for preparation of PVA–PAADDA–GA membrane.

Before the use, the membranes were treated by immersing in 1.0 M KOH solution for 24 h to convert it from  $\text{Cl}^-$  form into  $\text{OH}^-$  form, then washed with D.I. water until pH neutral and finally stored in D.I. water for another 24 h for measurements. It should be mentioned that considering the difficulty in characterizing membranes definitively in  $\text{OH}^-$  form, for example, by excluding  $\text{CO}_2$  rigorously as in a glove box, the anion conductivities reported here are all based on the membranes in bicarbonate form (ie., exposure to air) without further correction.

### 2.2. Characterization of PVA–PAADDA–GA membranes

The FT-IR spectra of PVA–PAADDA–GA membranes were recorded using Shimadzu-4200 FT-IR spectrometer with a wavenumber resolution of  $4 \text{ cm}^{-1}$  in the range  $500$ – $4000 \text{ cm}^{-1}$ . Samples in the form of thin films were sandwiched between two KBr plates and placed in the cell to be measured. Air was employed as a background reference.

The composite morphology was evaluated using an FEI Sirion 200 field-emission scanning electron microscope (SEM) operating at 5 kV. Prior to observations, the membrane samples were fractured in liquid nitrogen and sputtered with gold, then examined at  $5000\times$  magnification.

### 2.3. Thermal analysis

Thermogravimetric analysis (TGA) of the membrane was performed using a STA449C apparatus (NETZSCH). Samples of about 10 mg were loaded into an alumina pan, and then heated from 25 to 600 °C at a rate of  $10 \text{ }^\circ\text{C min}^{-1}$ . All measurements were conducted under nitrogen. The vacant alumina pan was used as a reference throughout the whole experiment.

### 2.4. Swelling behavior and ion-exchange capacity

The swelling behavior of the membranes was evaluated by both the water uptake (WU) and the methanol (99.8 wt.%) uptake (MU) from the mass change before and after complete dryness of the membrane. A dry membrane was swollen in D.I. water for 24 h, then the surface water was carefully wiped with a filter paper, and it was immediately weighed. After drying the sample overnight at 60 °C, the water uptake was calculated using the expression:

$$\text{WU} = (W_{\text{wet}} - W_{\text{dry}}) / W_{\text{dry}}$$

where  $W_{\text{wet}}$  and  $W_{\text{dry}}$  are the masses of the fully hydrated membrane and of the dry membrane, respectively. The methanol uptake was measured by the same procedures.

The ion exchange capacity ( $\text{IEC}_{\text{OH}^-}$ , mequiv  $\text{g}^{-1}$ ) of the membranes was determined using the classical titration method. Square pieces of each membrane were soaked in 25 ml of 0.1 M HCl solution and equilibrated for at least 24 h to replace the  $\text{OH}^-$  by chloride ions. The hydroxyl ions,  $\text{OH}^-$ , released in the exchange reaction were determined with a 0.1 M NaOH solution using phenolphthalein as an indicator. The  $\text{IEC}_{\text{OH}^-}$  value was thus estimated as  $\text{IEC} = \text{VN}/m_d$ , where  $V$  is the volume of the NaOH solution spent in the titration and,  $m_d$  is the mass of the dry membrane, ie., mequiv of quaternary ammonium groups per gram of dried sample.

### 2.5. Ionic conductivity measurement

The  $\text{OH}^-$  conductivity of the formed membrane was measured by an AC impedance technique using an electrochemical impedance analyzer (VMP2/Z, PAR), where the AC frequency was scanned from 100 kHz to 0.1 Hz at a voltage amplitude of 100 mV. Fully hydrated membrane was sandwiched in a Teflon conductivity cell equipped

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