

# An investigation of the proton conductivities of hydrated poly(vinyl alcohol)/boric acid complex electrolytes

M. Şenel · A. Bozkurt · A. Baykal

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**Abstract** Proton-conducting polymer complex electrolytes were prepared by incorporation of boric acid,  $H_3BO_3$  into poly(vinylalcohol), PVA, to form hydrated  $PVAxH_3BO_3$  where  $x$  denotes the number of moles of boric acid per polymer repeat unit. The dried materials were characterized via Fourier transform infrared spectroscopy, thermogravimetry, and X-ray diffraction. The proton conductivity of the hydrated complex electrolytes was measured by AC impedance spectroscopy.  $PVA2H_3BO_3$  with RH ~25% was found to be optimum composition that exhibited proton conductivity of  $1.3 \times 10^{-3}$  S/cm at 80 °C.

**Keywords** Polymer electrolyte · Boric acid · Proton conductivity · X-ray diffraction (XRD)

## Introduction

Proton exchange membranes (PEM) have gained prominence after they become applicable to various technological areas particularly on clean energy systems such as fuel cells. Hydrated perfluorosulfonic acid ionomers, typically Nafion, are the most commonly used membranes that separate into hydrophilic and hydrophobic domains up on swelling [1]. The conductivity occurs via transport of the protons throughout the hydrophilic channels. These membranes have been successfully used in the hydrogen/oxygen fuel cells (PEMFCs) due to their excellent chemical and mechanical stability as well as high proton conductivity [2, 3]. However, there are some limitations such as high cost

and the difficulty in recycling or disposal of the perfluoro-sulfonic acid membranes [4].

Poly(vinylalcohol), PVA, is a water-soluble, polyhydroxy polymer whose physical properties are dependent on the degree of polymerization and degree of hydrolysis. PVA has an excellent chemical resistance; thus, it can be used in many practical applications such as adhesives, textile, and pharmaceutical and biomedical industries due to nontoxic and biodegradable properties [5–7]. PVA can also be modified by chemical crosslinking, which is a highly versatile method to improve the chemical, thermal, and mechanical properties [8]. One of the most common methods is the reaction of hydroxyl groups of PVA with aldehydes to form acetal or hemiacetal [9]. PVA can also physically crosslink with boric acid through hydrogen bonding and ionic interactions in the hydrated state [6, 7].

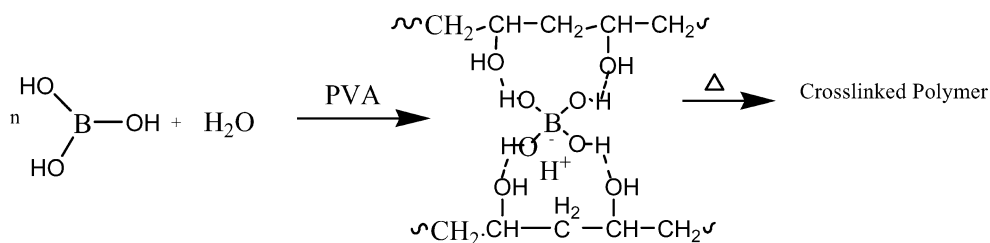
In the present work, we produced hydrated PVA-Boric acid systems at several stoichiometric compositions and investigated their proton-conducting properties. Moreover, the Fourier transform infrared spectroscopy (FT-IR), thermal, and morphology properties of the dried PVA/ $H_3BO_3$  samples were studied at several compositions.

## Experimental

Poly(vinyl alcohol), PVA (degree of hydrolization  $\geq 98\%$ ,  $M_w=72,000$ ), and boric acid were received from Merck. The complex electrolytes were prepared by mixing of PVA and  $H_3BO_3$  at several stoichiometric ratios in hot water to get  $PVAxH_3BO_3$  complex electrolytes, where  $x$  is the molar ratio of  $H_3BO_3$  to polymer repeat unit. Three different polymer electrolytes ( $PVA1H_3BO_3$ ,  $PVA2H_3BO_3$ , and  $PVA3H_3BO_3$ ) were produced. Water contents of the polymer electrolytes were measured by gravimetric mea-

M. Şenel · A. Bozkurt (✉) · A. Baykal  
Department of Chemistry, Fatih University,  
34500 Büyükçekmece-İstanbul, Turkey  
e-mail: bozkurt@fatih.edu.tr

**Fig. 1** Preparation and the structure of hydrated PVA/ $H_3BO_3$  complex electrolyte



surements, i.e., comparing the weight changes before and after complexation. The approximate RH values are 30% for PVA1 $H_3BO_3$ , 25% for PVA2 $H_3BO_3$ , and 15% for PVA3 $H_3BO_3$ .

FT-IR Spectra of the dried samples were recorded using Mattson Genesis II spectrophotometer.

Thermogravimetry (TG) measurements were carried out using Perkin Elmer Pyris 1. TG thermogram of PVA was recorded at a temperature-scanning rate of 10 °C/min, under  $N_2$  atmosphere.

The thermograms hydrated PVA $xH_3BO_3$  electrolytes were recorded by heating the samples from RT to 100 °C at a rate of 5 °C/min and then they hold at this temperature for 30 min under nitrogen atmosphere. Thereafter, the samples were further heated to 650 °C under nitrogen atmosphere at a rate of 10 °C/min.

The structural characterization of the samples were performed using X-ray diffractometer (XRD) model Huber JSO-DEBYEFLEX 1001 diffractometer (Cu  $K_{\alpha}$  radiation) operated at 40 kV and 35 mA. The samples were dried under high vacuum at 80 °C before XRD analysis.

Proton conductivity measurements were carried out in the Max-Planck Institute for Polymer Research, Mainz/Germany using a SI 1260-Schlumberger impedance analyzer. The hydrated samples were sandwiched between gold blocking electrodes and the conductivity was measured from 0 to 100 °C within the frequency range from 10 Hz to 1 MHz. The experiments were carried out under nitrogen atmosphere. Frequency-dependent AC conductivities ( $\sigma_{ac}(\omega)$ ) were measured using Eq. (1).

$$\sigma_{ac}(\omega) = \varepsilon''(\omega) \omega \varepsilon_0 \quad (1)$$

where  $\omega (=2\pi f)$  is the angular frequency,  $\varepsilon_0$  is the vacuum permittivity ( $\varepsilon_0 = 8.852 \times 10^{-14} \text{F/cm}$ ), and  $\varepsilon''$  is the imaginary part of dielectric permittivity.

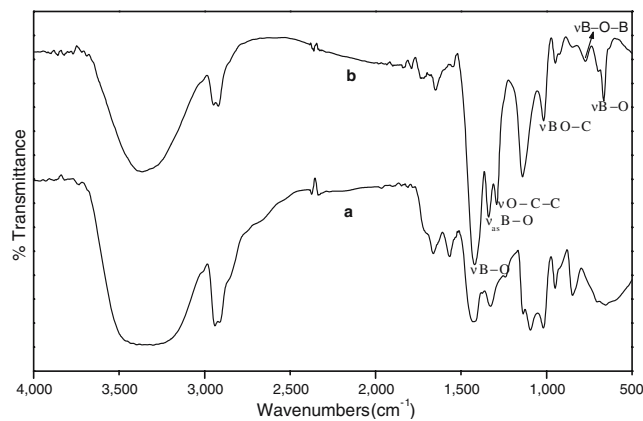
## Results and discussion

Polymer electrolytes were prepared by incorporation of  $H_3BO_3$  into PVA at several stoichiometric ratios in water. Boric acid and borates form very stable complexes with diols of PVA, forming hydronium ions (Fig. 1) [6, 7, 16]. In the meanwhile, the solvent water gets immobilized into matrix and hydrated PVA/ $H_3BO_3$  systems were produced.

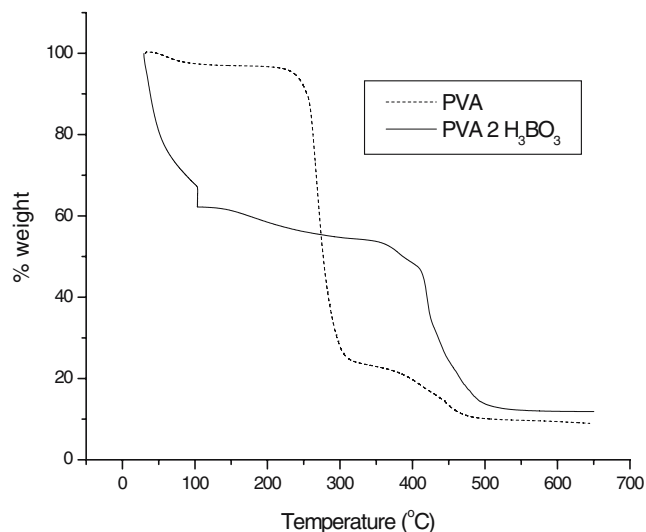
In acid-doped polymer electrolytes, there should be excess acid to attain high conductivity. However, the excess acid leaches out by the liquid water, which is inevitably change the conductivity of the membrane and decreases the efficiency of the fuel cell during operation [10–12]. In that respect, polymer-boric acid complexation or crosslinking seems to be alternative pathway which may inhibit proton solvent exclusions.

FT-IR spectra for the PVA and dried PVA1 $H_3BO_3$  are compared in Fig. 2. Characteristic main chain absorptions of the PVA are located at 3,350, 2,934, and 1,282  $\text{cm}^{-1}$ , corresponding to  $\nu$  O–H,  $\nu$  C–H, and  $\nu$ -C–C–O–, respectively (Fig. 2a). The peak at 1,145  $\text{cm}^{-1}$  (C–O,  $\nu=1,090$ –1,150  $\text{cm}^{-1}$ ) can be attributed to C–O stretching [13]. In Fig. 2b, the intense peak at 665  $\text{cm}^{-1}$  was attributed to vibration of B–O bond. In addition, the absorption band near 1,340  $\text{cm}^{-1}$  was assigned to the antisymmetric stretching vibration of the B–O bond,  $\nu_{as}$  (B–O) [14]. The band at 1,020  $\text{cm}^{-1}$  was due to the stretching of BO–C [14, 15], which confirms the condensation reaction of PVA with boric acid. The existence of B–O–B linkage was proved by the peak located at 768  $\text{cm}^{-1}$ , indicating the condensation boric acid with itself.

Figure 3 shows TG thermograms of the pristine PVA and PVA2 $H_3BO_3$  which are recorded from room temperature to 650 °C, under nitrogen atmosphere. As seen, the onset of the degradation temperature of PVA is approximately 225 °C. Hydrated sample, PVA2 $H_3BO_3$ , was first heated from ambient temperature to 100 °C at a rate of 5 °C/min and kept at this temperature for half an hour to see the expo-

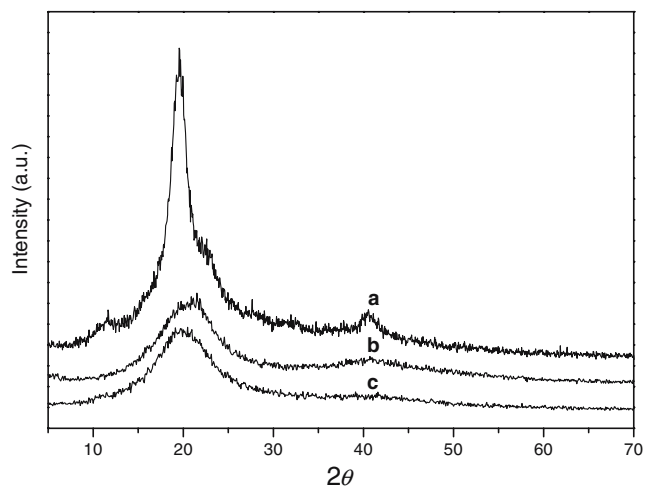


**Fig. 2** FTIR spectra of (a) PVA and (b) dried PVA1 $H_3BO_3$

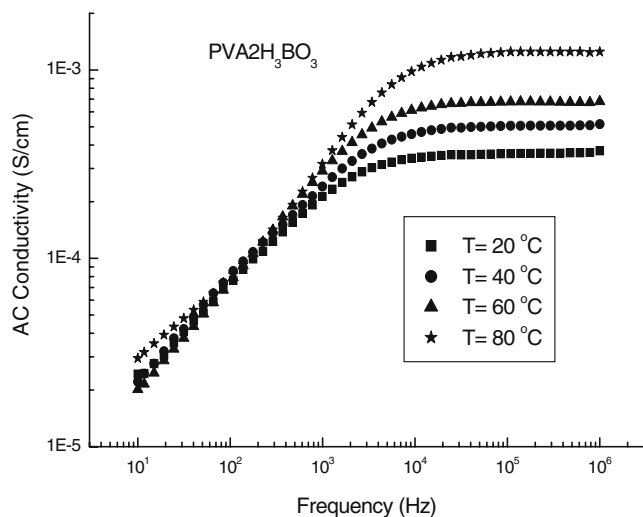


**Fig. 3** TG profile for pure PVA (*broken line*) at a temperature scanning rate of 10 °C/min. The thermogram of PVA2H<sub>3</sub>BO<sub>3</sub> (*solid line*) includes three steps: (1) heat from RT to 100 °C at 5 °C/min, (2) hold for 30.0 min at 100 °C, and (3) heat from 100 °C to 650 °C at 10 °C/min. All the experiments were carried out under nitrogen atmosphere

nential weight loss because of the evaporation of humidity as well as condensation reactions polymer electrolytes. Further increase of the temperature at a heating rate of 10 °C/min leads to a progressive degradation above 360 °C. Clearly, the addition of H<sub>3</sub>BO<sub>3</sub> results in the formation crosslinked polymers above 100 °C which shifted the degradation temperature of PVA about 135 °C to higher temperatures. The total weight change because of loss of free water and condensation (when  $T > 100$  °C) were found to be 45% for PVA1H<sub>3</sub>BO<sub>3</sub>, 42% for PVA2H<sub>3</sub>BO<sub>3</sub>, and 38% for PVA3H<sub>3</sub>BO<sub>3</sub>. By subtracting the percent weight changes from the free water contents (experimental part), one can conclude the respective weight losses because of condensation



**Fig. 4** X-ray diffraction patterns of (a) PVA, (b) dried PVA 1 H<sub>3</sub>BO<sub>3</sub>, and (c) dried PVA 2 H<sub>3</sub>BO<sub>3</sub>

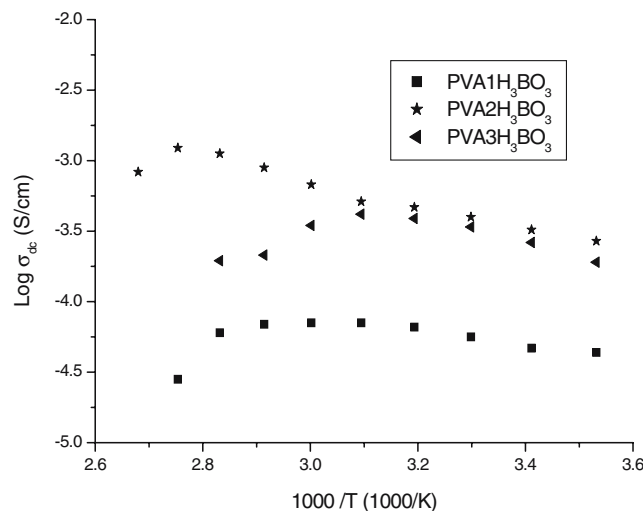


**Fig. 5** AC conductivity vs frequency (in log scale) at several temperatures

reactions at higher temperatures, i.e., 15% for PVA1H<sub>3</sub>BO<sub>3</sub>, 17% for PVA2H<sub>3</sub>BO<sub>3</sub> and 23% for PVA3H<sub>3</sub>BO<sub>3</sub>. Clearly, high temperature condensation increased in parallel with the boric acid composition.

The structures of the PVA and the dried crosslinked systems PVA1H<sub>3</sub>BO<sub>3</sub> and PVA2H<sub>3</sub>BO<sub>3</sub> were investigated using XRD analysis (Fig. 4). PVA shows a broad band centered at around 20° (2θ) indicated the semicrystalline structure of the homopolymer. The XRD patterns of the dried PVA1H<sub>3</sub>BO<sub>3</sub> and PVA2H<sub>3</sub>BO<sub>3</sub> samples shows that the intensity of the broad peak of PVA decreased with increasing H<sub>3</sub>BO<sub>3</sub> concentration. This behavior can be attributed to the chemical crosslinking that increased the amorphous character of the final product.

Proton conductivities of the hydrated polymer electrolytes, PVAxH<sub>3</sub>BO<sub>3</sub>, were measured using impedance spec-



**Fig. 6** Arrhenius plots of complex electrolytes: PVA1H<sub>3</sub>BO<sub>3</sub>, PVA2H<sub>3</sub>BO<sub>3</sub>, and PVA3H<sub>3</sub>BO<sub>3</sub>

troscopy. Frequency dependence of AC conductivity of the PVA2H<sub>3</sub>BO<sub>3</sub> at different temperatures is shown in Fig. 5. It can be observed that the conductivity is almost constant when  $F > 10^4$  Hz. However, deviations occur at lower frequencies because of electrode polarization. DC conductivity is derived from the plateaus by linear fitting and extrapolating to zero frequency.

Figure 6 shows the temperature dependence of proton conductivity of the gel electrolytes at different compositions as well as different water contents. It is obvious that the proton conductivities of the samples change with the temperature and composition.

The conductivity of hydrated PVA2H<sub>3</sub>BO<sub>3</sub> is higher than PVA1H<sub>3</sub>BO<sub>3</sub> where water content is higher for the latter. However, the proton conductivity of PVA3H<sub>3</sub>BO<sub>3</sub> is slightly lower than that of PVA2H<sub>3</sub>BO<sub>3</sub> at lower temperatures and the deviation is more pronounced when  $T > 60$  °C. This behavior can be attributed to low water content of PVA3H<sub>3</sub>BO<sub>3</sub> electrolyte as mentioned above. From these results, it can be concluded that PVA2H<sub>3</sub>BO<sub>3</sub> is the optimum chosen composition, which holds approximately 25% humidity and exhibits better conductivity. In these complex systems, proton transport is expected to occur throughout the water phase. The complex electrolyte PVA2H<sub>3</sub>BO<sub>3</sub> showed a remarkable conductivity of  $1.3 \times 10^{-3}$  S/cm at 80 °C. Clearly, conductivity decreases because of water loss when  $T > 80$  °C and continuous humidification is required to keep stable conductivity.

## Conclusions

The hydrogels of PVA-H<sub>3</sub>BO<sub>3</sub> were produced and the proton conducting properties were investigated. The physical properties were also changed with the boric acid composition as well as water content. We found that hydrated polymer

electrolyte PVA2H<sub>3</sub>BO<sub>3</sub> revealed a conductivity of  $4 \times 10^{-4}$  S/cm at RT and  $1.3 \times 10^{-3}$  S/cm at 80 °C. Clearly, PVAxH<sub>3</sub>BO<sub>3</sub> is a low temperature proton conductor and similar to perfluorosulfonic acid membranes, it becomes an insulator in the dry state. However, the dried and crosslinked PVA-H<sub>3</sub>BO<sub>3</sub> systems can be used as novel host material for anhydrous proton conductors where the protogenic solvents can be substituted into the matrix during synthesis.

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## References

1. Kreuer KD, Dippel Th, Meyer WH, Maier J (1993) Mater Res Soc Symp Proc 293:273
2. Rikukawa M, Sanui K (2000) Prog Polym Sci 25:1463
3. Motupally S, Becker AJ, Weidner JW (2000) J Electrochem Soc 147(9):3171
4. Schuster MFH, Meyer WH (2003) Annu Rev Mater Res 33:233
5. Reis EF, Campos FS, Lage AP, Leite RC et al (2006) Mater Res 9:185
6. Peppas NA, Mongia NK (1997) Eur J Pharm Biopharm 43:52
7. Hashimoto S, Furukawa K (1987) Biotechnol Bioeng 30:52
8. Kim DS, Yun TI, Seo MY, Cho HI et al (2006) Desalination 200:634
9. Martinelli A, Matic A, Jacobsson P, Börjesson L, Navarra MA, Femicola A, Panero S, Sacrosati B (2006) Solid State Ionics 117:2431
10. Xing BZ, Savadogo O (1999) J New Mater Electrochem Syst 2:95
11. Alberti G, Casciola M (2001) Solid State Ionics 145:3
12. Kufacı M, Bozkurt A, Tülü M (2006) Solid State Ionics 117:1003
13. Cotaes J (2000) Interpretation of infrared spectra. A practical approach. In: Meyers RA (ed) Encyclopedia of analytical chemistry. Wiley, New York
14. Pennarun PY, Jannasch P, Papaefthimiou S, Skarpentzos N, Yianoulis P (2006) Thin Solid Films 514:258
15. Mondal S, Banthia AK (2005) J Eur Ceram Soc 25:287
16. Cotton FA, Wilkinson G, Gaus PL (1995) Basic inorganic chemistry, 3rd edn. Wiley, New York