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Alkaline blend polymer electrolytes based on polyvinyl alcohol (PVA)/tetraethyl ammonium chloride (TEAC)

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Abstract

Alkaline blend polymer electrolytes based on PVA/TEAC were obtained by a solution casting technique. Tetraethyl ammonium chloride (TEAC) was added to PVA polymer matrix to form an alkaline blend polymer electrolyte exhibiting excellent ionic transport and mechanical properties. The ionic conductivity of the alkaline PVA/TEAC blend polymer electrolyte was found to be of the order of 10^{-2} S cm^{-1} at ambient temperature when the blend ratio of PVA:TEAC varied from 1:0.2 to 1:2. The characteristic properties of alkaline PVA/TEAC blend polymer electrolytes were examined using DSC, TGA, XRD, SEM, EA, stress–strain tests and AC impedance spectroscopy. The ionic transport properties for the blend polymer electrolytes were measured using Hittorf's method. It was found that the anionic transport numbers (t^-) were between 0.82 and 0.99; the membranes are highly dependent on the types of alkali metal salts and the chemical composition of the polymer blend. The ionic transport and mechanical properties were greatly improved at the expense of the ionic conductivity. In this work we demonstrate that alkaline blend polymer electrolyte can be tailored with a blend technique to achieve specific characteristic properties for battery applications.

1. Introduction

Solid polymer electrolyte (SPE) electrolytes can be applied for a variety of electrochemical devices such as cellular phones, smart credit cards and laptop computers [1]. Polymer complexes consisting of polyethylene oxide (PEO), plasticizers and alkali metal salts, discovered by Wright et al. [2, 3] and Armand et al. [4] are free of solvent polymer electrolytes. Alkaline SPEs based on PEO have been studied for application in Ni-Cd, Ni-Zn [5, 6] and Ni-MH secondary battery systems [7, 8]. These authors reported that alkaline PEO-KOH polymer electrolyte exhibited ionic conductivity around 10^{-3} S cm^{-1} at room temperature. Yang and Lin prepared alkaline polymer electrolyte based on PEO-PVA-KOH for use in secondary Ni–MH [9] and primary Zn-air batteries [10]. Lewandowski et al. [11] synthesized PEO-KOH polymer electrolyte for electrical double layer capacitors (EDLCs). Yang and Lin [12, 13] also reported PVA–KOH polymer electrolyte for use in Ni-MH and Zn-air batteries. Agel et al. [14, 15] prepared an alkaline anionic exchange membrane for fuel cells by grafting quaternary amines on the epichlorhydride polymer with ionic conductivities of about 10^{-2} S cm^{-1} and with anionic transport number (t^-) greater than 0.9.

There is little literature data on alkaline blend polymer electrolyte based on PVA/TEAC. In this work we report the preparation and characteristic properties of alkaline PVA/TEAC blend polymer electrolytes. Tetraethyl ammonium chloride (TEAC) was directly blended with PVA polymer to form an alkaline polymer electrolyte, so-called anionic ionomer membrane with very high t^-; it shows excellent ionic transport and mechanical properties.

Both DSC and TGA were used to analyze the thermal properties of the PVA/TEAC blend polymer electrolyte. XRD and SEM were used to investigate the crystal structure of the blend polymer film and examine its surface morphology, respectively. The TEAC content in the film was determined by elemental analysis (EA). The ionic conductivity was measured by AC impedance spectroscopy. The yield stress and elongation were examined by the stress–strain measurement. The ionic transport numbers were measured using Hittorf's method. Thus, the characteristic properties of PVA/TEAC blend polymer electrolytes with different compositions were compared and discussed.

2. Experimental

PVA (M.W. 75,000–80,000, Chang-Chung Chemicals), tetraethyl ammonium chloride (TEAC), $(C_2H_5)_4NCl$ (Aldrich), dimethyl sulfoxide (DMSO), $(CH_3)_2SO$ (Aldrich), and KOH (Merck) were used as received. The alkaline PVA/TEAC blend polymer electrolytes were prepared by a solution casting method. The appropriate weight ratios of the PVA and TEAC were directly dissolved in DMSO with agitation for about 12 h at 60 °C. After both PVA polymer and TEAC were completely dissolved in DMSO, the resulting polymer solutions were stirred continuously until the polymer solution took on a homogeneous viscous appearance. The resulting homogeneous solution was poured onto a petri disk and weighed immediately, and the excess DMSO was evaporated slowly at 80 °C in a vacuum oven. After the evaporation, the petri disk with the PVA/TEAC blend polymer was weighed again. The free standing film was washed several times with D.I. water in an ultrasonic bath to remove any trace of TEAC, and then dried again for further test.

The PVA/TEAC blend polymer films were immersed in 32 wt.% KOH solution for 24 h. After being immersed the films were reweighed and the thickness was measured by digital micrometer (TECLOCK PC-467, Japan) in the range between 0.4 and 0.5 mm. Conductivity measurements were made by an AC impedance method. The polymer electrolyte was sandwiched between SS316 stainless steel, ion-blocking electrodes, each with a surface area of 0.785 cm^2, in a spring-loaded glass holder. A thermocouple was positioned close to the blend polymer electrolyte film for temperature measurement. AC impedance measurements were carried out using an AutoLab from Eco Chemi, and a computer program GPE. The frequency range 1 MHz –10 Hz at an excitation signal of 10 mV was used. The AC impedance of the blend polymer electrolyte was measured from 30 to 70 °C. Temperature was maintained within ± 0.2 °C by a convection oven.

DSC thermal analysis was carried out using a Perkin Elmer Pyris 7 DSC system. Measurements were made at heating temperatures from 20 to 250 °C, and at a heating rate of 10 °C min^{-1} in a N_2 atmosphere with about 10 mg of sample. TGA thermal analysis was carried out using a Perkin Elmer Pyris 7 TGA system. Measurements were made at heating temperatures from 25 to 500 °C, at a rate of 10 °C min^{-1} under N_2 atmosphere with 10–20 mg samples. The crystal structures of the PVA/TEAC blend polymer films were examined using a Philips X'Pert X-ray diffractometer (XRD) with Cu Kα radiation of wavelength λ = 1.54056 Å for 2θ angles between 10 and 80°. The surface morphology and microstructure of the blend polymer film was examined using a S-2600H scanning electron microscope (Hitachi Co., Ltd.). EA was used to analyze the chemical composition of the films. Before analysis, a calibration curve was established by using several fixed weight ratios of PVA and TEAC. The compositions of C, H, N and S for various sample films were examined by an elemental analyzer (Perkin–Elmer EA2400). The mechanical strength was measured from stress–strain tests using an Instron model 5544 Universal Instruments.

The ionic transport properties were examined by using a dynamic Hittorf's method [15]. A test cell with two Pt electrodes was made for electrolysis. The PVA/TEAC blend polymer electrolyte was located and fixed in two separated compartments with the same 1 M KOH solution. The electrode reaction occurred on the Pt-cathode, producing H_2 and OH^-, and the Pt anode produced O_2. The balance of OH^- ions in each compartment led to transport numbers after a fixed amount of charge had been passed through the film. After electrolysis, the concentrations of OH^- ions in the two compartments were determined by titration with 1 M HCl stock solution. The cationic and anionic transport numbers were calculated as follows [15]:

$$t^+ = \frac{nF}{It}(C^0V^0 - C^+V^+) \text{ and}$$
$$t^- = \frac{nF}{It}(C^-V^- - C^0V^0) \qquad [1]$$

where n is the charge of the OH^- ion, F is the Faraday constant, 96,500 C mol^{-1}, I is the imposed current, t is the electrolysis time, C^0, C^+, C^- are the initial and final OH^- ion concentrations in the anodic and cathodic compartments, respectively, V^0 is the initial volume in each compartment, and V^+ and V^- are the final volume in the anodic and cathodic compartments, respectively. All blend polymer samples were tested at least three times. The scheme for the blend PVA polymer host with TEAC (quaternary amine) is shown in Figure 1.

3. Results and discussion

3.1. *Thermal analysis*

The DSC thermograph for the PVA polymer film and the PVA/TEAC blend films with different blend ratios are shown in Figure 2. An endothermic peak occurs at 240 °C, which corresponds to the melting temperature (T_m) of PVA. It has been reported that the T_m of pure PVA powder with 98–99% of hydrolysis degree is 225 °C [12]. It is found that the melting temperature, T_m, of PVA/TEAC blend polymer film shifts to a lower temperature ($T_m = 190$ °C) when TEAC is blended into PVA polymer with a ratio of 1:1. A lower T_m for the higher blend ratio indicates a change between a semi-crystalline phase and an amorphous phase.

TGA thermographs for the PVA/TEAC blend polymer films are shown in Figure 3. There is a weight loss of 13% at a temperature of 100 °C. This indicates that the film contains some free water. There is a constant weight plateau region between 100 and 250 °C. It is observed that the film shows multiple step degradation, which occurs in the region between 250 and 500 °C. The

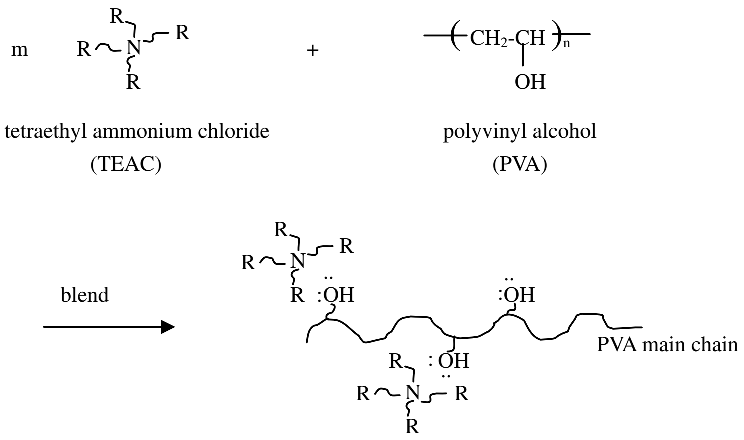


Fig. 1. Scheme for the PVA polymer blending with TEAC.

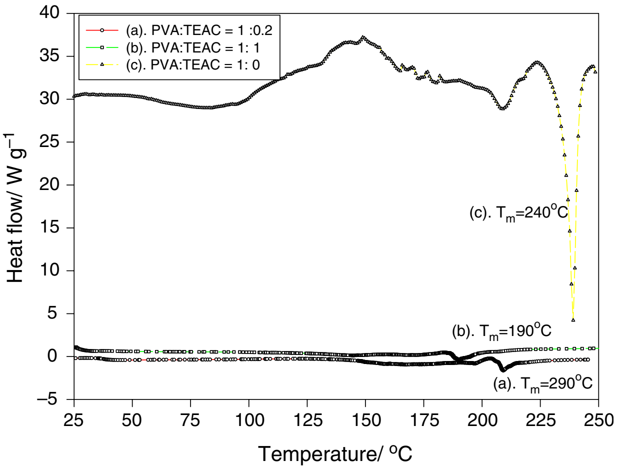


Fig. 2. DSC thermographs for PVA/TEAC blend polymer films.

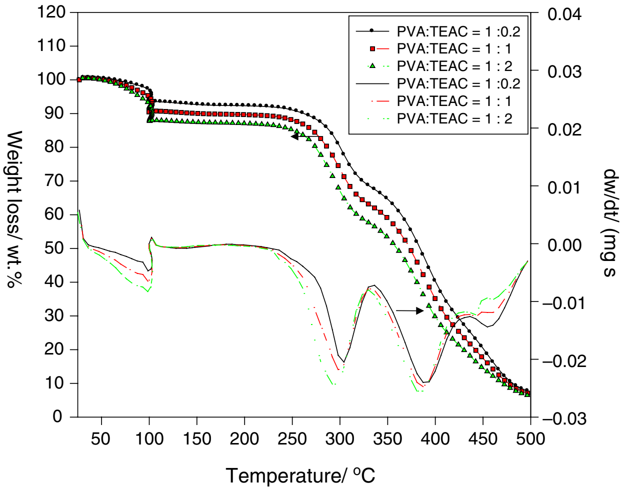


Fig. 3. TGA thermographs for PVA/TEAC blend polymer films with various blend ratios.

onset decomposition is 250 °C. The PVA/TEAC blend polymer is severely degraded over 250 °C. It is also found that the maximum degradation rates occur at two temperatures, 300 and 380 °C. It is clearly observed that the PVA/TEAC blend polymer film is stable in the temperature range 100 to 250 °C.

3.2. *Structural analysis and morphology*

Figure 4 shows the diffraction pattern for pure PVA polymer film and the PVA/TEAC blend polymer films. It was observed that the PVA polymer exhibited a semi-crystalline structure with a peak at a 2 θ angle of 20°. As more TEAC is added the intensity of the PVA peak is greatly reduced. This implies that the addition of TEAC to the PVA polymer matrix increases the amorphous region. As can be seen in Figure 4, a large broad peak at 2θ of 20° is revealed. This is known as the “amorphous hump”. This indicates that the PVA/TEAC blend polymer film becomes amorphous. The degree of amorphous material increases as the blend ratio of PVA:TEAC is higher. The actual mechanism of ionic transport in polymer electrolyte is still not clear. The amorphous characteristic of the PVA/TEAC blend polymer film produces much higher ionic transport. This is due to more flexible local chain segmental motion in the blend polymer.

SEM photographs for the blend polymer films with different blend ratios of PVA:TEAC are shown in Figure 5. The SEM photograph for the film at PVA:TEAC = 1:0.2 shows uniform surface morphology, as shown in Figure 5(a). Figure 5(b) shows the SEM photograph for the blend polymer film at PVA:TEAC = 1:2. This film also exhibits a uniform and homogeneous surface. It is found that there is no phase separation for any PVA/TEAC blend polymer films, and all films appear translucent. In addition, as can be seen from DSC result, there is only one T_m indicating that the PVA polymer blended with TEAC forms a homogenous and stable freestanding film.

3.3. *Conductivity measurement*

The AC impedance spectra of alkaline PVA/TEAC blend polymer electrolyte with PVA:TEAC = 1:0.2 at different temperatures are shown in Figure 6. The AC

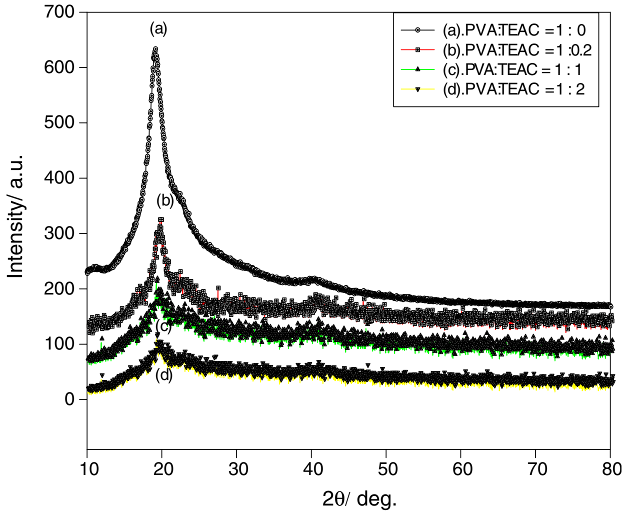


Fig. 4. XRD patterns for PVA/TEAC blend polymer films with various blend ratios.

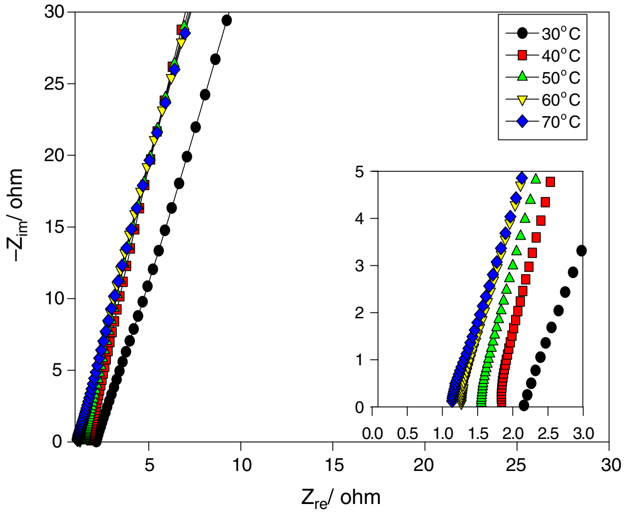
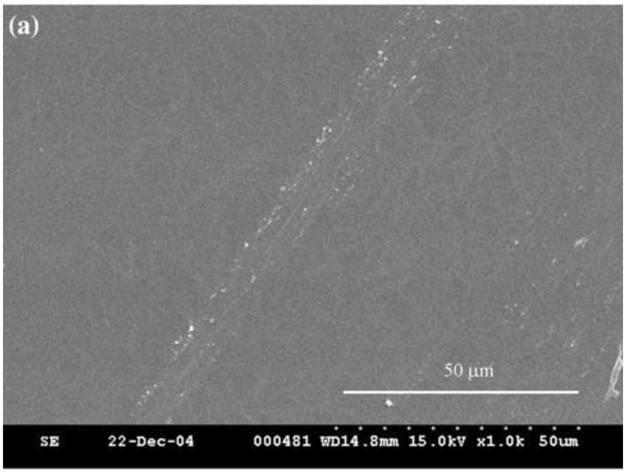


Fig. 6. AC impedance spectra for alkaline PVA/TEAC blend polymer electrolyte at a ratio of PVA:TEAC = 1:0.2 at different temperatures; the inset for high frequency region of spectra.

PVA:TEAC=1:0.2



PVA:TEAC=1:2

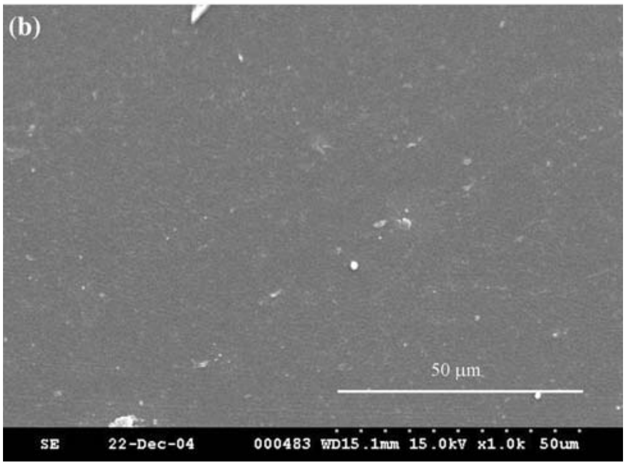


Fig. 5. SEM photographs for the PVA/TEAC blend polymer films. (a) PVA:TEAC = 1:0.2; (b) PVA:TEAC = 1:2.

spectra are typically non-vertical spikes for blocking electrodes, i.e., SS|PVA/TEAC blend SPE|SS cell. Typical AC impedance spectra show two well-defined regions. In the high frequency range, which is related to the ionic conduction process in the bulk of the polymer electrolyte, the bulk resistance (R_b) of the film can be obtained. In the low frequency range, a straight line parallel to the imaginary axis attributable the effect of blocking is found.

Since the stainless (block) electrode is used in impedance analyses, the electrolyte/electrode interface can be regarded as a capacitance. When the capacitance is ideal, it should show a vertical spike in the impedance diagram. However, an inclined spike at an angle (θ) less than 90° is found instead of the vertical spike. This is due to the non-homogeneous or rough electrolyte/electrode interface.

Analysis of the AC spectra yields information about the properties of the polymer electrolyte such as bulk resistance (R_b). The bulk resistance can be calculated from the intercept at the higher frequency side on the Z_{re} axis. The R_b value is converted into the ionic conductivity of blend polymer electrolyte, σ, using the equation $\sigma = l/R_bA$, where l is the film thickness (cm), A is the area of the blocking electrode (cm^2), and R_b is the bulk resistance (ohm) of the blend polymer electrolyte.

Typically, the values of R_b are in the range 1–3 ohm (as shown in the inset of Figure 6) and they are dependent on the composition of the blend polymer electrolytes. The value of ionic conductivity is of the order of 10^{-2} S cm^{-1}. Table 1 shows the conductivity values at different blend ratios at different temperatures. It is observed that the ionic conductivity at PVA:TEAC = 1:2 is higher than that at ratios of 1:0.2 and 1:1. As a result, the conductivity value of alkaline PVA/TEAC blend polymer electrolyte with PVA:TEAC = 1:2 (σ = 0.0459 S cm^{-1}) is close to that of alkaline PVA polymer electrolyte (σ = 0.0471 S cm^{-1}) at ambient temperature (Table 2).

The temperature dependence of the ionic conductivity of alkaline PVA/TEAC blend polymer electrolyte is of

Table 1. The conductivities (S cm^{-1}) of alkaline PVA/TEAC blend polymer electrolytes with various blend ratios at different temperatures

T/°C	Ratios		
	PVA:TEAC = 1:0.2	PVA:TEAC = 1:1	PVA:TEAC = 1:2
30	0.0106	0.0221	0.0459
40	0.0138	0.0223	0.0462
50	0.0164	0.0233	0.0464
60	0.0201	0.0249	0.0480
70	0.0224	0.0259	0.0497

Table 2. The conductivities (S cm^{-1}) of alkaline PVA/TEAC blend and PVA polymer electrolytes at ambient temperature

Properties	Ratios			
	PVA:TEAC = 1:0	PVA:TEAC = 1:0.2	PVA:TEAC = 1:1	PVA:TEAC = 1:2
σ/S cm^{-1}	0.0471	0.0106	0.0221	0.0459

the Arrhenius type [12–13]. The $\log_{10}(\sigma)$ vs $1/T$ plot, as shown in Figure 7, gives an activation energy (E_a), which is dependent on film composition. The E_a value for alkaline PVA/TEAC blend polymer electrolytes lies in the range 3–6 kJ mol^{-1}. It is experimentally found that the water content in all films is in the range 40–50 wt.%

3.4. *Mechanical properties*

The stress–strain test results for different compositions of PVA/TEAC blend polymer films are shown in Figure 8. Table 3 shows the experimental results of stress–strain measurements for various film compositions at 25 °C. The PVA/TEAC (1:0.2) blend film exhibits a stress property with a yield stress of 66.4 kgf cm^{-2}, but with good elasticity with an elongation-at-break value at 405%. Moreover, the PVA/TEAC (1:1) blend polymer film shows a yield stress of 88.3 kg_f cm^{-2} and with a high elongation-at-break value of 443%. Furthermore, the PVA/TEAC (1:2) blend film exhibits a low yield stress of 31.3 kg_f cm^{-2} and with a low elongation-at-break value of 86%. The higher the TEAC addition into the PVA host, the lower the mechanical strength of the blend polymer film. In addition, it is seen that the optimum composition for the PVA/TEAC blend polymer film is around 1:1, as shown in Table 3.

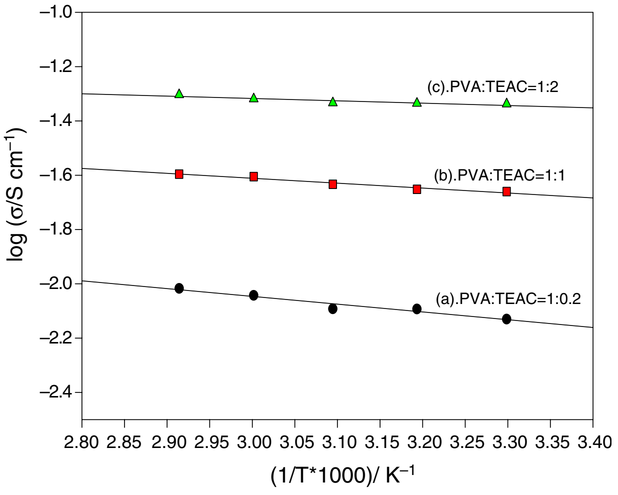


Fig. 7. Arrhenius plot for alkaline PVA/TEAC blend polymer electrolytes with various blend ratios.

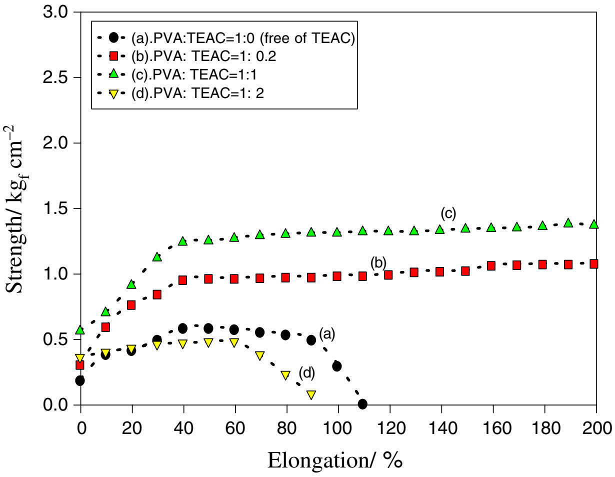


Fig. 8. Mechanical strength test results for the PVA/TEAC blend polymer films with various blend ratios.

Table 3. The mechanical strength test results of the PVA/TEAC blend polymer films at pull rate of 200 mm min^{-1} at 25 °C

Polymer film	Item				
	Thickness/ mm	Width/ mm	Strength/ kg_f	Stress/ kg_f cm^{-2}	Elongation/%
PVA:TEAC = 1:0	0.16	10	0.6	37.5	98
PVA:TEAC = 1:0.2	0.16	10	5.3	66.4	405
PVA:TEAC = 1:1	0.16	10	3.4	88.3	443
PVA:TEAC = 1:2	0.16	10	3.8	31.3	86

3.5. *Ionic transport properties*

The values of anionic transport numbers of the PVA/TEAC blend polymer films with different alkali metal salts measured using Hittorf's method are shown in Table 4. The anionic transport numbers (t^-) are measured as a function of composition and the types of alkali metal salt. All anionic transport number values at different compositions are in a range 0.96–0.99 in 1 M KOH solution, 0.91–0.96 in 1 M NaOH solution and 0.86–0.93 in 1 M LiOH solution. The t^- of the PVA/TEAC blend polymer in KOH solution exhibits the highest value. On the other hand, the t^- value of the PVA/TEAC blend film in LiOH solution is lowest.

Table 4. The anionic transport number values of alkaline PVA/TEAC blend polymer electrolytes with different alkalis metallic salts

Alkalis salts	Ratios			
	PVA:TEAC = 1:0	PVA:TEAC = 1:0.2	PVA:TEAC = 1:1	PVA:TEAC = 1:2
NaOH	0.86	0.91	0.95	0.96
KOH	0.93	0.96	0.99	0.99
LiOH	0.82	0.86	0.92	0.93

Yang et al. [18] prepared alkaline blend polymer electrolyte based on PVA/PECH for primary Zn-air batteries. The PVA/PECH (1:1) blend polymer electrolyte exhibits excellent chemical and mechanical properties, as listed in Table 5. The mechanical properties of alkaline PVA/PECH (1:1) blend films are greatly enhanced, compared with the PVA polymer films. The polymer membrane becomes strong and tough. However, it shows slightly poorer ionic transport ($t^- = 0.86$) and slightly reduces the ionic conductivity ($\sigma = 0.001$ S cm^{-1}) when compared with alkaline PVA polymer electrolyte ($t^- = 0.95$ and $\sigma = 0.0472$ S cm^{-1}). Table 5 compares the characteristic properties of PVA/TEAC polymer electrolyte and PVA polymer electrolyte. The ionic transport property of PVA/TEAC (1:1) blend polymer electrolyte is greatly increased up to $t^- = 0.99$, but the ionic conductivity is still of the order of 10^{-2} S cm^{-1}. Thus, characteristic properties such as mechanical strength, electrochemical stability and ionic transport properties for the PVA-based polymer electrolytes can be tailored by blending with quaternary amines.

3.6. *Composition of PVA/TEAC blend polymer electrolytes*

The TEAC content in the PVA/TEAC blend polymer film was determined by EA. The calibration curve for the TEAC content vs the content of N is shown in Figure 9. The compositions of C, H, N, and S are measured for various compositions of blend polymer films, as listed in Table 6. The TEAC content in the PVA/TEAC (1:0.2) blend polymer film is 16.35 wt.%; this value being close to the nominal value of 16.67%. However, the TEAC content in the PVA/TEAC (1:1) blend polymer film is 39.89 wt.%; its value is much lower than the nominal value of 50%. Moreover, the TEAC content in the PVA/TEAC (1:2) blend polymer film is 70.28 wt.%; this value is slightly higher than the nominal value of 66.67 wt.%. It can be concluded that the actual TEAC content in the PVA/TEAC blend polymer electrolyte is roughly consistent with the nominal blend ratio.

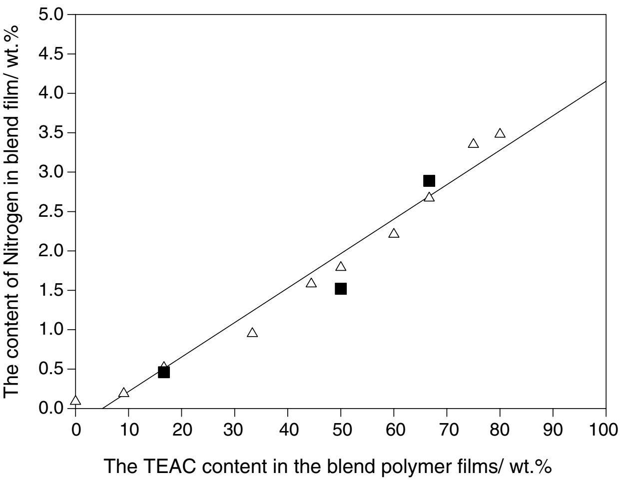


Fig. 9. The results of EA for the PVA/TEAC blend polymer films with various blend ratios; Line + triangle (Δ): calibration curve; solid square (■): exp. data.

Table 6 The results (wt.%) of EA for the PVA/TEAC blend polymer electrolyte at various blend ratios

Blend ratios	Elements				
	C	H	N	S	Actual TEAC content (wt.%) (Exp. data)
PVA:TEAC = 1:0.2 (nominal 16.66 wt.%)	51.08	10.11	0.46	0.04	16.35
PVA:TEAC = 1:1 (nominal 50.00 wt.%)	48.01	9.85	1.52	0.015	39.89
PVA:TEAC = 1:2 (nominal 66.67 wt.%)	46.76	9.76	2.89	0.02	70.28

4. Conclusions

The characteristic properties of alkaline PVA/TEAC blend polymer electrolyte were studied using DSC, TGA, XRD, SEM, EA, stress–strain tests, AC impedance spectroscopy and Hittorf's method. The films possessing

Table 5. Comparison of some characteristic properties of alkaline PVA-based polymer electrolytes

Properties	Types		
	PVA SPE	PVA/PECH blend SPE (PVA:PECH = 1:1)	PVA/TEAC blend SPE (PVA:TEAC = 1:1)
σ/S cm^{-1} at r.t.	0.0472	0.001	0.0231
Film thickness/mm	0.48	0.53	0.46
Mechanical stress/kg$_f$ cm^{-2}	8.3	262	88.3
Elongation/%	457	106	443
t^- (1 M KOH)	0.95	0.86	0.99

ionic conductivity of the order of 10^{-2} S cm^{-1} at ambient temperature were prepared. It was found that the PVA/TEAC blend polymer with KOH electrolyte exhibited excellent ionic transport properties with anion transport numbers (t^{-}) of approximately 0.96–0.99.

The electrochemical and ionic transport properties of PVA/TEAC blend polymer film was greatly improved; the blend film became more flexible and tough. It was observed that the PVA/TEAC (1:1) blend polymer film showed the best ionic transport and mechanical properties. In particular, it was found that the characteristic ionic transport properties of the PVA polymer films were greatly enhanced by the addition of quaternary ammonium chloride (TEAC).

Acknowledgement

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