



Alkaline solid polymer electrolyte membranes based on structurally modified PVA/PVP with improved alkali stability

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ABSTRACT

Novel alkaline solid polymer electrolyte membranes that can conduct anions (OH^-) have been prepared from poly(vinyl alcohol)/poly(vinylpyrrolidone) (PVA/PVP) by blending and chemical cross-linking, followed by doping in aqueous KOH solution. The physicochemical properties of these membranes have been studied in detail by FTIR, TG, and SEM analyses. The ionic conductivity was found to be greatly dependent on the concentration of KOH and the interpenetrated PVP in the PVA matrix. A maximum conductivity of up to 0.53 S cm^{-1} at room temperature was achieved for PVA/PVP in a mass ratio of 1:0.5 after doping in 8 M aqueous KOH solution. The membrane showed perfect alkaline stability without losing its integrity even upon exposure to 10 M KOH solution at up to 120°C . Scanning electron micrographs revealed a highly ordered microvoid structure uniformly dispersed on the membrane surface with a pore size of ca. 200 nm after heat-curing, which imparted the membrane with good liquid electrolyte (KOH) retention ability. FTIR spectra showed that these high ionic conductivities may be attributed to the presence of excess free KOH in the polymer matrix in addition to KOH bound to the polymer. Almost constant, highly stable, ionic conductivity while maintaining mechanical integrity was retained at room temperature for more than one month.

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1. Introduction

Solid polymer electrolyte fuel cells (SPEFCs) based on proton-conducting polymers have been identified as promising power sources for stationary and residential applications [1]. In SPEFCs, the ion-exchange membranes play a vital role in obtaining not only high ionic conductivity but also thermal and mechanical stabilities. Nafion[®], a perfluorinated ionomer developed by DuPont, is the common denominator in this technology. However, this still limits widespread application due to its high cost, unstable properties at high temperatures, high methanol permeability, and difficulties in synthesis and processing [2]. On the other hand, alkaline solid polymer electrolytes (ASPEs) find a market niche in a number of applications, such as in batteries [3,4], supercapacitors [5], and alkaline membrane fuel cells (AMFCs). For example, when the operational environment is alkaline, AMFCs have many advantages, including: (i) faster kinetics of oxygen reduction reactions in an alkaline medium, which allows the use of non-noble and low cost

metal electrocatalysts such as silver and nickel; (ii) improved water management since the electro-osmotic drag transports water away from the cathode, and (iii) lowered alcohol 'crossover' problem due to hydroxide ion transport from cathode to anode.

Up to now, some promising alkaline-exchange membranes (AAEMs) have been evaluated for use in AMFCs. Here, the membranes have been constructed mainly from copolymers, the quaternized comonomers of which feature an anion as the charge carrier, 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]. Unfortunately, the quaternized polymer is unstable in alkaline media at temperatures above 60°C and at high KOH concentrations [13–17]. Generally, many organic compounds are more stable under acidic conditions than under alkaline conditions. The chemical stability of cation-exchange membranes can be improved by perfluorinating the polymer backbone, as in the case of Nafion[®] membrane. However, the quaternary ammonium groups, which are functional groups in the AAEMs, decompose in concentrated alkali solutions via the Hofmann degradation reaction [18]. Due to the caustic environment in alkaline fuel cells, the alkaline electrolyte membrane must be chemically

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and thermally stable [19,20]. Therefore, the development of AAEMs with improved alkaline stability is still an urgent need [19,20,25].

Another kind of ASPEs consist of a neutral polymer doped with an inorganic base. This type of polymer electrolyte has a number of distinct characteristics, such as easy preparation (just dipping in alkali metal hydroxide, KOH), low cost, abundance of the basic components, and high ionic conductivity as compared with other solid polymer electrolytes [21]. ASPEs have also been used in studies concerning application to AMFCs and showed promising power performance, such as in an alkaline direct methanol fuel cell (ADMFC) [22–24] and an alkaline direct ethanol fuel cell (ADEFC) [13].

PVA is a polyhydroxy polymer that is very commonly used in practical applications because of its easy preparation and biodegradability [26]. 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 [27]. PVP, as a hydrophobicizer and stabilizer, can greatly improve membrane oxidative stability and chemical stability [28]. Based on this consideration, we report herein a novel alkaline solid polymer electrolyte membrane composed of KOH-doped poly(vinyl alcohol)/poly(vinylpyrrolidone) (PVA/PVP). The membrane structure is finished by blending PVA and PVP, and then chemical cross-linking of the hydroxyl groups of PVA with acetal ring formation by using glutaraldehyde as a cross-linker. The membrane properties, such as ionic conductivity, swelling behavior, water uptake, membrane microstructure, strong alkaline tolerance at high-temperature, thermal stability and long-term durability have been investigated systematically in order to pursue a membrane that has potential for electrochemical applications, such as in AMFCs.

2. Experimental section

2.1. Materials and membrane preparation

The membranes were formed by a 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 distilled water (500 mL) and then heating at 90°C with continuous stirring until a transparent solution was obtained. The polymeric additive, PVP, was prepared separately ($M_w = 40,000$; Aldrich). Appropriate amounts of the two solutions were then mixed in the selected blend ratios, 1:0, 1:0.25, 1:0.5, 1:1, and 1:2 PVA/PVP by mass. The resulting mixture took on a homogeneous and transparent appearance. After removal of the air in vacuo, the resulting solutions were poured into plastic Petri dishes, and water was evaporated under ambient conditions. When visually dry, the membrane was peeled from the plastic substrate, and had a thickness of about 60 – $80\ \mu\text{m}$.

2.2. Chemical cross-linking of PVA/PVP

Samples of square pieces of membranes (ca. $1.5 \times 2\ \text{cm}$) were soaked in a reaction solution containing 10 mass% glutaraldehyde (GA) (25 wt.% solution in water; Shanghai Guoyao) in acetone at 30°C for 60 min. Cross-linking proceeded between the $-\text{OH}$ of PVA and the $-\text{CHO}$ of GA in the membrane due to an acid-catalyzed reaction upon addition of a small amount of HCl to the solution. PVP was thus interpenetrated into the PVA network due to increased cross-linking density. Transparent, flat membranes were obtained with a thickness of the order of several tens of micrometers (60 – $80\ \mu\text{m}$). The thickness of the membranes could be easily controlled by adjusting the volume of the suspension.

2.3. Alkaline PVA/PVP membrane preparation

Fig. 1 schematically illustrates the preparation of chemically cross-linked alkaline PVA/PVP. To clarify the conducting mechanisms of KOH-doped PVA/PVP, the membranes were prepared in the following two ways. (i) The membranes were rendered conducting by immersion of PVA/PVP in KOH solution at various concentrations and equilibrated for at least 24 h. At this stage, PVA/PVP was doped with KOH (PVA/PVP/KOH), and then the membranes were taken out and used directly for ionic conducting measurements without any post-treatment. (ii) After completion of the doping, the membranes were taken out and rinsed repeatedly with deionized (D.I.) water to remove the adsorbed KOH on their surfaces, and then stored in D.I. water for final ionic conductivity measurements. Two types of membranes were thus prepared, which we denote as PVA/PVP/KOH-d (d = doped) and PVA/PVP/KOH-r (r = rinsed), respectively. A model of the inner structure of PVA/PVP/KOH and typical membrane images are given in Fig. 2.

2.4. Measurement of ionic conductivity and swelling behavior of the membranes

The OH^- ionic conductivity of the formed membranes was measured by an AC impedance technique using an electrochemical impedance analyzer (VMP2/Z, PAR), where the AC frequency was scanned from $100\ \text{kHz}$ to $0.1\ \text{Hz}$ at a voltage amplitude of $100\ \text{mV}$. Fully hydrated membranes were sandwiched in a Teflon conductivity cell equipped with Pt foil contacts [28]. The membrane was in contact with water throughout the measurements. Ionic conductivity (S/cm) was calculated according to the following equation: $\sigma = l/(RTW)$, where l is the length of the membrane between two potential sensing platinum wires, R is the membrane resistance, and W and T are the width and the thickness of the membrane, respectively. The temperature dependence of ionic conductivity was determined by controlling the temperature from 25 to 80°C . The cell was sealed with water throughout the duration of the measurements.

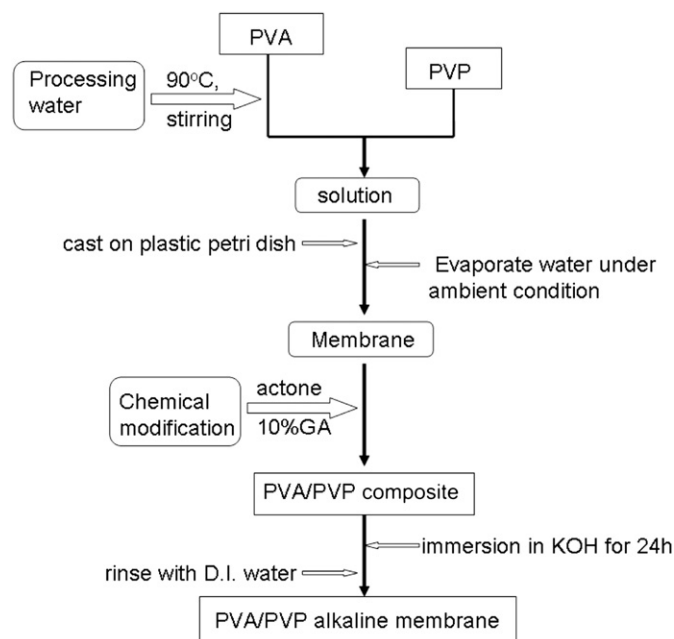


Fig. 1. Schematic diagram for the preparation of alkaline PVA/PVP composite by blending and chemical cross-linking.

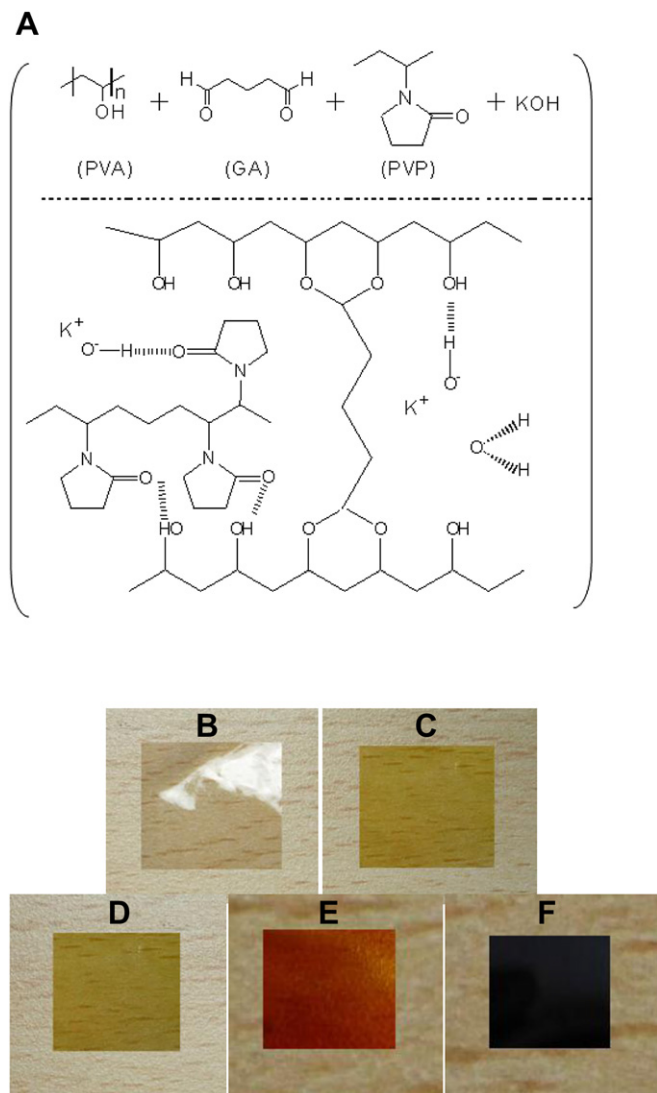


Fig. 2. Inner structure model of KOH-doped PVA/PVP (A) and Membrane pictures for (B) PVA conditioned in 4M KOH at 25 °C, (C) PVA conditioned in 4M KOH at 80 °C, (D) PVA/PVP conditioned in 10M KOH at 25 °C, (E) PVA/PVP conditioned in 10M KOH at 80 °C and (F) PVA/PVP conditioned in 10M KOH at 120 °C. Condition time: 24h, followed by complete removal of free KOH prior to testing. PVA/PVP = 1:1 in mass ratio.

The swelling of the membranes was evaluated by both the water uptake (WU) and the methanol uptake from the mass change before and after complete dryness of the membrane. A dry membrane was swollen in deionized water for a day, 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 (WU), was calculated using the expression: $WU = (W_{wet} - W_{dry})/W_{dry}$, where W_{wet} and W_{dry} are the masses of the fully hydrated membrane and of the dry membrane, respectively. The methanol uptake was measured by the same procedure.

2.5. Characterization of PVA/PVP/KOH membranes

The membranes were examined by Fourier-transform infrared (FTIR) spectroscopy in order to characterize their molecular structures after alkaline doping. IR spectra were recorded on an FTIR-4200 spectrometer (Shimadzu) with a wavenumber resolution of 4 cm^{-1} in the range 400–4000 cm^{-1} . Samples in the form of thin

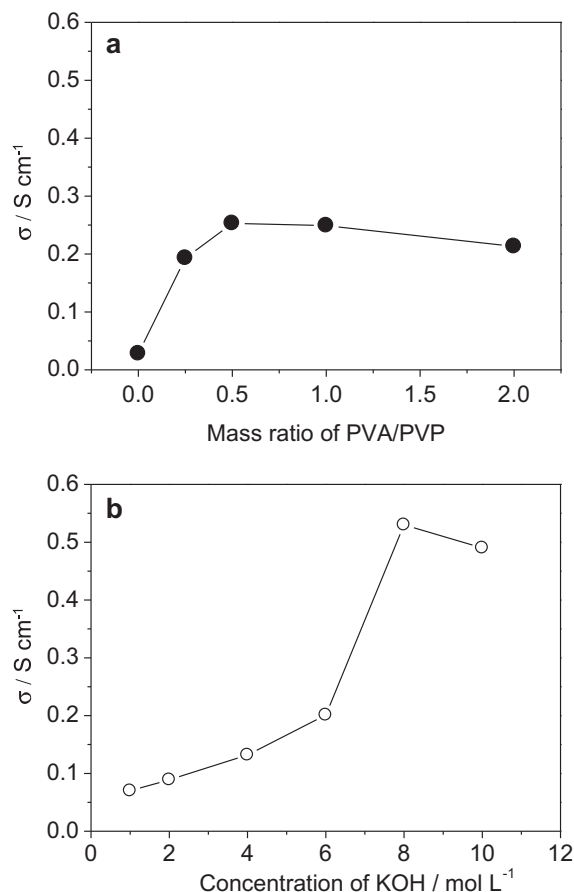


Fig. 3. (a) Ionic conductivity of PVA/PVP/KOH-d as a function of PVP content. (b) Conductivity changes with doping KOH concentration in aqueous solution. (a) Doping KOH concentration: 4 M. (b) Polymer composition: PVA/PVP = 1:0.5 in mass. Doping time: 24 h.

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 4000 \times , 6000 \times , and 10,000 \times magnifications. The element distribution in the cross-section was determined by means of an Oxford Instruments X-ray Microanalysis INCA, operating at 20 kV with a data collection time of 10 min.

2.6. Thermal analysis

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

3. Results and discussion

3.1. Ionic conductivity and water uptake

The alkaline PVA/PVP blend membranes appeared transparent and homogeneous with mechanical flexibility. When immersed in KOH solution, the membrane became orange in color, but it almost

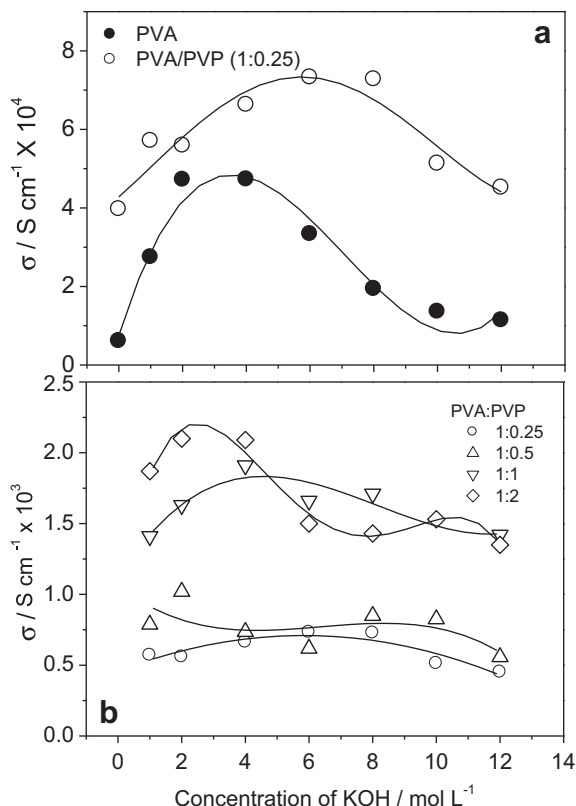


Fig. 4. Ionic conductivity of (a) PVA/KOH-r and (b) PVA/PVP/KOH-r as a function of doping KOH concentration in aqueous solution. Doping time: 24 h.

decolored completely upon rinsing in D.I. water. Fig. 3(a) shows the ionic conductivity of PVA/PVP doped with 4 M KOH, that is, PVA/PVP/KOH-d as a function of PVP content, where the PVA/PVP mass ratio ranged from 1:0 to 1:2. It can be seen that the ionic conductivity of the membrane at room temperature depended on the PVP content. The ionic conductivity increased from 0.023 S cm⁻¹ for PVA/PVP at a 1:0 mass ratio to a maximum of 0.25 S cm⁻¹ for PVA/PVP at a 1:0.5 mass ratio. This can be attributed to an increase in the number of charge carriers in the PVA polymer matrix due to the interpenetrating PVP domain. Due to the hydrophilic nature of PVP, the polymer would be swollen well in water. Hence, it allows the

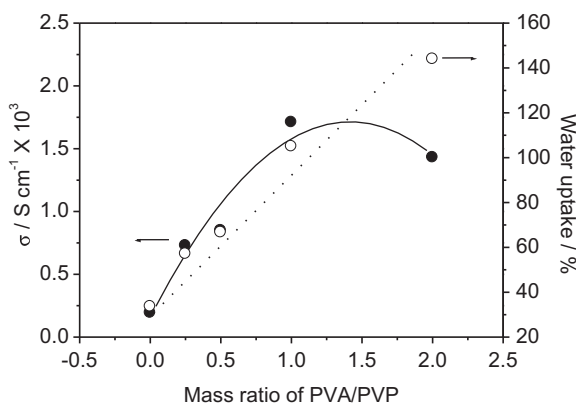


Fig. 5. Ionic conductivity and water uptake of PVA/PVP/KOH-r as a function of PVP content. Polymer composition: PVA:PVP = 1:1 in mass. Doping KOH concentration in solution: 8 M. Dondition time: 24 h.

excess KOH to remain fixed in the interspaces of the polymer matrix together with water, resulting in higher ionic conductivity. Similar trends were observed for the concentration dependence, where the ionic conductivity of PVA/PVP first increased to a maximum of 0.53 S cm⁻¹ as the KOH concentration was increased from 1 to 8 mol L⁻¹, and then decreased when the KOH concentration exceeded 10 mol L⁻¹ (Fig. 3(b)). The decreasing trend in the ionic conductivity with higher KOH concentration is a common phenomenon observed in polymer electrolytes and can be explained in terms of weak ionic mobility since the degree of

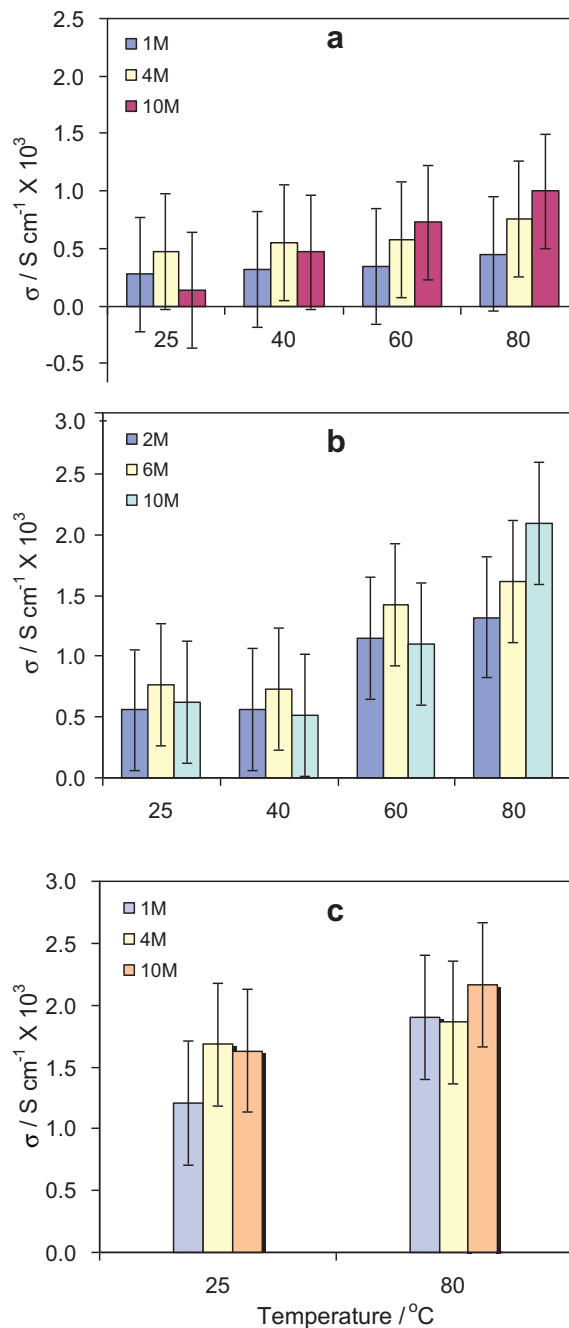


Fig. 6. Ionic conductivity of PVA and PVA/PVP composite after KOH conditioning at elevated temperatures. The membranes were conditioned in (a) 1, 4, 10 M KOH for PVA, (b) 2, 6, 10 M KOH for PVA/PVP (1:0.25 in mass), (c) 1, 4, 10 M KOH for PVA/PVP (1:1 in mass) at elevated temperatures for 24 h, followed by complete removal of free KOH prior to conductivity testing. The conductivity was measured at 25 °C.

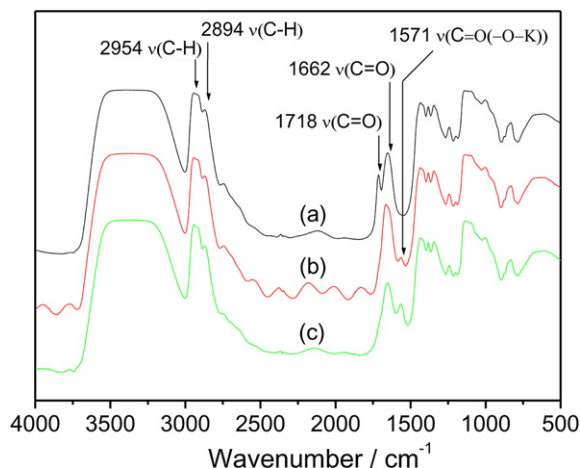


Fig. 7. FTIR spectra registered for PVA/PVP composite (a) without KOH conditioning (b) conditioning in 6 M KOH at 25 °C (c) conditioning in 6M KOH at 60 °C. Polymer composition: PVA/PVP = 1:1 in mass.

freedom of ion transport is reduced as so much KOH enters into the polymer matrix [29].

Compared to the PVA membrane, the ionic conductivity of the PVA/PVP (1:0.5 by mass) increased from 0.023 to 0.53 S cm⁻¹ at 25 °C. The σ value for the PVA/PVP (1:0.5 by mass) membrane was ca. 20 times that of the PVA membrane. It seems that our PVA/PVP (1:0.5 by mass) membrane is a highly ionic conducting ASPEM in comparison with recent outstanding results [22–25]. Here, PVP was also noted to have a great influence on the membrane mechanical stability. The membrane became brittle and easily broken when the PVA/PVP ratio was higher than 1:1.5 by mass. Therefore, it can be concluded that PVP functioned both as a plasticizer in stabilizing the polymer membrane and as a complexing reagent imparting a high σ value.

In order to clarify any interactions between the dopant KOH and PVA/PVP, Fig. 4 shows the change in the ionic conductivity of PVA/PVP/KOH-r with dopant KOH concentration in solution. It can be seen that the ionic conductivity measured at 25 °C by AC impedance spectroscopy reached a maximum value of 4.73×10^{-4} S cm⁻¹ for PVA after KOH doping from an aqueous solution of 2–4 mol L⁻¹. This conductivity value greatly increased to 7.73×10^{-4} S cm⁻¹ for PVA/PVP blend at a 1:0.25 mass ratio, and further increased to 1.77×10^{-3} S cm⁻¹ at a 1:1 mass ratio after KOH doping from an aqueous solution of 6–8 mol L⁻¹. Although the σ values of PVA/PVP/KOH-r (Fig. 4) are rather low compared with that of PVA/PVP/KOH-d (Fig. 3), they are of the same order as the ionic conductivity obtained by directly mixing a viscous PVA solution with a concentrated aqueous KOH solution, as reported elsewhere [30]. This clearly demonstrated that some KOH was taken into the polymer matrix, although the adsorbed KOH on the surface of the membrane was removed after repeated rinsing with D.I. water. Evidently, the ionic conductivity of PVA/PVP/KOH-r stems mainly from the “bond” KOH through chemical interactions such as hydrogen bonding and induction forces between C=O groups on PVP and KOH together with C–O and OH groups of PVA and the KOH dopant. On the contrary, for PVA/PVP/KOH-d, the high ionic conductivity stems mainly from the contribution of excess “free” KOH adsorbed on the membrane surface. It is reported that alkali-doped PVA with various additives, such as HAP [24], SSA [23], or PAA [25], and TiO₂ filler [22], among others, gives much higher ionic conductivities in excess of 10⁻² S cm⁻¹. Since the membranes were prepared by directly adding KOH to PVA solution [22] or by immersing the membrane in aqueous KOH solution [23–25] without any post-treatment such as rinsing

with D.I. water, it is concluded that the high ionic conductivity values in the above work were attributed to excess “free” KOH adsorbed on the membrane surface, as for PVA/PVP/KOH-d in this work.

As in the case of PVA/PVP/KOH-d, an additional doping concentration of KOH, i.e., larger than 4 M for PVA or 8 M for PVA/PVP, led to a decrease in the ionic conductivity of PVA/KOH-r or PVA/PVP/KOH-r. That is, an additional higher doping KOH concentration in solution does not simply make a further contribution to the conductivity. The membrane samples are found to be supernatant at high doping KOH concentration (>8 M) in solution. It seems that more OH⁻ could not be taken into the polymer due to the weak ionic mobility (owing to the formation of ion-pairs or increased viscosity), thus leading to a decrease in ionic conductivity [29].

The decrease in ionic conductivity seen when the PVA/PVP ratio exceeds 1:1 by mass may stem from the high water uptake of the membrane due to the increased hydrophilic effect of PVP. In order to see this trend, the ionic conductivity data in Fig. 4, obtained at a typical doping KOH concentration of 8 M, and the water uptake have been plotted again in Fig. 5 as a function of PVP content in the polymer. It can clearly be seen that the water uptake in the membrane increased sharply with increasing PVP content and exceeded 120% at PVA/PVP = 1:2 by mass. Larger sorption of water may be due to greater flexibility of the polymer chains or the microstructure of the polymer, which would allow more water to reside between the polymer chains. This, together with the hydrophilic character of PVP, results in large sorption of water at high PVP contents, which does not simply give improved ionic conductivity but rather a dilution of charge carriers [28].

3.2. Chemical stability

The chemical stability of alkaline electrolyte membranes is recognized as a key factor that affects their electrochemical applications, especially in alkaline media at temperatures above 60 °C and at high KOH concentrations [14,15,18,19]. The chemical stability of the membranes was assessed by immersing PVA and PVA/PVP in different concentrations of KOH at elevated temperatures for 24 h. This experiment was thus designed to test the tolerance of the membrane to base treatments at elevated temperatures [11]. After complete removal of the free KOH on the membrane surface, the ionic conductivity of the membranes was measured at room temperature. Fig. 6 shows the results of the typical runs at three concentrations each, specifically 1, 4, and 10 M KOH for PVA, 2, 6, and 10 M KOH for PVA/PVP at 1:0.25 by mass, and 1, 4, and 10 M KOH for PVA/PVP at 1:1 by mass, respectively. It is noted that each of the tested membranes displayed an increased conductivity with increasing KOH concentration at elevated treatment temperatures. The PVA soaked in 10 M KOH showed a rapid increase in ionic conductivity, and exhibited its highest conductivity of 9.77×10^{-4} S cm⁻¹ when treated at 80 °C (Fig. 6(a)). By incorporation of a small amount of PVP, i.e., at PVA/PVP = 1:0.25 by mass, membranes soaked in either 6.0 or 10 M KOH showed a rapid increase in ionic conductivity, attaining maximum values of 1.61 and 2.09×10^{-3} S cm⁻¹, respectively, after conditioning at 80 °C (Fig. 6(b)). Similarly, an increased ionic conductivity was observed for PVA/PVP = 1:1 by mass after conditioning the membrane in 10 M KOH at 80 °C (Fig. 6(b)).

It is known that AAEMs are frequently less stable since basic groups are inherently less stable than acidic groups [15,18,19,26]. Because of this, purely quaternized polymers are only stable over a limited range of KOH concentrations, typically up to 0.5 or 1.0 M at 80 °C. They are known to deteriorate at a KOH concentration of just 2.0 M at temperatures as low as 60 °C [11] or even in pure water at

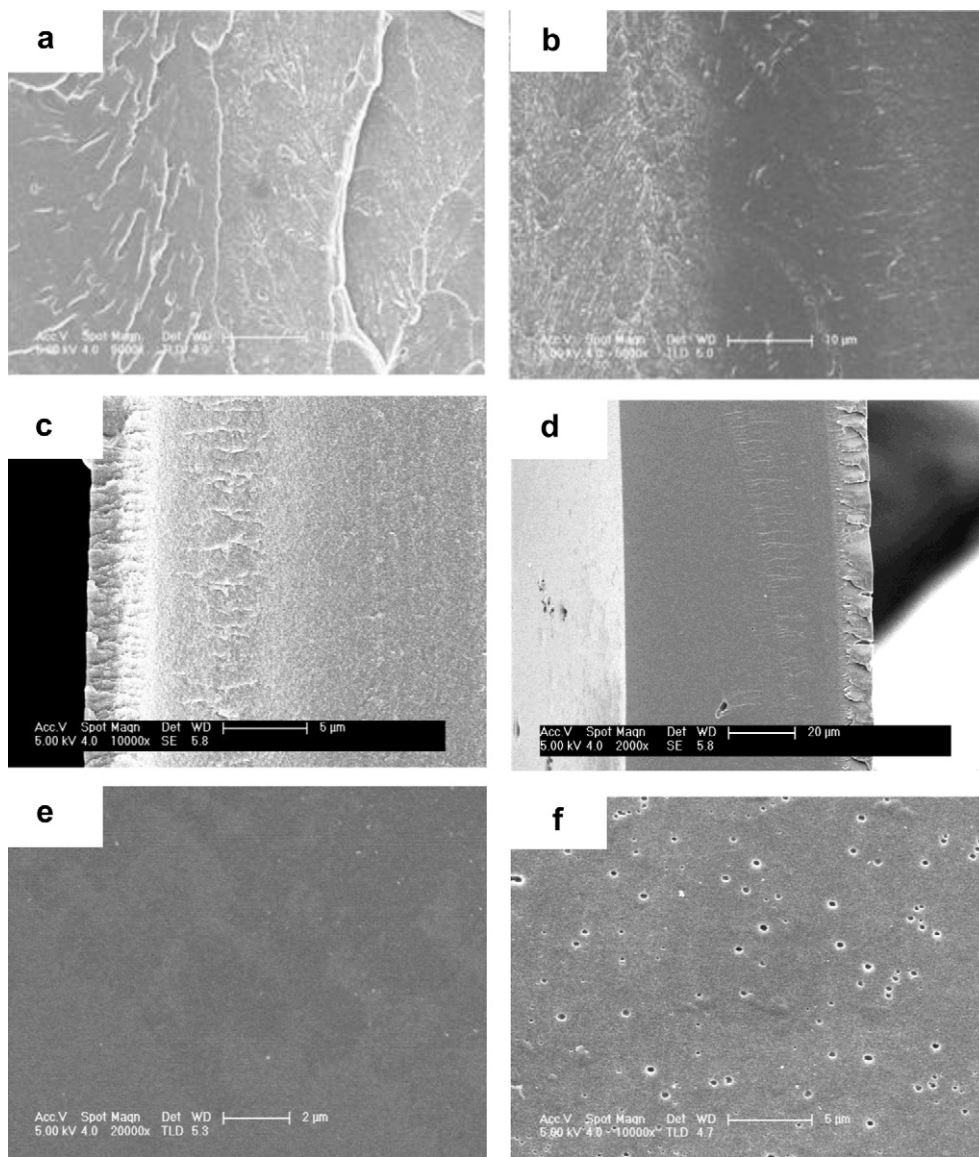


Fig. 8. SEM pictures of the cutview of (a) PVA membrane conditioned in 10 M KOH at r.t., (b) PVA membrane conditioned in 4 M KOH at 80 °C, (c) PVA/PVP composite conditioned in 10 M KOH at r.t., (d) PVA/PVP composite conditioned in 10 M KOH at 120 °C, (e) surface picture of PVA membrane conditioned in 10 M KOH at 80 °C, (f) surface picture of PVA/PVP conditioned in 10 M KOH at 120 °C. Condition time: 24 h, followed by complete removal of free KOH prior to testing. PVA/PVP = 1:1 in mass.

80 °C [10], whereupon the ionic conductivity is greatly decreased or can even no longer be measured. Hybrid PEO/SiO₂ membranes have also been found to undergo serious degradation upon immersion in a strongly alkaline solution [31]. However, no decrease in ionic conductivity was observed for PVA/PVP after immersion in a strongly alkaline solution at elevated temperatures. This demonstrates the perfect tolerance of the resulting PVA/PVP to base treatment, which may be attributed to the highly cross-linked PVA network and entrapped PVP in the PVA matrix. Therefore, the addition of PVP not only improves the ionic conductivity but also the chemical stability of the membranes.

3.3. FTIR

To clarify the conducting mechanisms of alkaline PVA/PVP membranes, FTIR spectra were recorded in the wavenumber region between 4000 and 500 cm⁻¹, which covers the whole range of all of the characteristic IR vibrations. Fig. 7 presents typical FTIR spectra

measured for PVA/PVP composite (1:1 by mass), with and without high-temperature conditioning, after doping in 6 M aqueous KOH solution. All of the spectra show an intense band between 3100 and 3750 cm⁻¹, which is ascribed to the stretching vibration of OH groups from the bound water. The bands at 2894 and 2954 cm⁻¹ arise from the stretching of CH₃–, –CH₂–, and CH– groups. Although the stretching absorption band at 1557 cm⁻¹, which is attributed to the II belt ν (C–N) of PVP could not be unambiguously assigned, a sharp peak at 1672 cm⁻¹, which is ascribed to the I belt ν (C=O) absorption from PVP, was clearly observed. The presence of cross-linking in the membrane has been proven by IR measurements, where the appearance of a sharp absorption band at 1718 cm⁻¹ (C=O) was observed due to the ‘free’ –CHO attached to GA. This indicates reduced accessibility to the reactive groups caused by an increase in the network density [28]. Interestingly, after conditioning the composite membrane in KOH solution, the peak at 1718 cm⁻¹ disappeared and a new characteristic absorption peak centered at 1571 cm⁻¹ appeared and intensified significantly with treatment

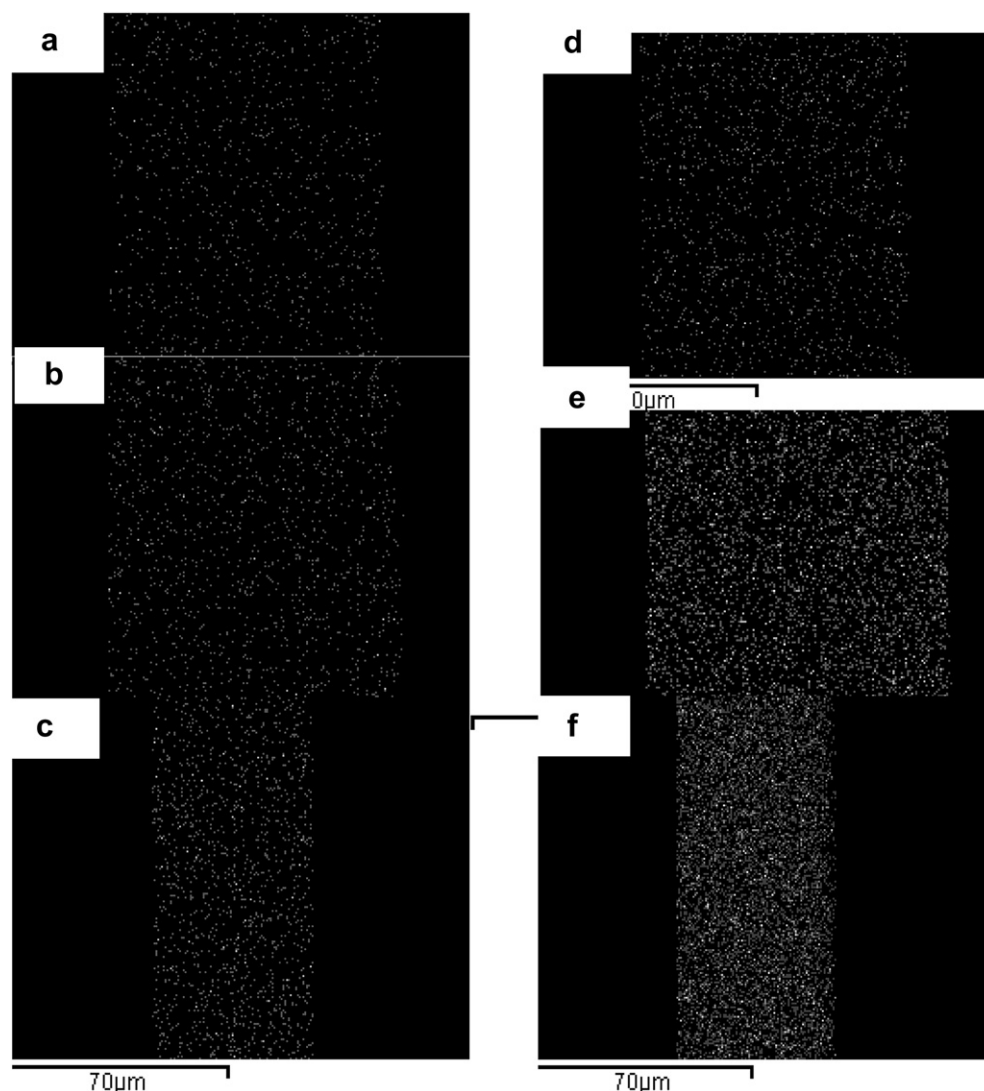


Fig. 9. EDX mapping of (a),(b),(c) potassium element and (d),(e),(f) oxygen element within KOH-doped PVA/PVP composite, respectively. Doping KOH concentration in solution: 10 M; (a),(d): conditioned at r.t.; (b),(e): conditioned at 80 °C; (c),(f): conditioned at 120 °C. Condition time: 24 h, followed by complete removal of free KOH prior to testing.

temperature. Since a disproportionation reaction of the ‘free’ —CHO occurs under alkaline conditions, which produces the alcohol and carboxylic acid [C=O(—O—H)], the [C=O(—O—H)] will further react with KOH to produce carboxylate [C=O(—O—K)]. Hence, the band at 1571 cm^{-1} band is assigned as the asymmetrical stretching vibration absorption of [C=O(—O—K)]. Therefore, it is concluded that the absorbent capacity of the PVA/PVP composite for KOH is highly improved after high-temperature treatment, and that the higher ionic conductivity is due to increased charge carriers in PVA/PVP.

3.4. Membrane morphologies

Fig. 8 shows SEM photographs of the cross-sectional views of PVA/PVP/KOH-r. These were obtained to assess whether the change in initial liquid electrolyte absorbent capacity is related to the ionic conductivity increment with the addition of PVP, in particular, after base treatment at elevated temperatures. For comparison, the corresponding SEM photographs of PVA/KOH-r are also provided. It can be seen that SEM observation of the sections of a membrane reveals a homogeneous and dense material. It was found that by increasing the dopant KOH concentration in solution and/or by conditioning at elevated temperatures, an orange color was induced

in the membranes, as shown in Fig. 2(b). However, no surface degradation or membrane damage, such as the appearance of holes or phase-separation phenomena, could be detected. The structure is seen to be very compact in the SEM images (Fig. 8(a) and (b)) for PVA/KOH-r conditioned either at high KOH concentration (10 M KOH) or at 80 °C. Moreover, no morphology changes were observed for PVA/PVP/KOH-r membrane after conditioning in KOH solutions of different concentrations at 25 °C (Figs. 2(b) and 8(c)). It should be mentioned that PVP has been reported to be used as a pore-forming agent since it leaches out during membrane casting, leaving pores typically ranging from 1 to 10 μm [32–34]. When the membrane is immersed in an electrolyte solution, the solution penetrates into the porous network, which makes the membrane ionically conductive. However, in the present work, there was no loss of PVP during casting. There were neither gaps nor cracks in the polymer matrix; rather, the PVA/PVP/KOH-r membrane exhibited a glassy and dense cross-sectional morphology, even after conditioning at high KOH concentration (10 M) in aqueous solution (Fig. 8(c)). In addition, the flexibility of the membranes was remarkably improved after KOH doping.

An intriguing result is that a compact structure of the PVA/KOH-r membrane persisted after high-temperature conditioning, while conditioning of PVA/PVP/KOH-r at 120 °C led to a microvoid

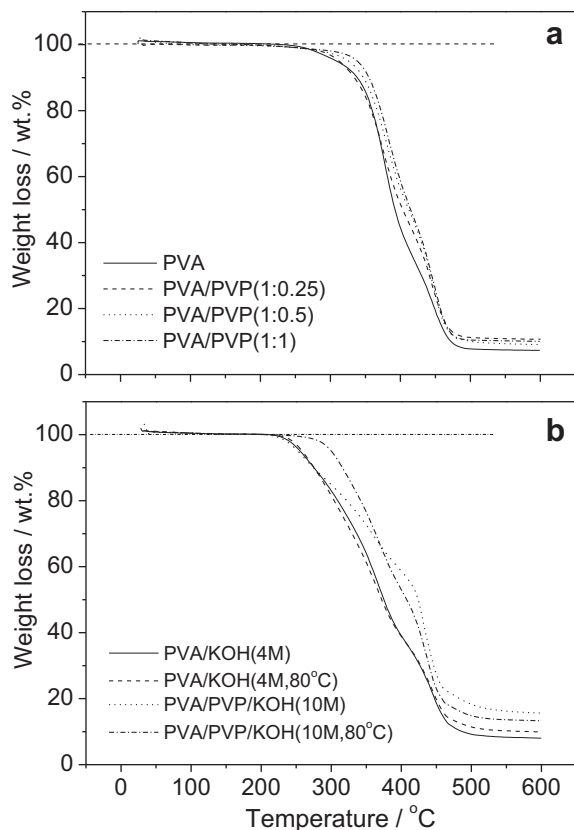


Fig. 10. TG profiles of PVA/PVP composite (a) without KOH conditioning (b) conditioned in different KOH concentration at 80 °C. Polymer composition: PVA/PVP = 1:1 in mass.

structure with pores of size ca. 200 nm uniformly dispersed on the membrane surface (Fig. 8(f)). The corresponding cross-sectional view of Fig. 8(d) also showed some microvoids, and a similar phenomenon was observed for PVA/PVP/KOH-r membrane conditioned at 80 °C. It is known that a liquid electrolyte solution is likely to evaporate and leak from a polymer structure with large pores (above 3 μm) with time, which leads to a detrimental increase in electrolyte resistance [35]. Therefore, a dense membrane showed better liquid retention with time, despite initial low liquid solution uptake. Compared with the room temperature conductivity of around $4.73 \times 10^{-4} \text{ S cm}^{-1}$ for the PVA/KOH-r membrane, the conductivity of the PVA/PVP/KOH-r membrane was as high as $1.77 \times 10^{-3} \text{ S cm}^{-1}$ at ambient temperature and close to $6.2 \times 10^{-3} \text{ S cm}^{-1}$ after treatment at 120 °C. Obviously, the increase in ionic conductivity for PVP/PVA/KOH-r is related to good initial liquid solution retention (KOH) due to PVP modifying the micro-phase structure. In other words, the liquid electrolyte retention is apparently improved for PVA/PVP. Thus, if the composite ratio is optimized (for example: PVA/PVP = 1:0.25 to 1:1 and the membrane is conditioned in aqueous KOH solution from 4 to 10 M at 60–100 °C), it is possible to obtain the best compromise between initial liquid electrolyte absorbent capacity and retention ability, even at high temperatures.

In the EDX mapping image shown in Fig. 9, the highlighted bright dots reveal high element concentration. It can be seen that the distributions of potassium and oxygen were homogeneous, indicating that KOH was well dispersed throughout the PVA/PVP membrane. In addition, EDX mapping of potassium and oxygen indicated higher concentrations of both after high-temperature conditioning than in the case of room temperature conditioning. This

is in good agreement with the conductivity obtained from Fig. 6 and the FTIR results, which further demonstrates the good initial liquid electrolyte retention ability of the membrane after temperature conditioning.

3.5. Thermal stability (TGA analysis)

Fig. 10 shows the thermogravimetric analysis curves of PVA/PVP/KOH-r membranes with different PVP contents and heat-conditioned at elevated temperatures, along with those of PVA/KOH-r for comparison. The membrane samples were dried at 110 °C prior to TG analysis. All of the samples displayed three major weight loss stages at around 80–200, 230–380, and 400–450 °C, followed by the final decomposition of the polymer matrix. For the samples exposed to air prior to TG analysis, the weight losses in the first, second, and third stages can be respectively attributed to the expulsion of water molecules from the polymer matrix or the moisture absorbed from the air, the decomposition of hydroxide groups, and the splitting of the main chain of PVA followed by decomposition of the polymer backbone above 450 °C.

Compared with organic anion-exchange membranes, for which the degradation of the quaternary ammonium groups occurs at a much lower temperature (150–190 °C) [10], our membranes show greatly enhanced thermal stability. Further analysis by D-TGA revealed that with increasing PVP content in the polymer, the onset degradation temperature was increased both for the membranes without KOH doping (from 235 to 280 °C) (Fig. 10(a)) and for those doped with KOH (from 200 to 238 °C) (Fig. 10(b)). The weight loss of the PVA/KOH-r membrane conditioned in 4 M KOH at 80 °C (47–48%) (Fig. 10(b) and Table 1) is almost as the same as that of the membrane conditioned at r.t., which illustrates the high thermal stability of the PVA network structure. In addition, the membrane thermal stability is greatly improved by the addition of PVP, such that the weight loss (31–32%) is much reduced in comparison with that from PVA/KOH-r (47–48%) at the maximum thermal decomposition temperature in the range 230–380 °C (Fig. 10(b) and Table 1), even when a PVA/PVP (1:1 by mass) membrane, for example, was conditioned in 10 M KOH at 80 °C. This confirms that the incorporation of PVP is critical to the improvement of the membrane's thermal stability.

3.6. Long-term stability of alkaline PVA/PVP blend membrane

In order to investigate the long-term stability of alkaline PVA/PVP membranes were conditioned in 10 M KOH at 80 °C and 120 °C, respectively, for 24 h, then rinsed and stored in D.I. water. Here, PVA/PVP with a 1:1 mass ratio is discussed as a representative example. We determined: (i) dimensional changes of the membrane; i.e. the changes in the length (L_x), width (L_y), and thickness (L_z) of the membrane after different storage times were evaluated as measures of membrane stability using the dimensions

Table 1
Thermal properties of PVA/PVP semi-IPNs after KOH doping.

PVA:PVP (in mass)	T ₁ -onset decomposition (°C)	T ₁ -max decomposition (°C)	Weight loss (%)
1:0–4M	203	367	47–48
1:0–4M–T80	200	364	47–48
1:1–10M	200	363	32–33
1:1–10M–T80	238	368	31–32

10%GA as a cross-linker. Cross-linking time: 1 h. 1:1–4M–T80 indicates that the membrane sample was conditioned in 4 M KOH at 80 °C for 24 h, then the adsorbed KOH on the surface of the membrane was completely removed by rinsing the membrane in D.I. water numerous times and so on.

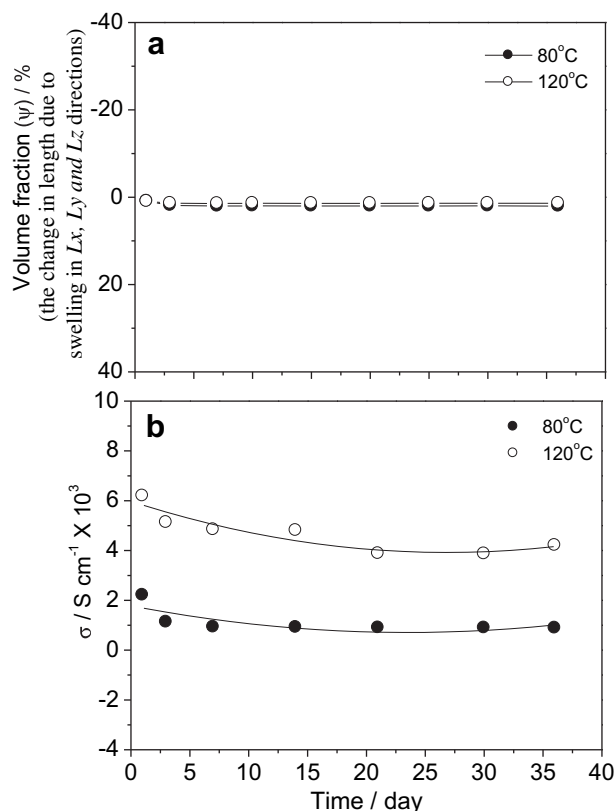


Fig. 11. Time courses of (a) dimensional change (ψ) and (b) the ionic conductivity of PVA/PVP composite conditioned in 10 M KOH at 80 °C and 120 °C, respectively, then stored in D.I. water. Condition time: 24 h, followed by complete removal of free KOH prior to testing. Polymer composition: PVA/PVP = 1:1 in mass.

at ambient conditions (10 M KOH, 25 °C) as standards; and (ii) changes in the ionic conductivity of the membranes.

The change in length due to swelling was found to be almost the same in all directions (i.e., in the L_x , L_y , and L_z directions), indicating a rather isotropic swelling of PVA/PVP/KOH-r membranes. The volume fractions, ψ , thus calculated from the Eqn. [36]: $\psi = (L_x L_y L_z - L_{x0} L_{y0} L_{z0}) / L_x L_y L_z$ are presented in Fig. 11. It can be seen that there was almost no change in ψ value for PVA/PVP/KOH-r with storage time in D.I. water for more than one month, neither for the membrane conditioned at 80 °C nor for that conditioned at 120 °C in 10 M KOH (Fig. 11(a)). The ionic conductivity of the same investigated membrane remained nearly constant, except for an initial decrease within the first 2–3 days (Fig. 11(b)). An interesting phenomenon was noted in that the membrane color changed to brown after conditioning at 80 °C and to black after conditioning at 120 °C, but gradually reverted to the original color after rinsing in D.I. water, in accordance with the constant ionic conduction. This suggests that the membrane morphology remained intact over the investigated storage time. The initial decrease in ionic conductivity may be due to incomplete rinsing of the membrane or extraction of surface-attached PVP during initial high-temperature conditioning. The solution was seen to become somewhat opaque after conditioning the membrane in 10 M KOH at 120 °C, but remained wholly transparent after conditioning at room temperature or at 100 °C. In short, the residual PVP molecules cannot escape from the membrane matrix because of strong entanglement of PVP entrapped in PVA networks, although no covalent bonds are formed between them. As a result, the membrane conductivity did not change during the whole storage time.

4. Conclusions

We have developed a novel alkaline solid polymer electrolyte membrane on the basis of PVA/PVP blending and chemical cross-linking, with doping by KOH, in which PVP serves as both a plasticizer and stabilizer. The ionic conductivity was found to be greatly dependent on the concentration of KOH and the PVP content. High ionic conductivity up to 0.53 S cm^{-1} was obtained at room temperature for PVA/PVP in a mass ratio of 1:0.5 after doping with 8 M aqueous KOH solution.

Perfect tolerance to base treatment of the resulting membrane has been demonstrated by the incorporation of PVP, with neither dimensional changes nor a decrease in ionic conductivity being observed after conditioning in 10 M KOH at 120 °C and then storing in D.I. water for more than a month. This is the highest chemical stability for alkaline solid polymer electrolyte systems reported so far. The incorporation of PVP has been shown to be critical for the improvement of the membrane's thermal stability. The above results may be due to the formation of interpenetrating polymer chains of PVP in the highly cross-linked PVA network, which improves not only the ionic conductivity but also the stability of the membranes.

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