Synthesis and Characterization of PVA Based Anion Exchange Membranes for Solid Polymer Electrolytes

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ABSTRACT

In this paper, a solid polymer electrolyte membrane based on poly vinyl alcohol (PVA) is formulated. The anion exchange membrane (AEM) is composed of dinonylnaphthaleindisulfunic acid and cross-linker triallylamine; while it is soaked in a potassium hydroxide (KOH) solution for 2h. Ionic conductivity was investigated with the variation of dinonylnaphthaleindisulfunic acid content and KOH concentration. The 15% acid modified membrane's conductivity reached 0.163 S/cm at room temperature while the neat membrane's conductivity was 10^{-3} S/cm. Though the mechanical testing revealed that with the increase of acid amount the modified membranes strength was decreased; however, the strength is sufficient to perform. The neat PVA membrane showed a Tg of about 84 °C, while the modified 15% acid membrane showed a Tg of 87 °C. Higher conductivities at room temperature, excellent thermal stabilities, and sufficient mechanical strength proved this AEM as a promising candidate for solid electrolyte fuel cell.

1. INTRODUCTION

The attention to polymer electrolyte membranes has been increasing continuously due to their potential use in electric vehicles, hydrogen sensors, electrochomic devices and fuel cells [1]. Because of global warming and a shortage of energy, fuel cell technology is an attractive alternative. Polymer electrolyte fuel cells emit no pollution and, in fact, produce water as a byproduct. A polymeric electrolyte membrane (PEM) replaces the traditional porous separator of batteries and resolves the problems that are caused by the use of a liquid phase electrolyte, such as internal shorting, leakage and the possibility of combustion at the surface of the electrode.

The polymer electrolyte membrane fuel cell (PEMFC) is popular due to its light weight, high power density and provision of continuous power [2]. There are two types of PEMs–a proton conducting membrane (PCM) and an anion exchange membrane (AEM). The PEMFCs exhibit some significant problems, the use of a PCM like Nafion suffers from the high methanol permeation and it needs a large amount of Pt catalyst to attain high power density [3,4]. In order to overcome these problems many works have been done to develop an efficient and better-performing membrane [5-8]. The AEM offered numerous advantages such as performance of electrode kinetics, ability of using non precious material as catalysts, and cost over the PCM [9]. In AEM, OH- anions are conducting instead of H+

though the membrane to provide current [3,5,8]. In alkali medium the oxygen reduction reaction occurs faster; here a non-precious material like silver or nickel can be used as a catalyst [10].

Wang et al. used a three step systemic method (chloromethylation, quarternization and alkalization) to prepare an AEM based on a poly-ether-imide [9]. This AEM had an ionic conductivity of 2.51×10^{-3} S/cm at room temperature. In chloromethylation, chloromethyl groups were added in order to load more hydroxyl ions in the polymer chain; during alkalization the OH- anions were bonded to the polymer matrix by replacing the Cl- ions. The effect of alkali concentration and temperature on the ionic conductivity was examined, achieving an ionic conductivity of 3.5×10^{-3} S/cm at 90 °C. The conductivity was approximately same at different KOH concentrations. The AEM system was improved by using a polysulfonade, where the ionic conductivity was studied with respect to temperature and amount of KOH concentration [8]. The highest number of chloromethyl groups were attained at 75 °C reaction temperature and 75 min reaction time and showed the maximum ionic conductivity of 7.33×10^{-2} S/cm.

Xiong et al. studied a PVA AEM for a fuel cell in an easier method than the thee step method [7]. PVA was grafted with trimethylammonium chloride groups by quarternization and then cross linked with gluteraldehyde (GA). The

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membrane showed anionic conductivity of 7.34×10^{-3} S/cm and improved the methanol properties compared to the Nafion 117 membrane. The quarternized polymer electrolyte is unstable in an alkaline environment above 60 °C [11]. To further investigate this, Qiao et al. prepared a new cost effective cross linked alkaline PVA membrane with GA for high chemical stability [3]. However, the higher concentration of KOH (4.0M) saturated the PVA matrix and made it too viscous for ion mobility. Hence the membranes were soaked in higher concentration of KOH, resulting in membranes with the ionic conductivities at 6.0M and 10.0M KOH of 8.47×10^{-4} S/cm and 9.77×10^{-4} S/cm, respectively. The absorbing capacity, i.e. the charge carrier concentration of PVA membrane, was increased and hence the ionic conductivity was increased. Qiao et al. modified the AEM membrane by blending the PVA with poly vinyl pyrolidone (PVP) and following the same procedure [11]. The 1:0.5 mass ratio of PVA/PVP showed the maximum ionic conductivity of 0.53 S/cm soaked in KOH prior to measure. The membrane was highly stable at higher temperature120 °C. The same high ionic conductivity was measured soaking in KOH for poly-acrylic acid (PAA) mixed with PVA and cross linked by triallylamine [6]. Increasing the amount of PAA resulted in an increase in ionic conductivity for the 24h KOH soaked membrane. A higher amount of OH⁻ ions can be rationalized to diffuse into PVA chain due to soaking in KOH solution for a longer time. In another study, Shang et al. demonstrated a PVA grafted with bis-crown ether monomer. It resulted with a higher conductivity of 0.235 S/cm at 80 °C comparing the other existing PVA membranes and alkaline stability [12].

In a study, a highly durable long side-chain polybenzimidazole (PBI) AEM (N-PBIs) were fabricated successfully; where the OH- conductivity of N-PBI membrane achieved 0.11 S/cm at 80 °C [13]. Another work based on imidazolium, AEMs showed conductivity up to 1.0×10^{-2} S/cm at 90 °C [14]. The ionic conductivity of most of the AEMs were measured in contact of water or doped in KOH solution prior to measurement and showed conductivity in the range of 10^{-3}-10^{-1} S/cm [3,7,10,11,15]. Results from some other research groups showed a conductivity of 10^{-1} S/cm and 10^{-2} S/cm at higher temperature [13-14, 16].

In previous studies the highest conductivity is found in the range of 10^{-1} S/cm which is measured at high temperature and soaked for longer time. Most of the reported membranes are soaked in alkaline solution for long time before measurement. To eliminate this longer time soaking, a cross-linked anion exchange membrane

based on PVA is fabricated here. The PVA solution with dinonylnaphthaleindisulfonic acid and a cross linker, triallylamine, is casted in a Teflon mold. The cross linker interacts with the hydroxyl group of PVA and builds up a crosslink structure. The fabricated membrane is soaked in KOH solution for 2h; and found stable in this alkaline environment. Ionic conductivity of the membrane is measured at room temperature (not soaked in water during measurement); at dry condition after doping in KOH solution. At room temperature this PVA solid electrolyte membrane showed a conductivity of 10^{-1} S/cm. Tensile and thermal properties of the membranes are also investigated.

2. EXPERIMENTAL PROCEDURE

2.1 Materials

Poly-vinyl-alcohol, dinonylnaphthalenedisulfonic acid, triallylamine and potassium hydroxide solution were used to fabricate anion exchange membrane. Poly-vinyl-alcohol (99+% hydrolyzed, molecular weight 89000-98000) in powder form was supplied by Sigma Aldrich. Dinonylnaphthalenedisulfonic acid was obtained from Sigma Aldrich as a deep brown viscous solution. The solvents were isobutanol (55 wt.%) and 2-methyl-1-propanol (45 wt.%). Liquid Triallylamine was used as cross linking agent and was provided by Sigma Aldrich. Potassium hydroxide (KOH, 56.11 gm/mol.) was obtained from Sigma Aldrich in white pellet form.

2.2 Fabrication of AEM

The neat PVA membrane was prepared by a simple solution casting method. PVA powder was mixed with distilled water at 90 °C for 20 minutes to make a 10wt.% solution. The solution is viscous and transparent after complete dissolution in water. This solution was poured onto a Teflon mold and dried at room temperature. When dry, the membranes were peeled out from the mold. The average thickness of the neat membranes was about 0.15-0.25 mm.

PVA anion conductive membranes were prepared by adding dinonylnaphthalenedisulfonic acid (wt./wt.) to the neat PVA 10 wt% solution. The PVA/acid mixture was stirred mechanically on a magnetic stirrer until a homogeneous solution was obtained. By varying the amount of acid, membranes of different acid concentrations (5 wt.%, 15 wt.%, 20 wt.%) were prepared. A 60 wt.%

of KOH and 3 wt.% of cross linker triallylamine based on wt.% of PVA were dissolved in distilled water. The KOH-cross linker solution was mixed with the homogeneous PVA/acid solution and stirred at 60 °C for about 2h until a homogeneous and clear solution was obtained. This solution was cast on a Teflon mold and then dried at room temperature. The average thickness of the modified membranes was about 0.60-0.75 mm.

The PVA membranes were soaked in an 8.0M KOH aqueous solutions for alkalization at room temperature and equilibrated for 2h. In this process KOH is doped into the PVA membrane [11]. Membranes were removed from the KOH solution, wiped and then dried at room temperature before conductivity measurement. Fig. 1 presents a block diagram describing the formulation procedure for the PVA anion exchange membrane.
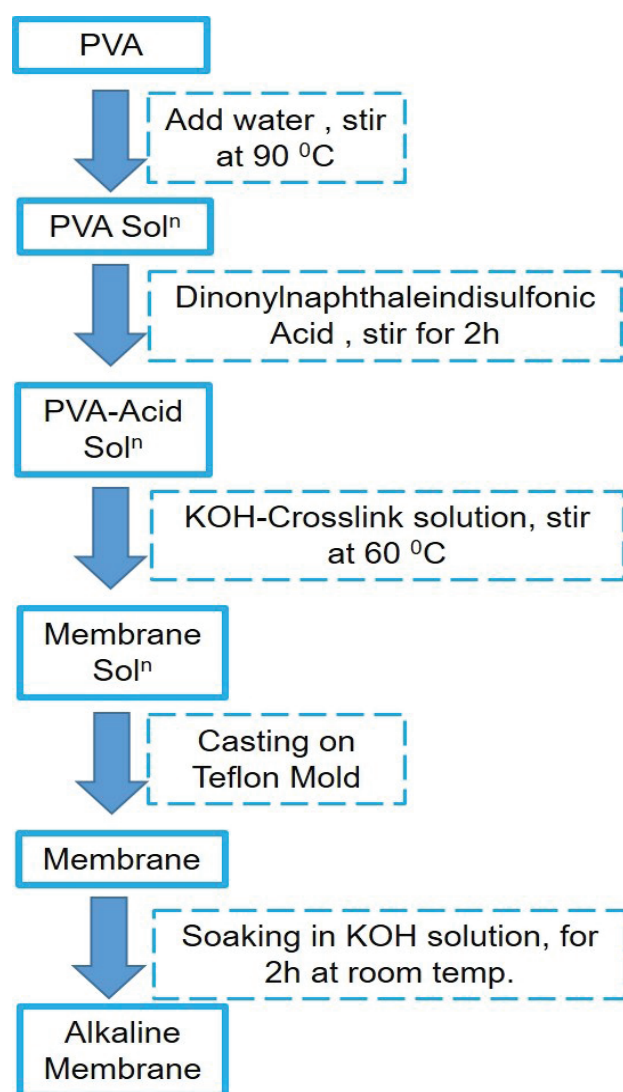

Fig. 1. Schematic diagram of preparation of PVA ion conductive membrane.

2.3 Characterization

Conductivity test: The anion conductivity of the membranes was calculated by the electrochemical impedance spectroscopy (EIS) method. The measurements were done using a PARSTAT 2273 (Princeton Applied Research Co., Power Suite Software) impedance analyzer in potentiostatic mode. The conductivity experiments were done at a frequency range of 10 Hz to 1.5 MHz; thirty points were collected within this frequency range. The electrode surface area was 2.51 cm^2. The resistance value was measured at the high frequency intercept of the impedance with the real axis. If the high frequency point didn't cut the real axis, the point was extrapolated to cut the real axis. The proton conductivity was calculated by using equation 1,

$$\sigma = t / (A \times R) \dots \dots \dots \dots \dots \dots \dots \dots \dots \text{(1)}$$

where σ represent the conductivity of the membrane (S/cm), R is the measured resistance on the membranes (Ω), t is the thickness of membranes (cm) and A is the cross-sectional area (cm^2) perpendicular to current flow. The membranes were cut in small pieces and clamped between two copper electrodes. Five samples from each membrane were tested and the average value was taken as the conductivity of the membrane.

Fourier transform infrared (FTIR) spectroscopy: FTIR spectra were obtained using a Thermo-Scientific Nicolet 6700 FTIR Spectrometer with Smart Orbit diamond attenuated total reflectance (ATR) accessory. IR spectra were obtained at a resolution of 4.0 cm^{-1} over a 400 to 4000 cm^{-1} wave number range and 32 scans.

Differential scanning calorimetry (DSC): TA Instruments DSC Q1000 was used for the thermal scans of the membranes in the presence of nitrogen. The PVA modified membranes were subjected to a heat/cool/heat cycle to remove any thermal history that existed. The DSC thermograms for the samples that are shown in this study are the result of the second heating of the samples. For the PVA samples the heat cycle was ramped from room temperature to 250 °C at 10 °C/min and the cooling cycle followed at a speed of 15 °C/min from 250 °C to room temperature.

Thermogravimetric analysis (TGA): Thermal gravimetric analysis (TGA) was performed using a TA Instruments TGA Q500. Measurements were run under nitrogen, using a scan rate of 10 °C min^{-1}. The PVA samples were heated to 700 °C.

Tensile test: Tensile tests were conducted on the neat, and modified PVA membranes with a 44.5 N load cell. The

samples were cut into dog bones according to ISO 527-2-5A. The thickness of the samples was measured using a thin membrane thickness gauge (Timetrade TT 260). Five samples from each membrane were tested and the average value was taken as the ultimate strength. The samples were tested at a crosshead speed of 2.54 mm/min.

3.   RESULTS AND DISCUSSION

3.1   Effect of Acid Amount on Ionic Conductivity

Fig. 2 shows the ionic conductivity of the PVA anion membranes as a function of acid concentration. The acid concentration was varied from 5% to 20% based on PVA wt.%. All modified membranes were dried after soaking in KOH solution. The highest ionic conductivity value of 0.163 S/cm was obtained by the 15% acid modified PVA membrane soaking at 8.0M KOH solution. Other two modified membranes also showed ionic conductivity of approximately 10^{-1} S/cm. The acid interpenetrated into the PVA matrix and resulted more charge carriers.

In this work, the fabricated PVA membranes showed 10 times higher conductivity compared to these established PVA membranes at room temperature [17-19]. The studies with established PVA anion exchange membranes found conductivity in the range of 10^{-2} S/cm at room condition. Shang et al. found a conductivity in the range of 10^{-1} S/cm at 80 ^{0}C; however, at room condition conductivity showed in the range of 10^{-2} S/cm [20].
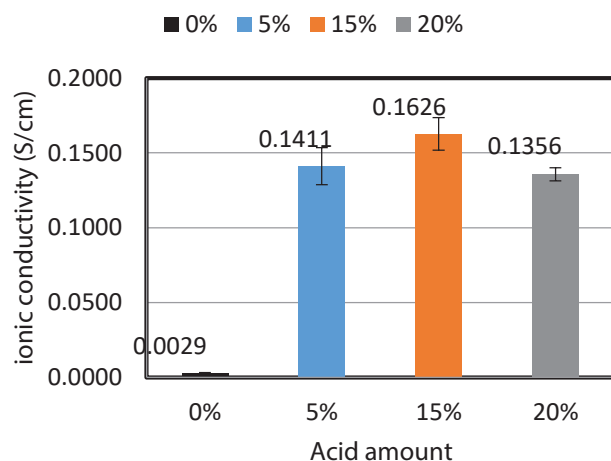

Fig. 2.   Ionic conductivity of PVA membranes as a function of acid amount.

The Nyquist plots (electrochemical spectra) for the modified PVA membranes are shown in Fig. 3. All the samples showed half semi-circle Nyquist plots. The

high frequency intercept part (squared part shown in Fig. 3) is shown in Fig. 4 in a larger form to describe the membrane's resistance. From the intercept point to the 'X' axis, resistance value can be read. The 15% acid membrane showed a minimum membrane resistance of 0.19 Ω, while 5% and 20% showed higher resistance value; which verify the ionic conductivity results in Fig. 2.
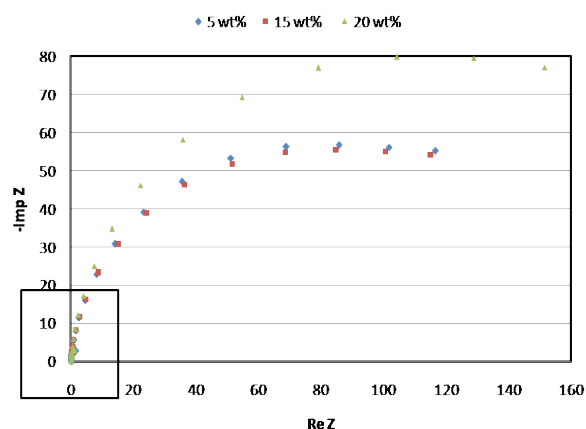
Fig. 3.   Electrochemical spectra for PVA modified membranes.
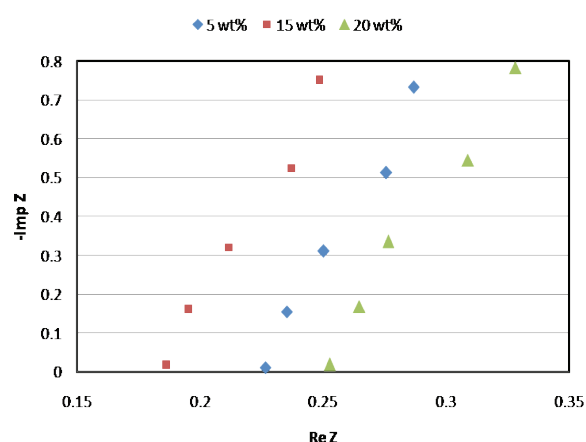
**Fig. 4:**   Intercept part of Nyquist plot.

3.2   Effect of KOH Concentration on Ionic Conductivity

To Investigate the ionic conductivity at different KOH concentrations, the 15% acid membrane was chosen because of its higher ionic conductivity. The ionic conductivity measurements for different KOH concentrations are shown in Fig. 5. The conductivities were measured at 1.0M, 4.0M, 8.0M and 10.0M KOH concentrations at room temperature. The conductivity is increased with the increasing concentration of KOH

up to 8.0M concentration. Higher concentrations of KOH resulted in greater impregnation of OH- into the composite membrane. This doping of KOH also enhanced the percentage of water in the polymer matrix [4]. Water binds to KOH on the membrane, which indicates a stable swelling behavior. Higher conductivity proves the higher uptake of hydrophilic groups in the polymer matrix. In a study the swelling ratio of PVA: PAA sample showed three times more than that of pure PVA polymer membrane due to the uptake of the hydrophilic groups in the PVA/PAA polymer membrane system [6].

However, 10.0M KOH concentration did not contribute more to the ionic conductivity. The higher concentration of KOH limited the movement of the free ions in polymer chain, referred to as weak ionic mobility [3, 11].
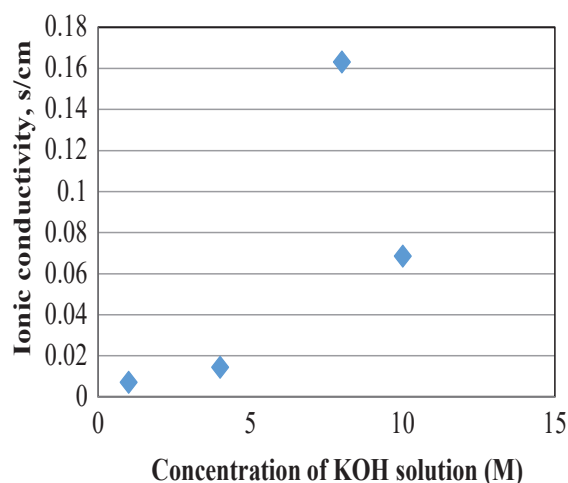
Fig. 5: Effect of KOH concentration on ionic conductivity of 15% PVA acid membrane.

3.3 FTIR STUDY

Fig. 6 shows the IR spectrum for neat PVA, 5% PVA acid and 15% PVA acid membranes. The characteristic peaks of neat PVA included 3252.0 cm^{-1} (-OH stretching vibration), 2936.5 cm^{-1} (C-H asymmetric stretching vibration), 1654 cm^{-1} (-OH symmetric wagging vibration), 1414 cm^{-1}, 1321 and 1085 cm^{-1} (C-H asymmetric and symmetric wagging vibrations) [21-22]. Compared with the spectrum of neat PVA, the relative intensity of the peaks around 3252 cm^{-1} and 2936 cm^{-1} decreased with the acid amount. This indicated possible interactions between the PVA polymer segment and the acid. The peaks at 1414 cm^{-1} and 1321 cm^{-1} for the acid containing membranes shifted closer and merged as one peak for 15% acid membrane. A new peak in the acid containing membranes at 1032 cm^{-1} was assigned to the -SO$_3$H group [23].
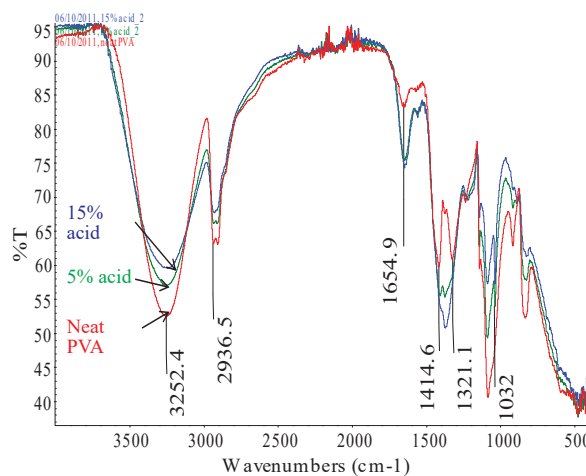
Fig. 6. FTIR spectra for neat PVA, 5% acid and 15% acid membranes.

3.4. Thermo-gravimetric (TGA) Analysis

Fig. 7 shows the TGA thermograms for neat PVA and acid containing modified PVA membranes. All the samples started to lose weight before 100 °C. The weight loss in the region between 80-150 °C was associated with the removal of water molecules from the polymer. After 150 °C, the neat PVA membrane showed a thermally stable region up to 240 °C. At 267 °C a 50% weight loss was observed due to the degradation of hydroxide groups on the polymer matrix [10-11]. The modified membranes showed a 35% weight loss at 180-200 °C region and 50% loss at 228 °C. The first loss at 35% was due to the decomposition of sulfonic acid groups [24] and the second loss at 50% was due to the decomposition of hydroxide groups. All the samples showed a weight loss in the 400-500 °C region due to the decomposition of main chain of PVA [11, 24]. In Fig. 7, it can be seen that the modified membranes contained higher residues at 680 °C than the neat membrane.
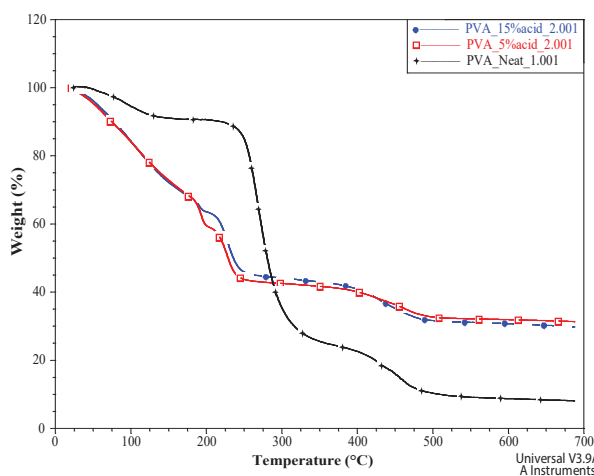
Fig. 7. TGA curves for neat PVA and acid containing PVA membranes.

3.5. DSC Analysis

Fig. 8 shows the second DSC thermal scans for the neat PVA and the 15% acid membranes. The glass transition temperature, T_g, of the neat PVA was 84.35 °C. The 15% acid membrane showed a T_g of 87.89 °C. Here the glass transition temperature is not changed significantly for the modified membrane in comparison to the neat membrane. In the first heating cycle the peak between 100 °C to 150 °C (not shown here) was due to removal of solvent water from the membranes. The melting of the neat membrane started at 210 °C and completely melted at around 228 °C. The degradation temperature of the acid membrane was 228 °C; this membrane was heated up to 210 °C. The melting peak of the acid membrane was not as clear as that for the neat membrane. However, it can be seen that the melting started at 200 °C for the acid membrane.
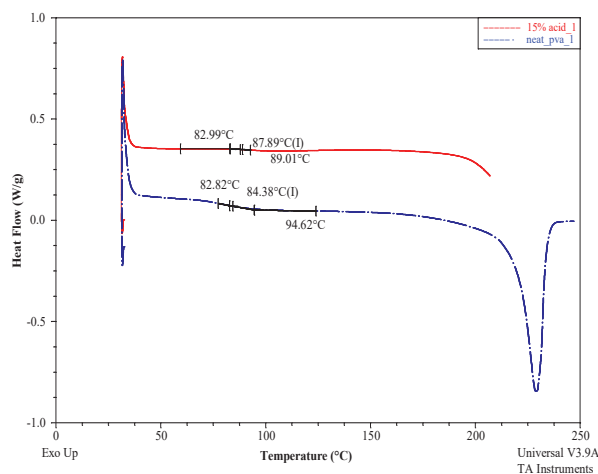

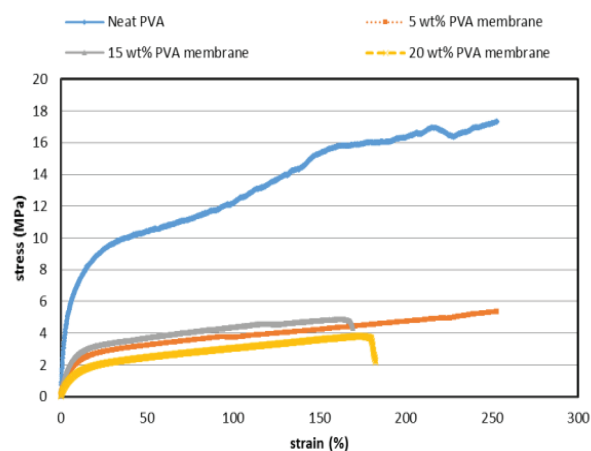**Fig. 8.** Thermal scans for neat PVA and 15% acid containing membranes.

Fig. 9. Mechanical behavior of modified PVA and neat PVA membranes.

The strength of neat PVA membrane was about 16.9 MPa similar to that reported by Chen et al. [25]. The 5% acid membrane displayed a mechanical strength of 5.23 MPa and the elongation at break was 235.33%. The 15wt.% and 20wt.% membranes showed strengths of 4.91 MPa and 3.91 MPa, respectively. The strength and strain decreased with acid content. In thermal analysis it can be seen that the melting of PVA was reduced when the acid was added to the PVA polymer. It indicated the amorphous phase was increased [26] and the ionic conductivity was also localized to the amorphous region [27]. It was assumed that acid amount penetrated the PVA matrix and made it more amorphous. Table I summarizes the stresses and strains of the tested membranes. These strengths were better compared to the strengths of the PVA/poly-acrylic-acid membranes [6].

Table I: Stress-strain data for neat and modified PVA membranes

	Average Ultimate Tensile Strength (MPa)	Average Strain (%)
Neat PVA	16.9 ± 0.4	252.33 ± 14.2
5 wt.% acid	5.23 ± 0.29	235.33 ± 30.59
15 wt.% acid	4.91 ± 0.08	194.67 ± 25.93
20 wt.% acid	3.91 ± 0.18	168.14 ± 19.14

4. CONCLUSION

In this paper, a PVA based AEM with high conductivity are synthesized and evaluated the tensile and thermal performance of the membranes. The membranes are fabricated by casting method while dinonylnaphthaleindisulfonic acid and a cross linker, triallylamine, are used. Three different modified membranes are studied here – 5%, 15% and 20% based on wt.% of acid content. The PVA polymeric membrane showed excellent film-forming ability and an excellent OH− conductivity with alkaline stability. The 15% acid modified membrane showed the highest anion conductivity of 0.163 S/cm (10^{-1} S/cm) at room temperature while the neat membrane's conductivity was 10^{-3} S/cm. The strength of the acid modified membrane revealed that increasing the acid amount reduced the strength of the membrane. The 5% acid membrane showed higher strength compared to 15% and 20% acid membranes. Thermal analysis of 15% acid membrane has shown that the Tg was 87 °C, which was higher than that of the neat PVA membrane (84 °C Overall, higher conductivity and thermomechanical properties proved the 15% acid modified membrane as a strong and reliable candidate for solid electrolyte membrane.

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