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Novel Proton Conducting Polymer Electrolyte Based on Poly(vinyl alcohol) and Trifluoromethane Sulfonic Acid

by A. Lewandowski[*] **and K. Skorupska**

Institute of Chemistry, Poznań University of Technology, PL - 60 965 Poznań, Poland

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A series of proton conducting, thin-film solid electrolytes, based on poly(vinyl alcohol), trifluoromethane sulfonic acid and water (PVA-CF_3SO_3H-H_2O) were prepared by the casting technique. The polymer electrolytes were transparent with a slightly brownish coloration. Maximum conductivity is obtained for samples containing about 40 wt.% of PVA, 36 wt.% of CF_3SO_3H and 24 wt.% of water, and reaches a level of *ca.* 10^{-2} S/cm at room temperature. The temperature dependence of the conductivity indicates the Arrhenius-type behaviour of the system for all compositions of the PVA-CF_3SO_3H-H_2O electrolytes, with activation energy of 30 kJ/mol (0.31 eV).

Key words: polymer electrolyte, trifluoromethane sulfonic acid, electrical conductivity, activation energy, protonic conductivity

Discovery of polymer-salt complexes as well as recognition of their potential application as solid electrolytes resulted in the development of numerous polymer electrolytes, including those with a protonic type of conductivity [1–26]. Generally, there are two types of proton conducting solid electrolytes based on a polymer matrix: (i) polyelectrolytes, composed of polymers, which possess ionogenic groups like –SO_3H, such as NAFION® and (ii) gels based on polymer + acid systems. Complexes of strong inorganic acids H_3PO_4 and H_2SO_4 with such polymers as poly(ethylene oxide) (PEO) [1,4,6,7], poly(vinyl alcohol) (PVA) [13], poly(ethylene imine) (PEI) [2,12], poly(acrylamide) (PAAM) [10,14,16], poly(methylmethacrylate) (PMMA) [14], poly(benzimidazole) (PBI) [19] or poly(vinyl acetate) (PVAc) [15] may serve as examples. This paper reports on some results of studies done on a new proton conducting polymer electrolyte, formed between poly(vinyl alcohol) and trifluoromethane sulfonic acid: PVA-CF_3SO_3H-H_2O. The main goal of the work was to prepare and to study the proton conducting gels based on an acid consisting of triflate anion, commonly applied in various systems, due to its non-complexing properties. Ion association, which occurs in systems containing H_3PO_4 and H_2SO_4, is one of the main factors determining the properties of polymer electrolytes, including their conductivity. The PVA–CF_3SO_3H system is compared to PVA–H_2SO_4 and PVA–H_3PO_4 proton conductors. Such an electrolyte could be useful in the construction of various electrochemical devices, such as batteries, supercapacitors or electrochromic devices.

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[*] To whom correspondence should be adressed; e-mail: andrzej.lewandowski@put.poznan.pl

EXPERIMENTAL

Poly(vinyl alcohol) (molecular weight 100000, Fluka), and trifluoromethane sulfonic acid (CF_3SO_3H, 99+ %, Aldrich) were used as received. A polymer suspension in water was left at 50°C for 24 hours. A homogenous solution of the swollen polymer was mixed with acid aqueous solution and stirred for *ca*. one hour to obtain a PVA+CF_3SO_3H viscous solution in water, which was cast on to a teflon plate and weighed immediately. Water excess was evaporated slowly at ambient temperature. After water excess evaporation, the plate with the foil was weighed again. Then, the foils with a thickness of approximately 0.05cm ÷ 0.10 cm were removed from the teflon surface.

Impedance spectra were taken using an ATLAS 9121 frequency response analyser coupled with an ATLAS 9131 electrochemical interface (both from Atlas-Sollich, Poland). The electrolytes were sandwiched between two platinum electrodes, each with a surface of 2.52 cm^2. Cyclic voltammetry curves were taken with the use of a μLAB universal electrochemical analyser (Eco Chemie, the Netherland). A saturated calomel electrode (SCE) served as a reference electrode. Electrolytes were placed between a counter electrode (platinum or gold with a surface of 1.90 cm^2) and a working microelectrode (with a surface of 0.0154 cm^2, 0.0040 cm^2 and 0.283 cm^2, in the case of platinum, gold and carbon as electrode materials, respectively). Microelectrodes were used in order to reduce IR drop and possible decomposition of the thin layers of electrolytes. The test vessel was thermostated by placing it in a water thermostat chamber. Thermal stability of the solid electrolytes was tested by placing them on a stainless steel plate heated at the rate of 5°C/min.

RESULTS AND DISCUSSION

The polymer electrolytes were transparent with a slightly brownish coloration, which increased with the acid content. No visible time changes were observed. The coloration of the PVA–H_2SO_4 [27] and PVA–H_3PO_4 [3] systems has also been noted. At the acid content higher than 40 wt.% the foils were too sticky to remove from the teflon plate. The PVA–CF_3SO_3H–H_2O foils are not stable in air above 140°C: they decompose to a brown, fragile material, which is due to evaporation of water followed by degradation of PVA. A similar treatment initiated some degradation with such polymers as PEI and PAAM [11]. The chemical stability of the PVA–H_3PO_4 films obtained by mixing aqueous solutions of acid and polymer, was not commented upon, but in the case of the PEO–H_3PO_4 it was necessary to use anhydrous AQN/THF solvents and dry argon atmosphere to avoid polymer degradation [2]. On the other hand, samples of Nylon-10x H_3PO_4 [11] were heated up to 100°C under vacuum or in air without noting any change (confirmed by stability of IR spectra). Polymer electrolyte PVA–CF_3SO_3H as well as PVA–H_3PO_4 [3] and PVA–H_2SO_4 [27] are soluble both in water and acid solutions. Thermal instability and water solubility of PVA based proton conducting electrolytes seem to be two basic limitations in their practical application.

***Ac impedance*:** Figure 1 shows a typical impedance plot obtained in the system Pt|electrolyte|Pt. It can be seen, that the spectrum is linear, both in low and high frequency sections, typical of the blocking electrodes. The impedance spectra were deconvoluted to separate the bulk resistance of electrolytes, R_b, from other possible components of the equivalent circuits, such as charge transfer resistance, Warburg impedance, resistance and capacity of passivation layer, or double layer capacity. Taking into account the electrolyte thickness, d, values of the bulk resistance, R_b, were converted into the electrolyte specific conductance: $\sigma\,(\Omega^{-1}cm^{-1}) = d\,(cm)/R_b\,(\Omega\ cm^2)$.

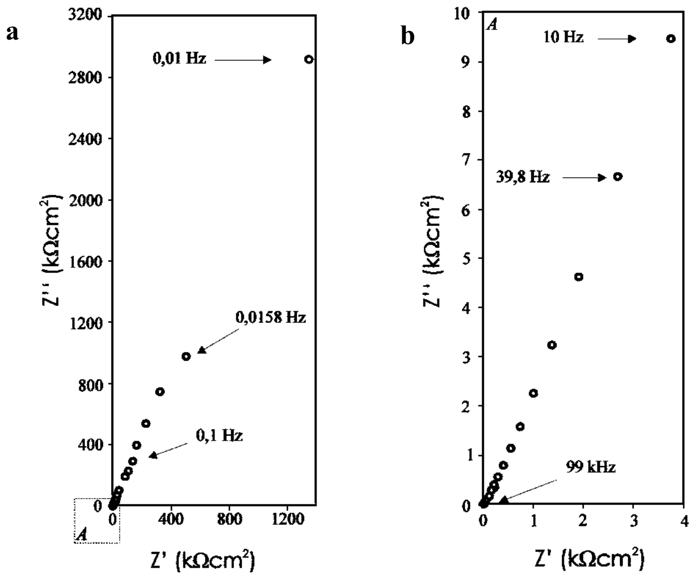

Figure 1. Low frequency (**a**) as well as high frequency (**b**) parts of the impedance plot for the symmetrical Pt|PVA (53.4 wt.%), CF_3SO_3H (36.2 wt.%), water (10.4 wt.%)|Pt cell. Electrolyte thickness: 0.08 cm. Room temperature.

***Dc conductivity*:** Table 1 contains specific conductivities of some representative PVA–CF_3SO_3H–H_2O polymer electrolytes, of different composition. The maximum value of the conductivity of the PVA–CF_3SO_3H–H_2O electrolytes is obtained for samples containing 40 wt.% of PVA, 36 wt.% of CF_3SO_3H and 24 wt.% of water, and reaches a high level of *ca.* 10^{-2} S/cm at room temperature. This value can be compared with the conductivity of other proton conducting polymer electrolytes. Two main factors determine the ionic conductivity, including protonic conduction, namely the number of carrier ions and their mobility. To obtain better properties at room temperature, the polymer must be modified to a larger proportion of the amorphous phase.

Table 1. Conductivity of some representative PVA–CF_3SO_3H–H_2O polymer electrolytes. T = 25°C.

	wt.%		
acid	PVA	water	[mS/cm]
23.7	57.2	19.1	0.51
27.4	59.6	13.0	0.71
31.3	45.2	23.5	5.2
34.3	49.3	16.4	7.2
36.5	39.9	23.6	9.7
36.2	53.4	10.4	3.9

The most common approaches to improve the conductivity include co-polymerization, preparing polymer blends as host materials, plasticization by a low molecular substance (addition of inorganic or organic soluble additives to increase the segmental motion of the polymer matrix network) or by the gel-electrolytes route. In the latter case, the polymer matrix acts as a host for a liquid solvent, which swells the polymer. Gel-type electrolytes (polymer-acid-solvent) consist of a polymer matrix swollen with water or organic solvent, and the proton transport takes place primarily in the solution entrapped in the polymer matrix. In aqueous systems, an acid dissociates to form hydrated protons, H_3O^+, and the system exhibits liquid-like ionic conductivity, while preserving the dimensional stability of a solid system. Literature data indicate that the conductivity of non-aqueous binary polymer-acid systems is of the order of 10^{-5}–10^{-4} S/cm [1–8,11–16,19,22]. The conductivity of the anhydrous polymer-acid system mainly increases with increasing the atmosphere humidity. In order to obtain a stable system, the residual water must be removed completely. In almost all papers dealing with protonic conductivity of anhydrous systems, the hydration-dehydration equilibrium is ignored. In the nonaqueous systems based on PVA doped with H_3PO_4, the maximum conductivity is not better than 10^{-5} S/cm at ambient temperatures [5]. Replacing the binary system polymer-acid by a ternary system polymer(1)-polymer(2)-acid decreases the degree of the system crystalinity and therefore increases the conductivity. For instance, the system PEO–H_3PO_4 exhibits a conductivity of 10^{-5} S/cm [1], while the conductivity of a system PEO–PMMA–H_3PO_4 is two orders of magnitude higher (10^{-3} S/cm) [6,7]. Proton conducting polymer electrolytes plasticized with organic solvents exhibit conductivity usually of the order of 10^{-4} S/cm [14,20,25]. The ternary aqueous systems: polymer–acid–water exhibit higher conductivity, usually of the order of 10^{-3} S/cm or even better [10,16,23,26]. The conductivity of PVA–H_3PO_4–H_2O system for H^+/VA = 0.77 is *ca.* 10^{-3} S/cm at 30°C [13]. The PVA–H_2SO_4–H_2O shows better conductivity: 10^{-2} S/cm [27]. Moreover, it has been reported recently that dissolution of aqueous H_3PO_2 in PVA produces membranes whose room temperature conductivity is even better than 10^{-2} S/cm [23]. One may conclude, that the polymer electrolytes based on PVA as polymer matrix, PVA–acid–H_2O (acid is H_2SO_4, H_3PO_4, CF_3SO_3H or H_3PO_2) exhibit a high conductivity at the level of 10^{-3}–10^{-2} S/cm at room temperature.

Figure 2 shows the temperature dependence of the conductivity as $\log\sigma = f(T^{-1})$. The straight line seen at the figure indicates the Arrhenius-type behaviour of the system. The activation energy for the conductance process, obtained from the slope of the straight line is of the order of 30 kJ mol^{-1} (0.31 eV), a value typical for proton conducting polymer electrolytes. Systems with the ion transport mediated by segmental motions can be described by the Vogel-Tamman-Fulcher equation, derived from the free volume theory. The Arrhenius type of behaviour, found here, indicates rather a conductivity controlled by a proton hopping mechanism. For weakly basic polymers such as PEO or PVA, hydrogen bonding can be proposed to explain the interaction between the acid and the polymer.

Voltammetry**:** High conductivity is not sufficient to make a given polymer electrolyte suitable for many practical applications. Other parameters, such as electrochemical stability window can be important factors. The behaviour of the electrolyte at gold, platinum and glassy carbon electrodes was investigated by cyclic voltammetry (Figures 3–5).

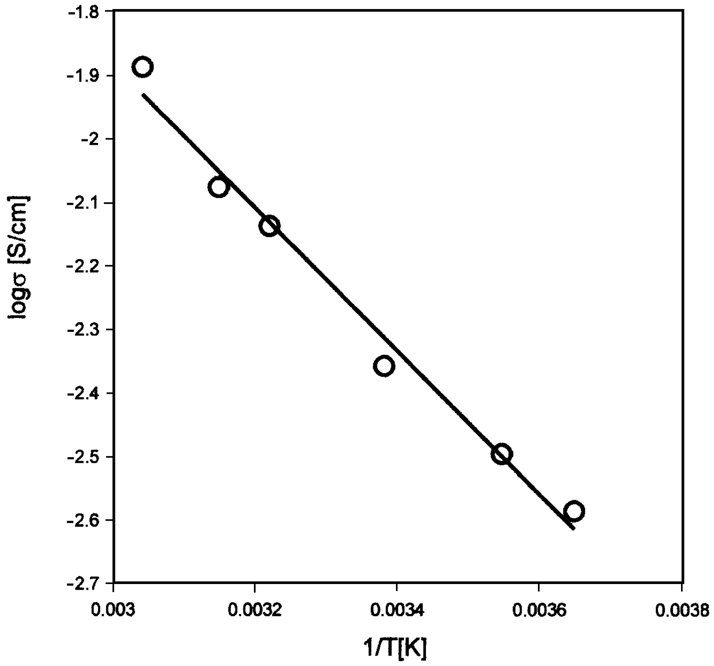

Figure 2. Arrhenius plot for the PVA (53.4 wt.%), CF_3SO_3H (36.2 wt.%), water (10.4 wt.%) electrolyte.

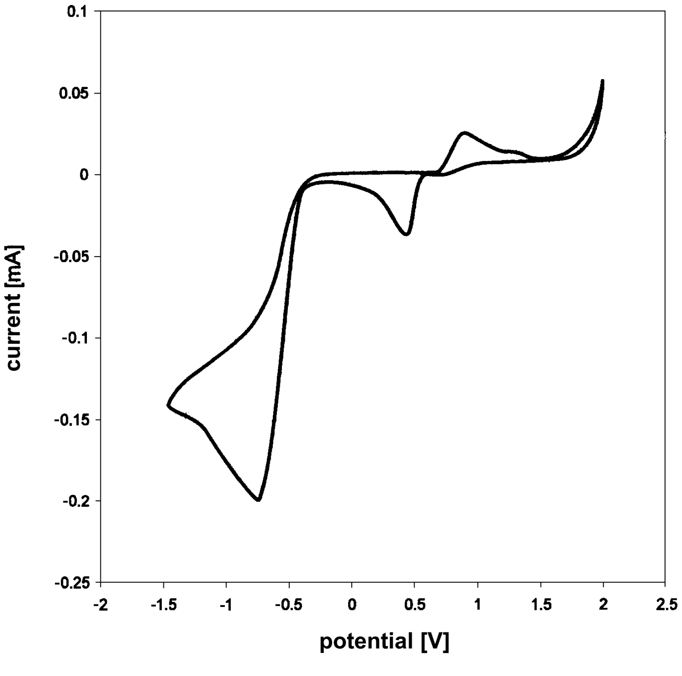

Figure 3. Cyclic voltammetry for the Au|PVA (41.5 wt.%), CF_3SO_3H (29.0 wt.%), water (29.5 wt.%)|Au cell. Electrolyte thickness: 0.08 cm. Working Au electrode area: 0.0040 cm^2. Room temperature. Sweep rate: 5 mV s^{-1}.

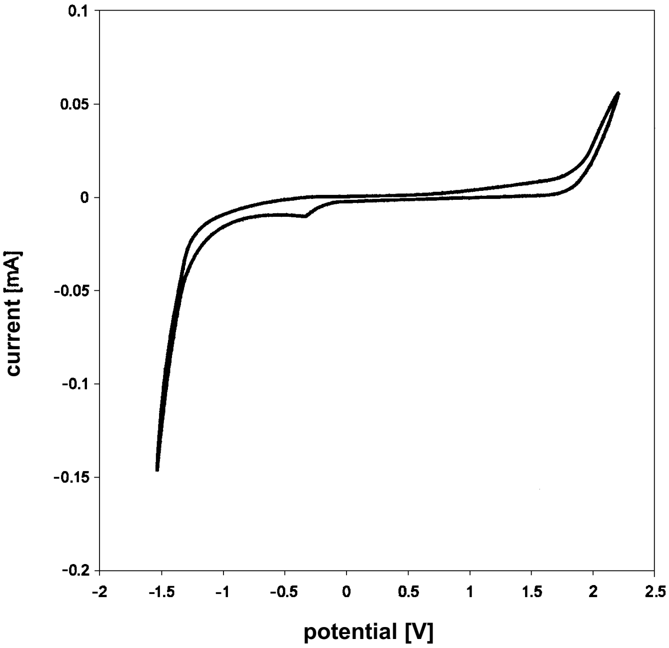

Figure 4. Cyclic voltammetry for the Pt|PVA (36.9 wt.%), CF_3SO_3H (27.0 wt.%), water (36.1 wt.%)|Pt cell. Electrolyte thickness: 0.03 cm. Working Pt electrode area: 0.0154 cm^2. Room temperature. Sweep rate: 5 mV s^{-1}.

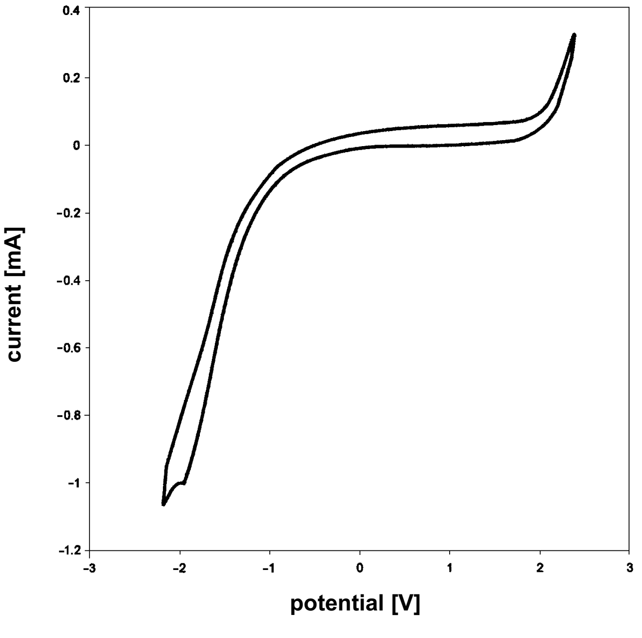

Figure 5. Cyclic voltammetry for the C|(41.5 wt.%), CF_3SO_3H (29.0 wt.%), water (29.5 wt.%)|Pt cell. Electrolyte thickness: 0.06 cm. Working carbon electrode area: 0.283 cm^2. Room temperature. Sweep rate: 1 mV s^{-1}.

A peak of metallic gold oxidation with a maximum at *ca*. + 1.0 V at the anodic scan; and a peak of gold cations reduction with a maximum at *ca*. +0.5 V at the reverse scan, can be seen in Figure 3. At negative potentials a peak of proton reduction to hydrogen (maximum at *ca*. –0.7) is present. The proton reduction at platinum (Figure 4) and carbon (Figure 5) electrodes takes place at much more negative potentials. It is worth noting that the voltammogram for carbon as an electrode material shows a relatively broad electrochemical stability window, which can be useful in the case of the electrolyte application for the construction of acidic supercapacitors based on activated carbons.

CONCLUSIONS

It has been shown that poly(vinyl alcohol) swollen in water forms with CF_3SO_3H thin films of good mechanical properties and conductance of the order of 10^{-2} S/cm, acceptable for various practical applications. The system can be used as a proton conducting plastic binder and a polymer electrolyte in the manufacture of flat electrochemical devices (batteries, supercapacitors, electrochromic devices, photogalvanic cells *etc*.) necessary for the development and construction of small electric appliances. The flexibility of such a material can compensate for the usual problems with volume changes of electroactive species during charging and discharging processes. Further experiments performed in our laboratory proved that the electrolyte is a viable candidate for application in supercapacitors [28]. Polymer electrolytes PVA–CF_3SO_3H (as well as PVA–H_3PO_4 [3] and PVA–H_2SO_4 [27]) are soluble both in water and acid solutions. Thermal instability and water solubility of PVA based proton conducting electrolytes, including the PVA–CF_3SO_3H system, are two basic limitations in their practical application.

Acknowledgments

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