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Proton conducting gels for electrochemical devices

Zbigniew Florjańczyk* [a], Wojciech Bzducha [a], Michał Kędzierski [b]

[a] Faculty of Chemistry, Warsaw University of Technology, ul. Noakowskiego 3,
00-664 Warsaw, Poland

[b] Institute of Industrial Chemistry, ul. Rydygiera 8, Warsaw, Poland

SUMMARY: The state of art on composite, polymeric proton conductors is presented in the paper. This includes binary systems composed of a Brønsted acid and proton coordinating macromolecules like poly(ethylene oxide), poly(ethylene imine), polyacrylamide, poly(vinyl pyrolidone), polybenzimidazole, and ternary gels containing a polymeric matrix, Brønsted acid and polar solvents like water, propylene carbonate, and dimethylformamide. The conductivity mechanism in these systems and possibilities of practical application in fuel cells and electrochromic devices have been discussed.

Introduction

Proton conducting polymeric membranes have become the object of the increasing academic and industrial interest with respect to their potential application in various electrochemical devices. In the industrial scale they have been already used for H_2O and HCl electrolysis and chlorine alkaline production. Most of the recent studies are stimulated by the development of fuel cells which deflagrate hydrogen or methanol in electrochemical way producing the stream of electrons that flow spontaneously from the fuel to the oxidant and diverts it for use in an external circuit[1-6] (1).

$$\begin{array}{lll} \text{Anode} & H_2 \rightarrow 2H^+ + 2e & E_0 = 1.23\ \text{V} \\ \text{Cathode} & {}^1\!/_2O_2 + 2H^+ + 2e \rightarrow H_2O & P = 1\text{–}2\ \text{W}\cdot\text{cm}^{-2} \\ & & \\ \text{Anode} & CH_3OH + H_2O \rightarrow 6H^+ + 6e + CO_2 & E_0 = 1.21\ \text{V} \\ \text{Cathode} & 1{}^1\!/_2O_2 + 6H^+ + 6e \rightarrow 3H_2O & P = 0.1 - 0.2\ \text{W}\cdot\text{cm}^{-2} \end{array} \qquad (1)$$

These types of cells are expected to see service as an energy source in electric vehicles and small stationary or portable-mobile power systems.

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The big market for proton conducting membranes may offer the electrooptical industry producing displays, optical modulators, antiglare rear view mirrors, variable light transmission windows controlling energy transfer within buildings and in vehicles and other electrochromic devices which can change the color reversibly and in a persistent manner on application of a voltage pulse[7,8)]. This results from the reversible insertion of ions in the electrochromic electrode. The most classical example of such electrode material is tungsten oxide, WO_3 (2).

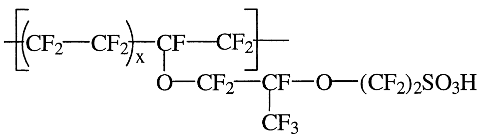
$$WO_3 + xM^+ + xe \rightleftharpoons M_xWO_3 \qquad (2)$$

pale yellow *deep blue*

where $0 < x < 0.25$ and M^+ can be typically H^+ or Li^+

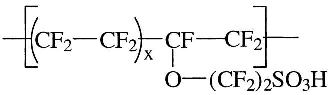
Several proton conducting polymeric systems have been also successfully applied in various humidity or gas sensors and electrically driven chemomechanical systems employing intelligent gels capable of changing shape when immersed in an electric field[9-11)].

Up to now the polyelectrolytes consisting of perfluorosulfonate ionomers have been almost the only materials used for the preparation of commercially available proton conducting membranes[12-15)]. The typical examples of this class of materials are the NAFION family produced by Du Pont and experimental DOW products (3).



$$-\!\left[(CF_2-CF_2)_x-\underset{\substack{|\\ O-CF_2-\underset{\substack{|\\ CF_3}}{CF}-O-(CF_2)_2SO_3H}}{CF}-CF_2\right]\!-$$

NAFION® x = 6–10



$$-\!\left[(CF_2-CF_2)_x-\underset{\substack{|\\ O-(CF_2)_2SO_3H}}{CF}-CF_2\right]\!-$$

DOW® x = 3–10

(3)

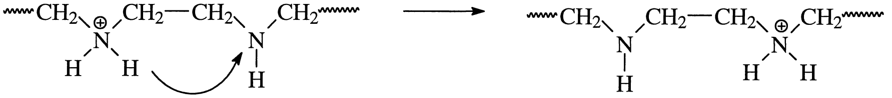
The greatest barrier to commercialization of these membranes on a large scale is their high cost (of the order U.S. $ 800–2000 /m^2). During the last decade several alternative polyelectrolytes containing chemically bonded sulfonic acid groups have been developed in the laboratory scale and tested in electrochemical devices. These include sulfonated trifluorostyrene polymers, polyimides, polysulfones, polyarylketones and organically modified silicates. Savadogo has recently reviewed the general preparation method and electrochemical properties of these materials [16)].

This paper will discuss the progress of another type of polymeric proton conductors named polymeric electrolytes. This term may refer to solvent free (solid) systems where the ionically conducting phase is formed by dissolving Brønsted acids in proton coordinating macromolecules and to gel electrolytes formed by dissolving acids in a polar liquid and adding the polymer network to provide the material with mechanical stability.

Solid electrolytes

H_3PO_4 and H_2SO_4 are the most often used acids in solid polymeric electrolytes. Poly(ethylene imine) (PEI) of a linear or branched structure[17-20)], poly(ethylene oxide) (PEO)[21, 22)], poly(vinyl alcohol) (PVA)[23)], polyacrylamide (PAAM)[24)], poly(vinyl pyrolidone) (PVP)[25)] and polybenzimidazole (PBI)[26, 27)] were used as polymeric matrices. The acid-polymer complexes were prepared by casting films from water or organic solvent and in some cases by immersion of polymer films in aqueous acid solutions.

In several systems, e.g. PEI–H_3PO_4, PEI–H_2SO_4, PAAM–H_2SO_4 it has been demonstrated through IR spectroscopy that the polymer is protonated and inorganic anions are formed. In such electrolytes the cation transportation may occur via proton hopping between coexisting protonated and unprotonated functional groups (4).



(4)

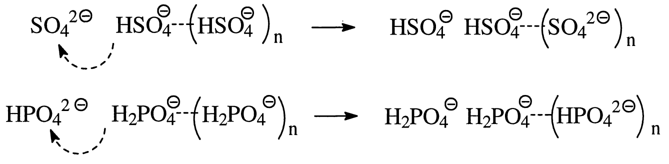
Potentiometric titration studies showed that 20–30% of amine groups in PEI can not be protonated due to the strong nearest neighbor interactions of charged atoms along the polymer chain[28, 29)]. This causes that in the systems with H_3PO_4 or H_2SO_4 at acid/monomeric unit molar ratio (x) above 0.35–0.4, the PEI chain remains in the protonated state and only HPO_4^{2-} or SO_4^{2-} can act as weak proton acceptors.

The ambient conductivity of these complexes is usually in the range of 10^{-10}–10^{-5} S·cm^{-1} (Table 1).

Tab. 1. Conductivity values σ for solid electrolytes based on linear (L)[18] and branched (B)[19] PEI for various acid/monomeric unit molar ratios x

Acid	PEI	x	σ_{RT}	$\sigma_{100°C}$
			S · cm^{-1}	S · cm^{-1}
H_3PO_4	B	0.20	5×10^{-6}	1×10^{-3}
H_3PO_4	B	0.35	2×10^{-7}	5×10^{-4}
H_3PO_4	B	1.80	9×10^{-4}	
H_2SO_4	B	0.20	4×10^{-5}	3×10^{-3}
H_2SO_4	B	0.35	9×10^{-7}	2×10^{-4}
H_3PO_4	L	0.10		2×10^{-5}
H_3PO_4	L	0.40	6×10^{-10}	5×10^{-7}
H_3PO_4	L	1.20	1×10^{-5}	5×10^{-5}

It increased as the x value was increased to 0.1–0.2, and then experienced a significant drop to a minimum at x equal 0.35–0.4. Additional acid beyond this point caused the conductivity to increase and reach the plateau for x higher than 1.8[20]. The plausible explanation is that at high acid concentration only $H_2PO_4^-$ or HSO_4^- anions serve as a stronger proton donor rather than ammonium cations. The protonated PEI, in effect, only provides the framework and proton transportation occurs along anionic chain, which is formed *via* hydrogen bonds (5).



(5)

Higher conductivity values obtained for H_2SO_4 complexes are attributed to the easier reorientation and higher acidity of HSO_4^- than to those of $H_2PO_4^-$. Non-dissociated acid molecules can also serve as proton donors.

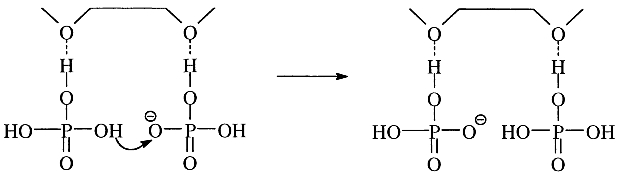
The temperature dependence of conductivity for samples with x lower than 0.4 can be described by Arrhenius-type relationship typical for an activated process based on Boltzman statistics. The plots for $x > 0.6$ are reminiscent to Wiliams-Landel-Ferry (WLF) and Vogel-Tamman-Fulcher (VTF) relationships describing visco-elastically related properties of amorphous polymers. These applied to the dependence of conductivity σ on absolute temperature T for polymer electrolytes have the form (6):

$$\sigma_{(T)} = A \bullet T^{-1/2} \exp\left[-E_a / R(T - T_0)\right] \tag{6}$$

The curved temperature dependence in $\log\sigma$ *v/s* $1/T$ plot observed is interpreted in terms of cooperative interaction between charge carriers and polymer chains. This means that the actual activated process is diffusion rather than conduction, whose rates become vanishingly small as thermodynamic glass transition temperature T_0 is approached. In practice σ is negligible below the experimentally determined T_g.

The DSC studies showed that T_g values increase from –47°C for pure PEI to 0°C for an acid to monomeric unit ratio of ~0.35, owing to an increase in NH---O hydrogen bonding as the polymer becomes protonated. Then, at about $x = 0.4$ it decreases slowly due to the plasticizing effect of inorganic anions arrays.

In the case of polymeric matrix of moderate nucleophilic properties like PEO or PAAM the degree of protonation is rather small and the interaction with acids occurs mostly via hydrogen bonds[19, 22)]. Conductivity, DSC, NMR and neutron quasi scattering studies of $PEO(H_3PO_4)_x$ conductors described by Armand and coworkers[30)] have shown that ion movements in these systems occur in amorphous phase and are governed by the segmental motion of polymer chain. The minimum value of conductivity was observed for $x \approx 0.7$ over a wide range of temperature T. The phase diagram shows existence of a crystalline complex of this stoichiometry (melting point ~73°C), which does not contribute to the bulk conductivity. The complex forms an eutectic with PEO and H_3PO_4, respectively of melting point below 40°C. The mechanism of proton conductivity in this system was not elucidated. One of the possibilities is the proton-vacancy type conductivity in PEO/acid complexes (7).



(7)

The proton vacancies can be formed by protonation of the polymer chain or by self-dissociation of the acid. It was suggested that this type of mechanism could operate also in the case of neutral or basic proton conductors like for example sulfonamides[30, 31], which have a $pK_a \approx 11$, corresponding to the acid-base equilibrium (8)

$$RSO_2NH_2 \rightleftharpoons H^{\oplus} + [RSO_2NH]^{\ominus} \tag{8}$$

The conductivity of such system can be increase by addition of a strong external base (e.g. guanidine) which shifts the equilibrium and enhances the proton vacancies. Ambient temperature conductivities exceeding 10^{-5} $S \cdot cm^{-1}$ were achieved for various PEO complexes depending on the doping level and crystallinity of conducting matrix. The ambient temperature conductivity as high as 10^{-3} $S \cdot cm^{-1}$ was reported for PEO complexes with low molecular weight polyethers terminated by SO_3H groups[32]. In this case sulfonic acid acts both as a proton donor and plasticizer.

Very high conductivity in the range of $10^{-3} - 10^{-2}$ $S \cdot cm^{-1}$ was observed for PAAM– H_3PO_4 at high acid content ($x > 1.5$)[25]. This results probably from the high intrinsic conductivity of the acid itself. However, the potential applications of these systems are limited due to poor mechanical properties and chemical instability.

The mechanical properties of conducting complexes can be improved after introduction of 20–30 wt % of neutral supporting polymers like poly(methyl methacrylate) or poly(vinylidene fluoride). In certain systems, for example PEO/H_3PO_4 /poly(methyl methacrylate) composites this results also in an improvement of conducting properties (Fig. 1). An increase in the flexibility of the conducting phase due to a decrease in the crosslinking density of the PEO chains by the acid molecules may be the reason for this[22].

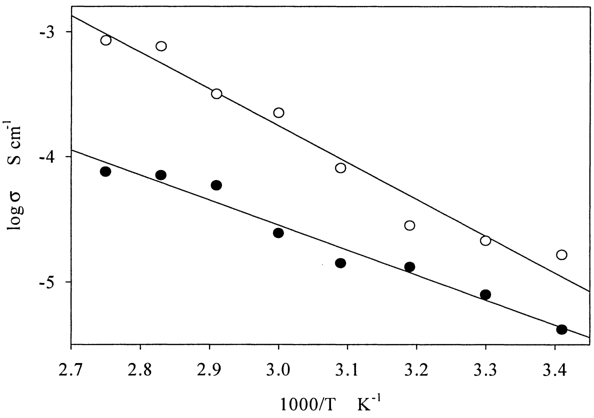


Fig. 1: Ionic conductivity vs. reciprocal temperature dependence for: (●) $P(EO)_{10}\cdot H_3PO_4$ electrolyte and (○) $P(EO)_{10}\cdot H_3PO_4$ – PMMA (20 wt %) blend

The conductivity of polymeric proton electrolytes clearly increases in the presence of water, which acts as a plasticizer, ion solvating agent, and at high concentration as the conducting phase. Some complexes of hydrophobic properties, as e.g. polybenzimidazole / H_3PO_4[26, 27)] or PEI / H_3PO_4[20)] spontaneously lose water to reach an equilibrium water content dependent on temperature and ambient humidity similarly like for a membrane based on perfluorosulfonic polyelectrolytes. These materials can be processed as thin film electrolytes of ambient conductivity 10^{-3} – 10^{-2} $S\cdot cm^{-1}$ and 0.01–0.1 $S\cdot cm^{-1}$ at 120–200°C. The electrolytes based on hydrophilic linear polymers like poly(vinyl alcohol), polyacrylamide, poly(vinylpyrolidone) or PEO are very soft and water soluble which limits the possibility of their practical application. Water insoluble, highly conducting membranes of reasonably good mechanical properties can be fabricated by development of interpenetrating polymer network systems[33)].

One of the most efficient methods consists in the free radical copolymerization of acrylamide with bisacrylamide in the presence of acids and agar or other natural polymers[34)]. The dimensionally stable membranes obtained can incorporate approximately 100% by weight of water. Their conductivity usually increases with an increase in the water concentration up to about 30–35 wt % and then remains almost constant for higher water concentration (Fig. 2).

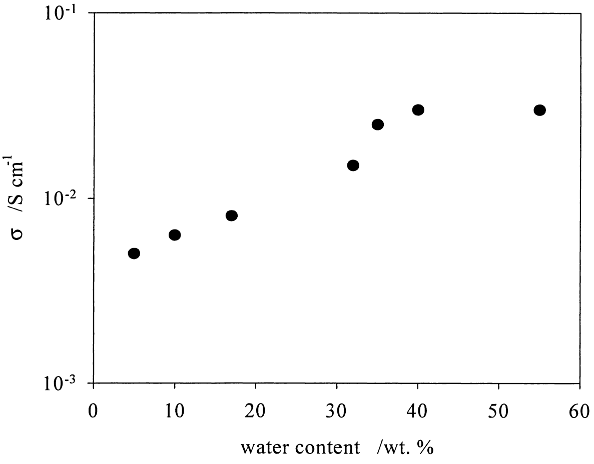


Fig. 2: Ionic conductivity vs. water concentration (wt %) in a PAAM based protonic electrolyte (H_3PO_4 / AAM = 1.6 : 1) at 25°C

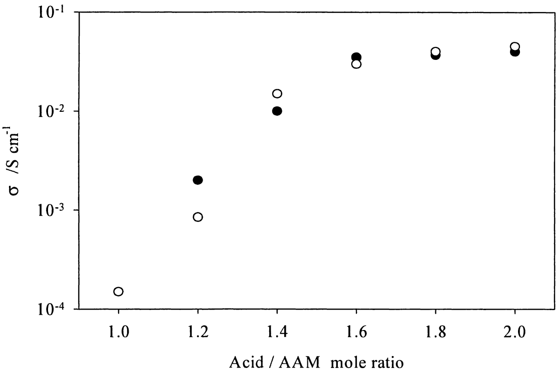


Fig. 3: Room temperature isotherms of the ionic conductivity of acrylamide (AAM) based protonic gel electrolytes as a function of the acid / AAM molar ratio. Data for samples doped with H_3PO_4 (●) or H_2SO_4 (○). Samples contain 20 wt % of water

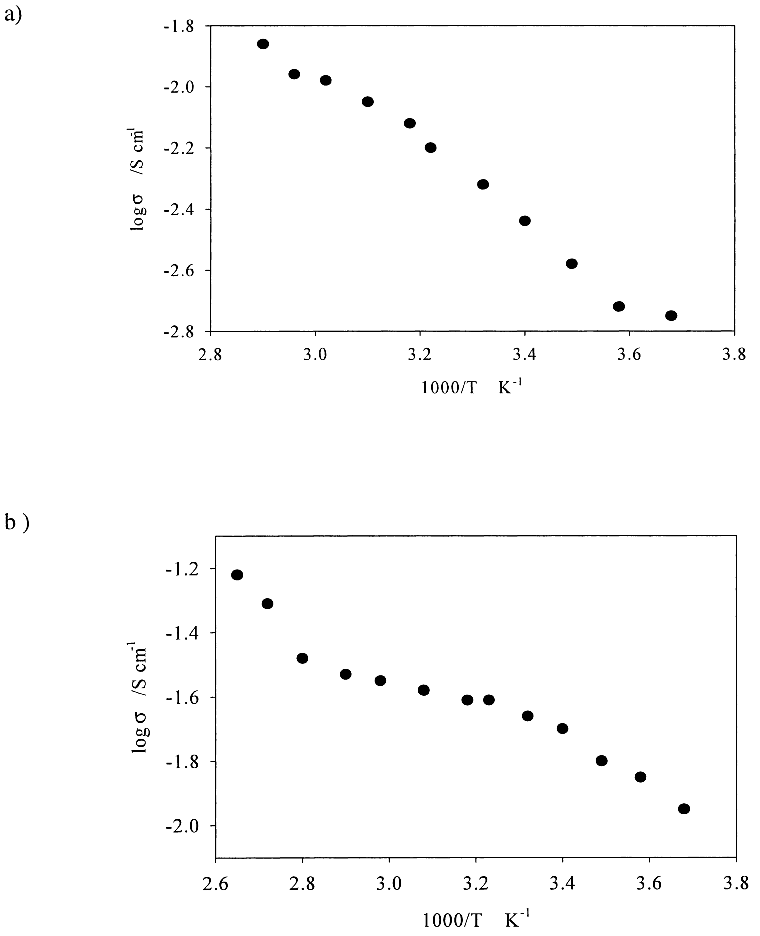


Fig. 4: Ionic conductivity vs. reciprocal temperature for PAAM based protonic electrolytes containing various amounts of water (H_3PO_4 / AAM = 1.6 : 1); (a) 20 wt % of water; (b) 40 wt % of water

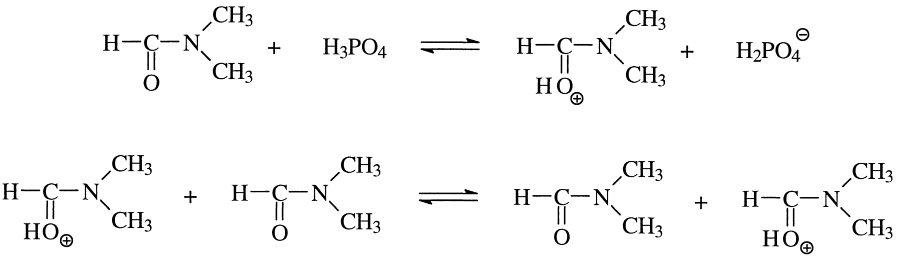
Figure 3 shows a typical acid concentration dependence of the conductivity at fixed water concentration. One can observe that conductivity initially rises sharply with increasing acid content to reach an almost constant value for *x* higher than 1.6. In the plateau region for the room temperature exceeds 10^{-2} S·cm^{-1} and is comparable with that reported for hydrated Nafion. At low water content (~20 wt %) the temperature dependence of conductivity (Fig. 4a) exhibits a typical VTF curvature which suggests that ion transportation is strongly coupled with segmental motion of the polymer chain. In fully hydrated membranes this interaction is smaller and the temperature dependence of conductivity cannot be described either by VTF or Arrhenius type relationships (Fig. 4b).

The DSC curves for gel protonic electrolytes based on H_3PO_4 and polyacrylamide base matrices show no traces of first order transition in the temperature range −100 – +120°C which suggests that water is tightly bonded with the polymer and inorganic component. The degradation processes leading to a decrease in mechanical integrity begin at about 140°C35). The tensile modulus of highly conducting polyacryamide gel electrolytes are in the range 300–400 g·mm^{-2}, which is ~6 times lower than those for hydrated Nafion36).

Nonaqueous protonic gel electrolytes

The electrochemistry of nonaqueous gels containing alkali metal salts is well developed because of the possible application in batteries. However, little is known about the properties of analogous materials exhibiting high protonic conductivity. Nonaqueous protonic gels incorporating H_3PO_4 have been synthesized using propylene carbonate (PC), dimethylformamide (DMF), 1-methyl-2-pyrolidone, ethylene glycol and several polyglycols as entrapped solvents37). The polymeric matrices were prepared by copolymerization *in situ* of methyl methacrylate (MMA) with glycidyl methacrylate (GMA), triethylene glycol dimethacrylate (TEGDM) or N,N'-methylenediacrylamide. The highest values of conductivity in the range 10^{-4} – 10^{-3} S·cm^{-1} at room temperature were reported for gels containing DMF and PC (Fig. 5).

On the basis of conductivity and FT-IR studies it was suggested that proton transportation might occur in this systems according to two different mechanisms. The first one consists in the protonation of the solvent followed by proton exchange between protonated and unprotonated solvent molecules (9).



(9)

This type of conduction was attributed to the DMF gels at low acid concentration. As can be seen from the Fig. 6 the activation energy for ion transportation in these systems is relatively low, thus the values of conductivity can be reached even in subambient temperature (exceeding 10^{-4} S·cm^{-1} at −50°C).

Another mechanism (typical for gels containing PC and another solvent which cannot be easily protonated) involves self dissociation of H_3PO_4 (10).

$$2\,H_3PO_4 \rightleftharpoons H_2PO_4^{\ominus} + H_4PO_4^{\oplus} \qquad (10)$$

The polyatomic anions formed are probably the dominant charge carries at low acid concentration. Here the solvent is not involved in proton transportation which results in lower ambient temperature conductivity and higher activation energy for conduction than in analogous systems containing DMF. For high H_3PO_4 concentration, acid based pairs like $H_2PO_4^-$ / HPO_4^{2-} are present leading to the possibility of proton exchange within the inorganic component array and therefore an increase in the conductivity is observed similarly like in solvent free systems. At ambient temperature this type of transportation is more effective in PC which has a higher dielectric constant (65) than DMF (37). At subambient temperature the conductivity is governed by electrolyte viscosity and the curvature of temperature dependence on conductivity reflects the changes in fluidity of solvent acid solutions. The cross-link density and the type of polymer matrix used seemed to have a rather negligible effect on the conductivity of gels$^{37)}$.

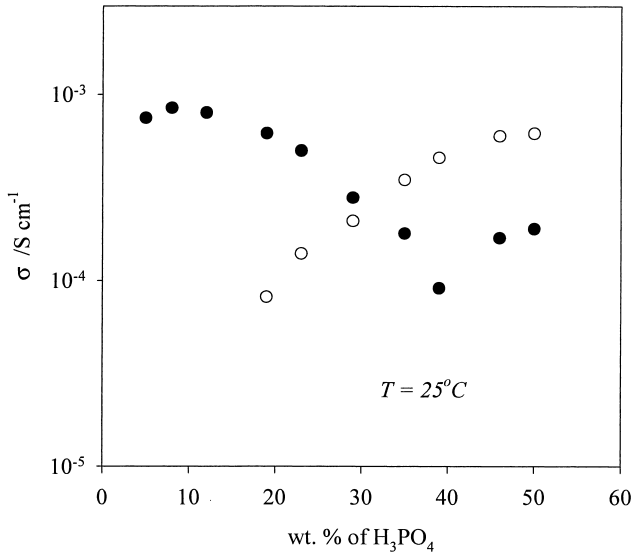


Fig. 5: Isotherms of ionic conductivity of (●) DMF-H_3PO_4 and (○) PC-H_3PO_4 gel electrolytes *vs.* wt % of H_3PO_4. Samples containing 10.5 w % of polymer matrix (GMA and MMA based, respectively)

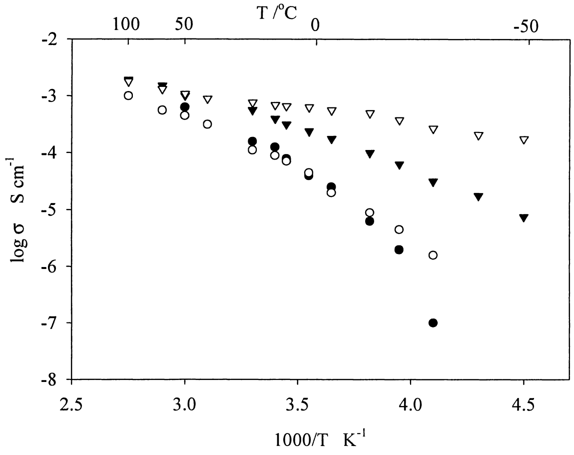


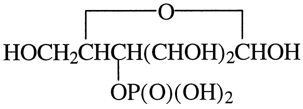
Fig. 6: Ionic conductivity of DMF-H_3PO_4 entrapped gel electrolytes as a function of inverse temperature. Samples containing 10.5 wt % GMA based polymer matrix with: ● =50, ○ =39, ▼ =23, ▽ =7.4 wt % of H_3PO_4

Recently it was found that highly conducting protonic gels can be prepared by swelling of poly(vinylidene fluoride) (PVdF) in H_3PO_4 / DMF electrolyte[38]. In this case the network structure is probably built *via* small crystallites of PVdF which act as physical crosslinks.

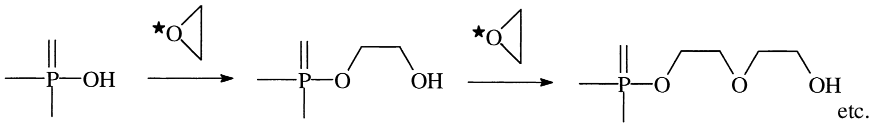
Phosphoric acid esters as components of conducting gels

Many phosphoric acid mono and diesters are characterized by strong acidic properties, and some of them have even higher values of the first ionization constant pK_1 than the parent acid (see e.g. Tab. 2). From initial studies carried out in our laboratory it results that monomeric or oligomeric esters of phosphoric acid enable the obtaining of electrolytes of higher conductivity than systems containing phosphoric acid solutions, especially in an organic solvent medium. For example, the replacing of phosphoric acid with diphenyl ester in gels containing PVdF and DMF cause an increase in conductivity by about one order of magnitude over a wide temperature range (Fig. 7).

Tab. 2. Apparent ionization constants of some orthophosphate derivatives

Compound	pK_1	pK_2	pK_3
$OP(OH)_3$	1.97	6.82	12
$(CH_3)(O)P(OH)_2$	1.54	6.31	
$(CH_3O)_2(O)P(OH)$	1.39		
$(C_2H_5O)_2P(OH)$	1.39		
$(nC_4H_9O)_2P(OH)$	1.72		
 $\mathrm{HOCH_2CH\overbrace{\underset{OP(O)(OH)_2}{C}H(CHOH)_2C}^{O}HOH}$	0.84	5.67	

The reaction of phosphoric acid with mono or diepoxides is a very convenient and economic method of synthesis of phosphoric acid esters. In the case of using monoepoxides the oligomeric mono, di and triesters terminated by hydroxyl group are formed as a result of oxirane addition to the P–OH bond followed by oxirane oligomerization according to the activated monomer mechanism[39] (11).



(11)

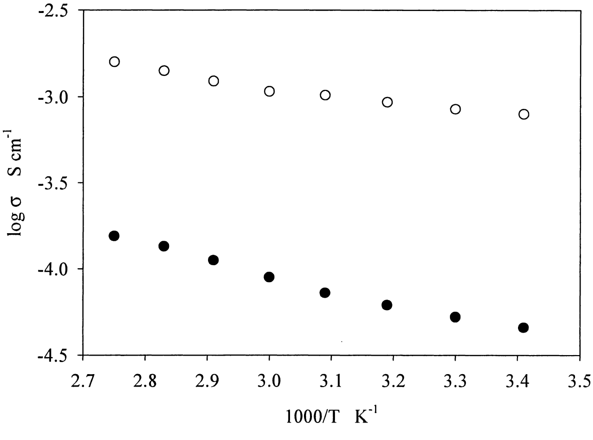
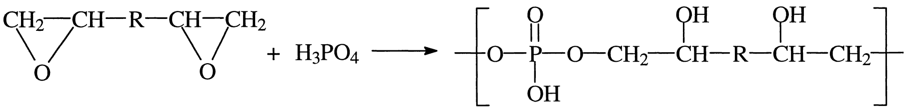


Fig. 7: Ionic conductivity of gel electrolytes as a function of inverse temperature; ● = gel containing 15 wt % of PVdF, 10.6 wt % of H_3PO_4; ○ = gel containing 15 wt % of PVdF, 13 wt % of diphenyl phosphate

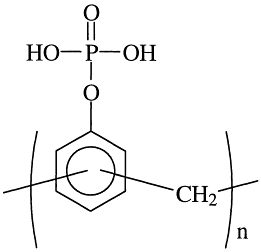
Phosphoric acid oligomeric esters were obtained when using glycidyl methacrylate as the oxirane, which were then subjected to free radical polymerization in the presence of DMF$^{37)}$. The gels obtained in these reactions exhibited conductivities higher than phosphoric acid solutions of the same concentration (over 10^{-4} S·cm^{-1} at ambient temperature).

The general scheme of H_3PO_4 addition to diepoxides can be presented by the following equation (12):



(12)

However, it is known from studies carried out by Penczek et al.[40)] that in many solvents gels are formed *in situ* due to physical crosslinking (via hydrogen bond) and chemical crosslinking (oxirane addition to side hydroxyl groups). The gels containing 50 wt % of dioxane and the product of the addition of phosphoric acid to the bisphenol A diglycidyl ether obtained in our laboratory exhibited ambient temperature conductivities of 10^{-5} S·cm^{-1}. The products of the condensation of phenyl monoester and formaldehyde also appeared to be very active components of proton conducting membranes[41)]. These products were obtained at 110 – 120°C using trioxane as the source of formaldehyde. Oligomers of a number average molecular weight 550 – 760 of from 2 to 5 monomeric units of the ester containing ~31% of *pp'*, 46.5% of *op'* and 22.5% of *oo'* isomers (13) were obtained under these conditions.



(13)

Studies carried out by the MALDI TOF and FAB techniques showed that oligomers from which one acid molecule abstracted, are also formed under these conditions.

Phosphorylated phenol-formaldehyde resins in aqueous solutions in the form of gels based on bisacrylamide and acrylamide copolymers exhibited at ambient temperature conductivity above 5×10^{-2} S·cm^{-1}, i.e. higher than those of membranes from perfluorosulfonated acids. Unfortunately, they easily underwent hydrolysis at elevated temperature. This process can be considerably limited by appropriate crosslinking of the resin.

Attempts were also made to use aromatic polyphosphates[42)] as components of proton conducting membranes. These products were obtained from the hydrolysis of the condensation products of bisphenol A with $POCl_3$. Carrying out the reaction in chloroform led to the obtaining of soluble oligomeric compounds of a branched structure of a number average molecular weight determined osmometrically equal to 2200. MALDI TOF mass spectroscopic studies showed the presence of oligomers (of molecular weights of 597 to 1097) containing 2–4 aromatic units and phosphate moieties. These compounds during heating for many hours in water did not undergo hydrolysis maintaining the branched structure.

Poly(vinylidene fluoride) (PVdF) - a film-forming polymer, was added to the phosphates formed in order to obtain proton conducting membranes. At a phosphate content not greater than 50 wt % membranes could be obtained of good mechanical properties with a uniformly dispersed conducting phase. After saturating with water such systems exhibit proton conductivity of 10^{-5} - 10^{-3} $S \cdot cm^{-1}$ at room temperature and 10^{-4} - 10^{-3} $S \cdot cm^{-1}$ at 90°C. In order to increase the hydrophilic character these membranes were modified additionally by the addition of N,N'-methylenediacrylamide, which was polymerized during the solvent removal. At the content of this component up to 10 wt % and 50-60 wt % of PVdF membranes are obtained characterized by very good mechanical properties capable to absorb about 40 wt % of water. The membrane becomes flexible in the hydrated form and its conductivity at room temperature reaches $\sim 1.5 \times 10^{-3}$ $S \cdot cm^{-1}$ and at 90 °C it is close to 8×10^{-3} $S \cdot cm^{-1}$.

Conclusions

Solid polymeric electrolytes composed of Brønsted acids and proton conducting macromolecules are an interesting object for fundamental studies on the conducting mechanism in solid state, but attempts of their practical application in electrochemical devices[23, 43, 33)] did not provide satisfactory results due to the too low conductivity values.

Several hydrogel protonic electrolytes exhibit ambient temperature conductivity comparable with these of hydrated perfluorosulfonated membranes ($\sim 10^{-2}$ $S \cdot cm^{-1}$). Studies on the application of these materials in ambient temperature hydrogen and methanol fuel cells showed that power obtained (in the range 15–60 $mW \cdot cm^{-2}$) is usually lower than that of Nafion based devices[34, 45)].

A majority of proton conducting hydrogels cannot be applied at elevated temperature due to the too week mechanical properties and inadequate chemical stability. Membranes in which polybenzimidazole is the matrix are a characteristic exemption here, which exceed with their chemical stability the perfluorosulfonated ionomers and can be applied in devices operating at 150–200°C[16, 46)]. This is especially important in the case of methanol cells, since in that temperature range electrode processes proceed in a very high yield. Moreover, a great advantage of these membranes is the relatively low methanol vapor permeability which causes that the loss of current density due to methanol crossover is significantly lower in comparison to that with perfluorinated materials. It should be also noted that the modulus of the doped polybenzimidazole is ca. 1000 times that of Nafion. These systems are now extensively studied and may also be extended to other heterocyclic polymers like polybenzimidazo-benzonantholines, which exhibit excellent thermal and mechanical properties. The hydrogels of ambient conductivity exceeding 10^{-5} S·cm^{-1} can be applied in various types of sensors[47)].

Nonaqueous protonic gel electrolytes seem to be very promising candidates for application in electrochromic devices. Their ambient and subambient conductivity in the range of 10^{-3} – 10^{-5} S·cm^{-1} is sufficient to ensure the coloration-bleaching response time shorter than 1 s. However, several important problems should be resolved, in particular the long-term transparency of electrolytes and reactions between the acid and conducting material.

The replacement of Brønsted acids by phosphoric acid organic mono- and diesters, which exhibit weaker hydrophilic properties, may be one of the routes for the development and ultimate manufacture of inexpensive reliable electrochromic mirrors and windows.

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