Proton conducting polymer electrolytes based on phosphorylated phenol–formaldehyde resins

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

[a] *Industrial Chemistry Research Institute, ul.Rydygiera 8, 01-793 Warsaw, Poland*
[b] *Department of Chemistry, Warsaw University of Technology, ul.Noakowskiego 3, 00-664 Warsaw, Poland*

Available online 24 March 2006

Abstract

Phosphorylated phenol–formaldehyde (PPF) resins were synthesized and investigated as the acidic components of proton conducting polymer electrolytes. The synthesis of PPF resins was carried out by melt polycondensation of monophenyl phosphate and formaldehyde (in the form of trioxane). The structure and molecular weight characterization of PPF resins were performed employing ^{1}H-, ^{13}C- and ^{31}P-NMR spectroscopy, Fast Atom Bombardment mass spectrometry and elemental analysis. PPF resins may be cured with an excess of formaldehyde. Depending on the curing conditions, products of different crosslinking density (expressed by equilibrium swelling ratio) and total ion-exchange capacity up to 9 mequiv. g^{-1} may be obtained. The soluble and crosslinked PPF resins were examined from the viewpoint of conducting properties and hydrolytical stability. Crosslinked PPF resins embedded in poly(vinylidene fluoride) binder form ion-exchange membranes of ambient conductivities above 0.05 S cm^{-1}. These composite membranes have been investigated in a methanol fuel cell and showed stable performance during several hours of cell operation.
© 2006 Elsevier B.V. All rights reserved.

Keywords: Phosphorylated phenol–formaldehyde resin; Proton conductivity; Membranes; AC impedance; DMFC

1. Introduction

Proton conducting polymeric membranes receive broad attention due to their potential applications as electrolytes in fuel cells, supercapacitors, electrochromic displays and other electrochromic devices [1–3]. Pefluorinated sulfonic acid membranes, best known by the trade name Nafion, are the most commonly used conductors. They combine the high ability of proton conductivity in hydrated state with long term electrochemical stability [4–6]. In search for a less expensive alternative to Nafion, various types of polyelectrolytes containing chemically bonded sulfonic acid groups with similar superior physicochemical characteristics have been developed in a laboratory scale. This includes perfluorosulfonate ionomers, sulfonated trifluorostyrene polymers, polyimides, polysulfones, polyarylketones and hybrid inorganic–organic systems synthesized by the sol–gel method [7–9]. These types of materials are expected to see service in automotive fuel cells or power stations operating at temperatures well above 100 °C. In applications where less stringent requirements are imposed on the electrolyte (like for example in small portable fuel cells working at ambient temperature), also inexpensive membranes based on hydrocarbon polyelectrolytes or inorganic acids immobilized in proton coordinating polymeric matrix have been extensively studied [9–12].

Attempts were also made to use mono- and diesters of phosphoric acid as components of proton conducting membranes [12–16]. In order to maintain their mechanical strength the conducting phase was often embedded in film forming polymers like for example poly(vinylidene fluoride) (PVdF). After saturation with water or polar organic solvent, such a system exhibits conductivity 10^{-5} to 10^{-3} S cm^{-1} at room temperature. Unfortunately, a majority of phosphoric acid esters underwent hydrolysis and after a certain period of time phosphoric acid was gradually washed up from the membrane. We have found, however, that some aromatic polyphosphate obtained from bisphenol A and phosphorus oxychloride [16] maintain high hydrolytic stability and may be used in membranes working at moderate temperature under conditions of low water content.

In the work reported here the phosphorylated phenol–formaldehyde (PPF) resins (Eq. (1)) were tested as a possible inexpensive acidic component of composite proton conducting

membranes

(1)
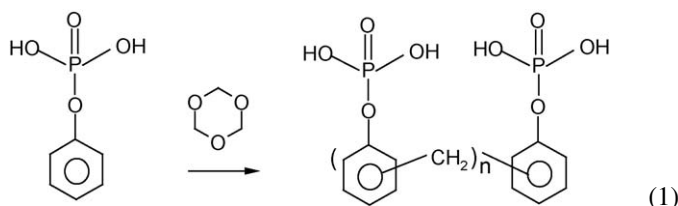
The condensation of monophenyl phosphate (MPPA) with formaldehyde or substances which generate formaldehyde upon decomposition is the most convenient way to synthesize the PPF resin [17,18]. Earlier [19], we described in detail the synthesis method, in which trioxane was applied as the source of formaldehyde. It permits to obtain both oligomers as well as crosslinked products. In this paper we mostly focused on the structure, conductivity and hydrolytical stability of PPF resins before and after crosslinking. The results of preliminary studies on the performance of ion-exchange membrane composed of crosslinked resins and PVdF binder in direct methanol fuel cells are also presented.

2. Experimental

2.1. Materials

Phenol (Polish Chemical Reagents, POCh, Gliwice, Poland), phosphorus oxychloride (Merck), sulfuric acid (Tech. Grade, 95 wt.%), N,N-dimethylacetamide (Merck) and poly(vinylidene fluoride) (PVdF) (M_w 275 000, M_n 107 000, Aldrich) were used without further purification. Trioxane (Tech. Grade from Tarnow Nitrogen Works) was purified by distillation.

2.2. Synthesis of phosphorylated phenol–formaldehyde (PPF) resin

Monophenyl phosphate (MPPA) was synthesized according to a known method [17]. A solution of phenol (86.5 g, 0.92 mol) in dry toluene (400 ml) was added dropwise to refluxing phosphorus oxychloride (101 ml, 1.10 mol) containing anhydrous AlCl$_3$ (1.25 g). The refluxing was continued for 3 h, the reaction mixture was filtered, and then the excess of POCl$_3$ and toluene was distilled off under atmospheric pressure. Dichlorophosphoryloxybenzene was then distilled at 84–86 °C/3 mmHg (90.9 g), and hydrolyzed with excess water. After evaporation, crude MPPA (74.2 g, 46.3%) was obtained, which after two recrystallizations from a chloroform-ethanol mixture gave colorless plates of m.p. 98–99 °C. ^{1}H-NMR (acetone-d$_6$) (δ ppm): 7.1–7.2 (3 H, (o, p) ArH), 7.3–7.4 (2 H, (m) ArH), 10–13 (2 H, P(O)(OH)); ^{31}P-NMR (D$_2$O) (ppm): −3.7.

MPPA (10–25 g) was melted in a three-necked flask provided with a mechanical stirrer and a reflux condenser and placed in an oil bath preheated to 120 °C. Trioxane (for molar ratio see Table 1) was progressively added with vigorous stirring. The melt was stirred at 120–125 °C for 30–60 min. The obtained resins were found to be soluble in water, methanol and DMSO and insoluble in acetone. The degree of polycondensation (DP)

Table 1
Phosphorylated phenol–formaldehyde (PPF) resins synthesized by polycondensation of monophenyl phosphate (MPPA) with trioxane

PPF resin	MPPA:CH$_2$O molar ratio	PA[a] (wt.%)	DP[b]
1	1:0.8	13	3.6
2	1:0.9	9.5	4.1
3	1:1	10.5	5.5

[a] PA, free phosphoric acid content.
[b] DP, degree of polycondensation calculated from ^{1}H-NMR spectra.

values were calculated on the basis of integrals corresponding to methylene (δ_{CH2} 3.4–4.2 ppm) and aromatic (Ar) (δ_{ArH} 6.6–7.4 ppm) protons in ^{1}H-NMR spectra (Fig. 1a) according to the following equations:

$$Ph = [ArOH] = \frac{1}{5}([ArH] + [CH_2])$$

$$DP = \frac{1}{1 - 0.5[CH_2]/Ph}$$

This method of M_n evaluation assumes no cyclic oligomers being present and may be applied to the resins of low DP values. This assumption is legitimate, since studies of the reaction mixture composition by the mass spectroscopy method shows that in the systems studied signals characteristic of cyclic products are not present (Fig. 2).

2.3. Curing of PPF resins

(a) PPF resin (1.88 g) was added to 95 wt.% sulfuric acid (4 ml), and this mixture was stirred at room temperature for 1 h and left for 22 h. Then, trioxane (0.28 g) was added in several portions and the resulting solution was left for 46 h. The insoluble product was then filtered off, triturated and washed several times with deionized water and dried. The yield of cured resin was 0.6 g (30%).

(b) PPF resin was prepared by melt polycondensation of 20 g of MPPA (115 mmol) and 2.8 g of trioxane (92 mmol) carried out in a flask placed in an oil bath at 125 °C for 35 min. Then, 13 ml of 37% formaldehyde aqueous solution (171 mmol)
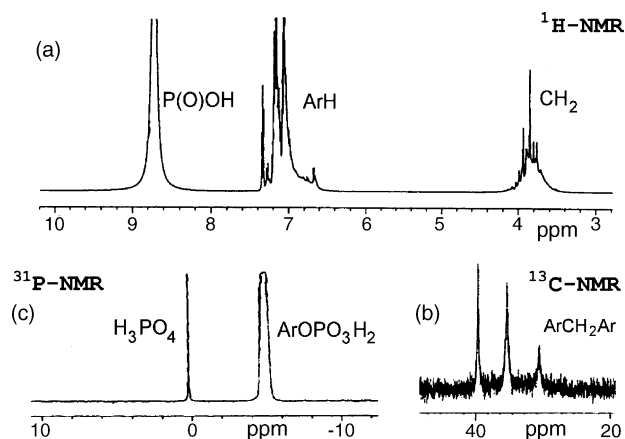

Fig. 1. NMR spectra of phosphorylated phenol–formaldehyde resin.
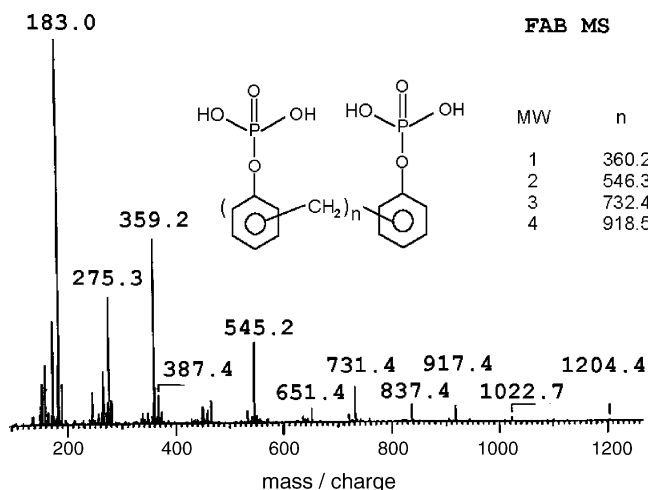
Fig. 2. Negative-ion FAB mass spectrum of $[M–H]^-$ for phosphorylated phenol–formaldehyde resin (DP = 3.6 calculated from NMR data, peak at *m/z* 183 is due to matrix).

was added and left overnight at room temperature. Water was distilled off under reduced pressure, and the resinous residue was heated at 120 °C for 2 h. The insoluble product was then filtered off, triturated and washed several times with deionized water. After drying in vacuum at 80 °C the yield of cured resin was 16 g (76%). Cured PPF resins were ground and sieved (mesh size 430 μm).

2.4. Preparation of PVdF–PPF resin composite membranes

Crosslinked PPF resin was ground to the particle size below 0.12 mm and suspended in 10 wt.% solution of poly(vinylidene fluoride) in dimethylacetamide. The resulting suspension was stirred for 15–30 min, then poured onto a glass plate and the solvent was evaporated off at 50–60 °C. The composite was then immersed in deionized water, dried in air and hot pressed using hydraulic press PRECO Inc. at 170–180 °C to obtain 200–300 μm thick membranes. The pressing cycle consisted of 2 min heating with subsequent deaeration and 2–3 min heating under pressure at a load of 10 t.

For the determination of water uptake, membranes were dried at 120 °C under reduced pressure to constant weight, then immersed for 66 h in distilled water, and weighed after blotting excess water with filter paper.

2.5. Experimental techniques

The NMR spectra were obtained by using a Varian INOVA 500 MHz spectrometer.

^{1}H-NMR measurements were performed by using DMSO-d$_6$ as a solvent and TMS as internal standard. For the purpose of quantitative analysis, the insoluble fraction of resin was removed by centrifugation prior to measurements. ^{13}C-NMR and ^{31}P-NMR analyses were carried out in aqueous solutions diluted with D$_2$O by using a pulse angle of 30°, with relaxation delays of 4–8 and 25 s, respectively. The ^{13}C-NMR chemical shifts were measured relative to dioxane ($\delta = 66.5$ ppm) as internal reference.

^{31}P-NMR spectra were referenced to phosphoric acid (85%) as external standard. Negative fast atom bombardment (FAB) mass spectrum was taken with a Finnigan MAT 95 spectrometer by using liquid secondary ion mass spectrometry. The Cs$^+$ ion (13 keV) source was operated at −4.8 kV accelerating voltage. Glycerol was used as a matrix compound.

Phosphorus elemental analysis was performed by heating the sample in a mixture of perchloric and nitric acid followed with titration of the resulting phosphate ion with lanthanum nitrate. Hydrolytic stability of PPF resins was investigated by refluxing its aqueous solutions (1 mol kg^{-1}). A progress of hydrolysis was followed with ^{31}P-NMR spectra showing changes in the content of phosphate ester groups ($\delta \sim 4$–5 ppm) and free phosphoric acid ($\delta \sim 0$ ppm). In the case of cured PPF resin the hydrolytic stability was studied by extraction with water using a Soxhlet apparatus, followed by determination of phosphorus content in the resin.

Ionic conductivity of electrolytes was determined using the complex impedance method. The samples of electrolytes were sandwiched between two stainless steel blocking electrodes (of diameter 7.8 mm, electrolyte thickness 1.6 mm) and placed in a temperature-controlled furnace. The impedance measurements were carried out on a computer-interfaced Solartron Schlumberger 1255 impedance analyzer. The frequency range used was 1 Hz to 1 MHz.

Fuel cell performance tests were carried out using a Globe Tech GT 60 station adapted to work in a system supplied with aqueous methanol solution (2 mol L^{-1}). The Pt catalyst loading of anode was 2.03 mg cm^{-2} and that of cathode was 2.24 mg cm^{-2}. Methanol was supplied at 2 atm pressure and flow rate of 2.4 ml min^{-1}. Oxygen was delivered at 3 atm pressure and flow rate of 2.4 ml min^{-1}. The operating temperature of the cell was varied between 30 and 120 °C.

3. Results and discussion

3.1. Physicochemical characteristics of PPF resins

PPF resins obtained as products of spontaneous condensation of molten MPPA and trioxane are oligomers of average degree of polycondensation (DP) between 3 and 6 (Table 1). The DP value is dependent mostly on the molar ratio of reagents and increases with increasing the trioxane content in the reaction mixture. As a result of reaction with formaldehyde, phenolic moieties in MPPA undergo substitution at ortho and para ring positions, and further condensation results in a mixture of products containing approximately 20% ortho–ortho, 50% ortho–para and 30% para–para methylene linkages. The share of these linkages can be estimated on the basis of the relative intensity of signals of methylene groups carbon nuclei in the ^{13}C-NMR spectra (Fig. 1b) [20]. In Fig. 2 is presented an exemplary FAB mass spectrum of PPF resin of calculated DP = 3.6. This spectrum includes a sequence of deprotonated molecular ions $[M–H]$ corresponding to the oligomers of DP in the range from 2 to 5. No signals characteristic for parent peaks of cyclic oligomers are observed. However, several peaks of lower intensity may be

Table 2
Properties of crosslinked phosphorylated phenol–formaldehyde (PPF) resins

PPF resin	PPF resin:CH$_2$O molar ratio	IEC[a] (mequiv. g^{-1})	Phosphorus (wt.%)	ESR[b] (vol.%)	EW[c] (g mol^{-1})
1	1:0.65	8.96	14.3	930	112
2	1:0.8	7.72	–	330	129.5
3	1:1	8.63	13.8	280	116
4	1:1.5	8.60	13.7	154	116
5	1:2	8.93	12.6	55	112

[a] IEC, ion exchange capacity.
[b] ESR, equilibrium swelling ratio in water.
[c] EW, equivalent weight.

assigned to the molecules formed by elimination of one phosphate ester group. This means that under the synthesis conditions partial hydrolysis of the P–O bonds takes place and phosphoric acid is present in the system, besides the resin. On the basis of analysis of ^{31}P-NMR spectra of the products (Fig. 1c) it can be estimated that 10–13% of ester groups undergoes hydrolysis at this stage of synthesis at 120–125 °C. Despite this, the method assures the obtaining of a higher concentration of acidic groups than the alternative solution consisting in the reaction of phenol–formaldehyde resins with POCl$_3$. From the literature data [17,18], and also from our studies [19] it appears that in this latter method it is not possible to obtain products of the degree of esterification greater than 65%.

Crosslinked products were obtained from the reaction of PPF resins with an excess of trioxane or formaldehyde. The reaction with trioxane was carried out at room temperature in a concentrated sulfuric acid solution. The amount of trioxane was calculated to obtain the products of low crosslink density, with the capacity to absorb high quantities of water. The resins cured in this way contain over 3 wt.% of sulfur that remains even after multiple washing of the resin with water. It may result from the partial sulfonation of aromatic rings.

Products of higher crosslinking density were obtained by dissolving the PPF resin in an aqueous formaldehyde solution followed by the evaporation of water and heating the residue at 125 °C. In both cases, curing proceeds under the anhydrous or near anhydrous conditions. For example, after the replacement of 95% of sulfuric acid by its 25 wt.% aqueous solution, no gelation was observed during several days.

Crosslinked PPF resins were characterized by the determination of total ion exchange capacity (IEC), phosphorus content and equilibrium swelling ratio in water (Table 2). IEC value in the range of 7.7–9 mequiv. g^{-1} and P weight content near 14% correspond to about 80–85% of the theoretical content of acidic phosphate groups in the resin. The volume swelling ratio in water varies from 50 to 950%, depending on the amount of hardener used. On the basis of IEC values, the equivalent weight (EW) of PPF resin, i.e. weight of dry resin per mole of acidic sites, was calculated in the range of 112–130 g mol^{-1}.

3.2. Hydrolytic stability of PPF resins

Hydrolytic stability is one of the important properties, which are required from proton conducting polymers for fuel cell applications. Being the monoesters of phosphoric acid, PPF
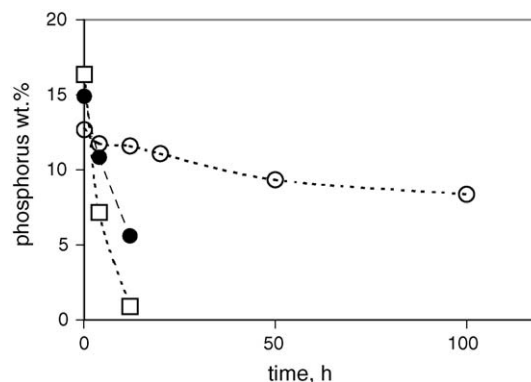

Fig. 3. Hydrolytic stability of monophenyl phosphate (□), phosphorylated phenol–formaldehyde (PPF) resin (●) and crosslinked PPF resin (○) at 100 °C.

resins undergo hydrolysis in aqueous solutions, resulting in the reproduction of phenolic hydroxyl group and the formation of orthophosphoric acid. Progress of hydrolysis may be followed with ^{31}P-NMR spectra, which display changes in the content of acidic phosphate groups ($\sigma \sim 4-5$ ppm) and free H$_3$PO$_4$ ($\sigma \sim 0$ ppm). At room temperature the hydrolysis process is relatively slow. In 40% aqueous solutions of the resin about 5% of ester bonds per year undergoes hydrolysis. However, at 100 °C about half of the ester groups underwent hydrolytic cleavage after 10 h of reflux (Fig. 3). Over the same period, nearly 95% of MPPA undergoes hydrolysis. The resistance towards hydrolysis
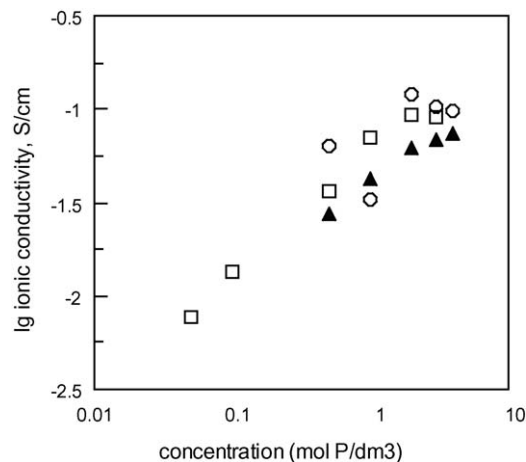

Fig. 4. Ambient temperature ionic conductivity of aqueous solutions of phosphorylated phenol–formaldehyde resin (□), monophenyl phosphate (○) and phosphoric acid (▲).

Table 3
PVDF/crosslinked phosphorylated phenol–formaldehyde (PPF) resins composite membranes

Membrane	ESR of resin[a] (vol.%)	PPF content (wt.%)	EW[b] (g mol^{-1})	Water uptake[c] (wt.%)	
				(1)	(2)
1	930	50	224	7.3	12.9
2	930	70	160	20.4	26.8
3	154	70	166	11.0	15.7
4	930	80	140	16.1	27.8

[a] ESR, equilibrium swelling ratio in water.
[b] EW, equivalent weight.
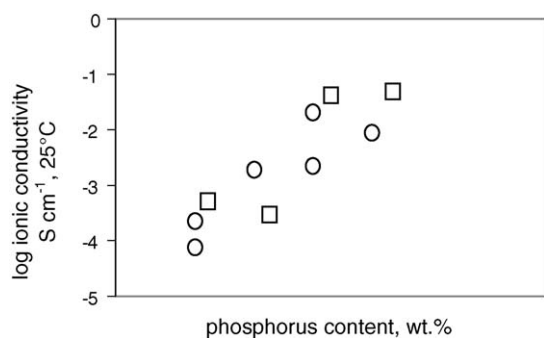[c] water uptake (1), initial, (2), after drying and rehydration.

Fig. 5. Ambient temperature ionic conductivity of composite membranes PVDF/crosslinked phosphorylated phenol–formaldehyde (PPF) resin (equilibrium swelling ratio in water of PPF resin: 154 vol.% (○), 930 vol.% (□)).

slightly increases with an increase in the degree of polycondensation. The hydrolytic stability of cured resins was studied by the extraction with boiling water using a Soxhlet apparatus and subsequent determination of phosphorus content by elemental analysis. Cured resins are, according to expectations, less susceptible to hydrolysis and for example, the resin of the highest degree of crosslinking lost one third of phosphorus content after 100 h of extraction (Fig. 3).
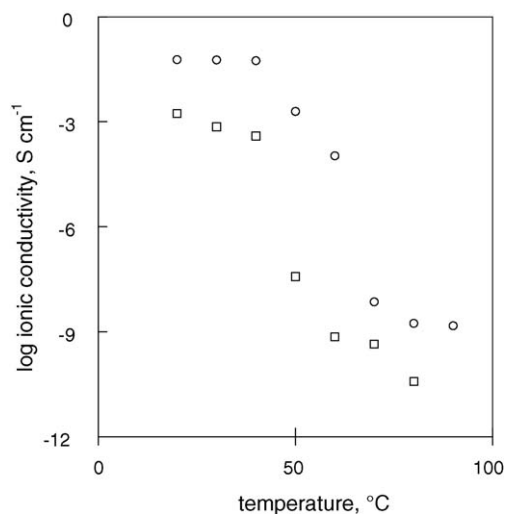

Fig. 6. Effect of temperature on the ionic conductivity of composite membranes: PVDF/crosslinked phosphorylated phenol–formaldehyde resin (wt. ratio: 30:70 (□), 20:80 (○)).
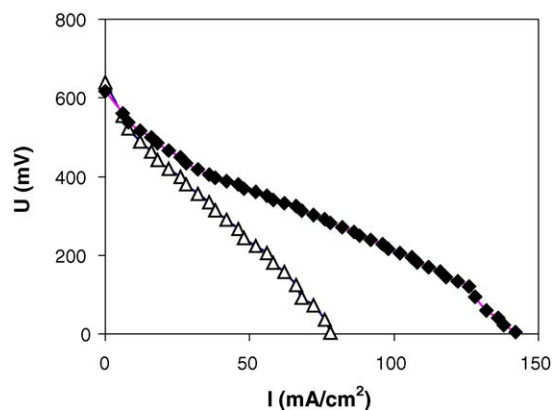

Fig. 7. Polarization curve for composite membrane PVDF/crosslinked phosphorylated phenol–formaldehyde (PPF) resin (80:20 wt. ratio, equilibrium swelling ratio in water of PPF resin: 154 vol.%) in methanol fuel cell working at 90 °C; initial (△), after 7 h of cell operation (■).

3.3. Ionic conductivity of PPF resins

Fig. 4 shows ambient ionic conductivity of aqueous solutions of one of the soluble PPF resins, MPPA monomer and orthophosphoric acid in dependence of acidic group concentration. One can observe that the conductivity values for electrolytes containing the resin or monomer are distinctly higher than those of orthophosphoric acid solutions. The phosphoric acid monoesters
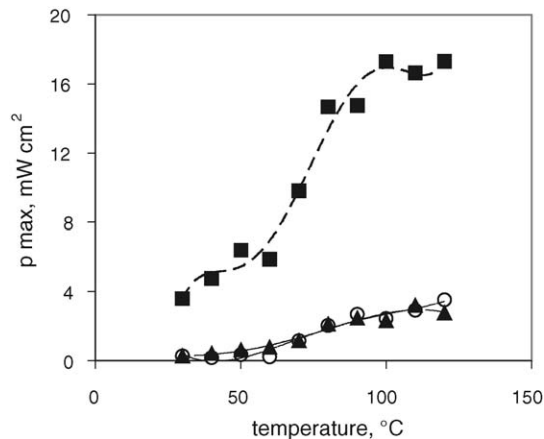

Fig. 8. Maximum power density vs. temperature for composite membranes PVDF/crosslinked phosphorylated phenol–formaldehyde resin (wt. ratio: 40:60 (○), 30:70 (▲), 20:80 (■)) in methanol fuel cell.

Table 4
Performance of PVDF/crosslinked phosphorylated phenol–formaldehyde (PPF) resins (20:80 wt. ratio) membrane in methanol fuel cell[a]

Temperature (°C)			p_{max}[b] (mW cm^{-2})	OCV[c] (mV)
Fuel cell	MeOH	O$_2$		
30	120	90	3.6	502
70	110	80	9.8	606
80	120	90	14.7	599
90	140	100	13.8	608
100	140	110	17.3	622
120	140	120	17.3	665
90[d]	140	100	21.9	625
30	120	90	3.6	502
70	110	80	9.8	606

[a] C methanol = 2 mol dm^{-3}; p MeOH = 2 atm; p O$_2$ = 3 atm; F methanol = 2.4 cm^3 min^{-1}; F oxygen = 0.3 dm^3 min^{-1}.
[b] p_{max}, maximum power density.
[c] OCV, open circuit voltage.
[d] After 7 h of cell operation at 90 °C.

are usually a stronger acid than H$_3$PO$_4$ itself as shown by their pK_1 values [21]. This probably results in a higher degree of dissociation and therefore larger fraction of charge carriers in electrolytes based on esters. For high resin concentrations the conductivity exceeds 10^{-1} S cm^{-1} at ambient temperature, which is about two orders of magnitude higher than that for commercially available hydrated proton conducting membranes.

To obtain membranes with good mechanical properties, the cured resins were powdered and dispersed in a PVdF matrix. A two-step procedure was applied, which involved casting of the blend composed of crosslinked PPF resin and PVDF from the suspension in dimethylacetamide, followed by hot-pressing of the resulting composite to form a 0.2–0.3 mm thick membrane. The obtained composite membranes, containing up to 80 wt.% of crosslinked PPF resin, showed reasonably good mechanical properties (tensile strength at break about 5.4 MPa, tensile elongation at break 1.2%) and water uptake in the range 7–20 wt.% (Table 3). The ambient temperature conductivity of hydrated membranes depends on the PPF resin content and reaches the highest value about 5×10^{-2} S cm^{-1} (Fig. 5). This results from the increase in the concentration of carriers and greater amount of embedded water. The water uptake increases after drying of the membrane and repeated imbedding with water. It was also found that after the extraction with boiling water for 10 h, the composite membranes with 80 wt.% PPF resin increase the water uptake to 26 wt.% and ionic conductivity to 6×10^{-2} S cm^{-1}, which suggests that some additional conducting channels might be formed at higher temperature. In the case of commercial Nafion 117 membranes the maximum water imbedding at 20 °C is ca. 17% and the ambient temperature conductivity is ∼4×10^{-3} S cm^{-1} [22]. The higher conductivity of the composite membranes obtained results probably from the higher content of acidic groups. Equivalent weight (EW) of the membrane, i.e. the amount in grams of polymer per mol of fixed acidic groups for NAFION 117 is 1100 and for composite membranes studied, ranges from 145 to 230. The conductivity of composite membranes does not change significantly up to about 60 °C, but at higher temperature, it decreases due to the membrane dehydration (Fig. 6).

3.4. Fuel cell testing

Several composite membranes with different PPF resin/PVdF ratio were fabricated into membrane–electrode assemblies and tested in a methanol powered fuel cell. The current–voltage characteristics were measured over the temperature range from 30 to 120 °C. Fig. 7 presents typical polarization curves obtained in these experiments, whereas Fig. 8 and Table 4 present the maximal values of power density and open circuit voltage of the cell. At fixed reactant pressure and methanol concentration values, the cell performance depends significantly on the working temperature as well as the PPF resin content in the membrane. The highest power density and OCV values were observed in the case of the membrane containing 80 wt.% of PPF resin. It should be noticed that cell performance usually was improved after several hours of performance. For example in the case of the membrane of highest resin concentration at the initial period of cell performance, the maximum value of power density at 90 °C was near 14 mW cm^2 and after 7 h it increased to about 22 mW cm^2 (the cell voltage was 280 mV at a current density of 80 mA cm^2). The gradual increase in the water content in the membrane and the increase in the membrane conductivity are probably the reasons for this. One cannot exclude, however that a small amount of H$_3$PO$_4$ is liberated from the membrane surface and thus the wetting of the electrode is certainly improved. The maximum power density reached is so far approximately three times lower than that for Nafion 117 membranes [22], despite that composite membrane exhibit superior conducting properties. The main reason for this is probably the higher methanol permeability of the composite membrane.

4. Conclusions

In our search for cost effective proton conducting membranes, phenol–formaldehyde resins esterified with acidic phosphate groups were obtained and characterized. Low molecular weight phosphorylated phenol–formaldehyde PPF resins in aqueous solutions exhibit high ambient temperature protonic conductivities, however, their hydrolytic stability at high tem-

peratures is rather limited. The resistance to hydrolysis may be improved by the crosslinking of PPF resins with an excess of formaldehyde, leading to products of total ion-exchange capacities up to $9\,\mathrm{mequiv.\,g^{-1}}$ and equilibrium swelling ratio in water up to 930 vol.%. Crosslinked PPF resins were investigated as acid components of composite proton conducting electrolytes in combination with PVdF as an inert film-forming binder. This type of membranes shows high values of ambient temperature ionic conductivities (above $0.05\,\mathrm{S\,cm^{-1}}$). The PVDF/crosslinked PPF resin composite membranes have been investigated in a methanol fuel cell and showed stable performance during several hours of cell operation. Although composite membranes were found to be good conductors, improvements are still needed to be competitive with Nafion as polymer electrolytes for low temperature fuel cell. Ongoing work is focused on the impregnation of porous membranes of different hydrophilicity with PPF resins, followed by direct crosslinking at ambient temperature and on chemical modification of the resin structure to produce a film that is less permeable to methanol than Nafion 117.

Acknowledgments

References

[1] J.C. Lasseques, in: P. Colomban (Ed.), Proton Conductors: Solids, Membranes and Gel Materials and Devices, Cambridge University Press, Cambridge, 1992 (Chapter 20).

[2] K.V. Kurdesch, G.R. Simander, Chem. Rev. 695 (1995) 197.

[3] J. Jacoby, Chem. Eng. News 81 (2003) 32.

[4] T.A. Zawodzinski, T.E. Springer, F. Uribe, S. Gottesfeld, Solid State Ionics 60 (1993) 199.

[5] K.D. Kreuer, Chem. Mater. 8 (1996) 610.

[6] G. Alberti, M. Casciola, Solid State Ionics 145 (2001) 3.

[7] V. Di Notto, M. Furlani, S. Lavina, Polym. Adv. Technol. 7 (1996) 759.

[8] O. Savadogo, J. New Mater. Electrochem. Syst. 1 (1998) 47.

[9] M. Rikukawa, K. Sanui, Prog. Polym. Sci. 25 (2000) 1463.

[10] Z. Florjańczyk, E. Zygadło-Monikowska, E. Wielgus-Barry, K. Kuźwa, J. Paśniewski, Electrochim. Acta 48 (2003) 2201.

[11] Ch.W. Walker Jr., J. Power Sources 110 (2002) 144.

[12] W. Wieczorek, Z. Florjańczyk, J.R. Stevens, Electrochim. Acta 40 (1995) 40.

[13] Z. Florjanczyk, W. Bzducha, M. Kędzierski, Macromol. Symp. 152 (2000) 223.

[14] D. Raducha, W. Wieczorek, Z. Florjańczyk, J.R. Stevens, J. Phys. Chem. 100 (1996) 20126.

[15] G. Żukowska, W. Wieczorek, M. Kędzierski, Z. Florjańczyk, Solid State Ionics 144 (2001) 163.

[16] Z. Florjańczyk, W. Bzducha, R. Wróblewski, P. Cieślicki, E. Zygadło-Monikowska, Polimery 44 (1999) 18.

[17] C.K.S. Pillai, V.S. Prasad, J.D. Sudha, S.C. Bera, A.R.R. Menon, J. Appl. Polym. Sci. 41 (1990) 2487.

[18] R. Antony, C.K.S. Pillai, J. Appl. Polym. Sci. 54 (1994) 429J.

[19] M. Kędzierski, Z. Florjańczyk, Polimery 46 (2001) 511.

[20] T.A. Yamagishi, M. Nomoto, S. Ito, S.I. Ishida, Y. Nakamoto, Polym. Bull. 32 (1994) 501.

[21] R. van Wazer, Phosphorus and Its Compounds, vol. 1, Interscience, New York, 1958, p. 583.

[22] Z. Florjańczyk, E. Wielgus-Barry, Z. Połtarzewski, Solid State Ionics 145 (2001) 119.