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Ion exchange membranes based on vinylphosphonic acid-co-acrylonitrile copolymers for fuel cells

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ABSTRACT

Poly(vinylphosphonic acid-co-acrylonitrile) with various concentrations of vinylphosphonic acid polymer units were prepared by free radical solution polymerization. The membranes were prepared by casting polymer solutions in N,N´-dimethylformamide and evaporating the solvent. Thermogravimetric analysis showed the stability of prepared membranes up to 175°C, and membranes were stable in oxidative Fenton reagent for 1 h at 70°C. The membranes of polymers containing more than 16 mol% of units with phosphonic acid group swelled excessively in water. The ionic conductivity of membranes increased with the increasing concentration of polymer units with a phosphonic acid group in the polymer chain and with temperature. The conductivity of a membrane with 15.5 mol% of polymer units with a phosphonic acid group was 5.15 S m^{-1} at 35°C. Membrane containing 15.5 mol % phosphonic acid units in polymer was tested in fuel cell.

Keywords: Vinylphosphonic acid; Poly(vinylphosphonic acid-co-acrylonitrile); Ionic conductivity; Membrane; PEM FC

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1. Introduction

Polymeric aliphatic ion exchange perfluorosulfonic acid membranes, such as Nafion, are now widely used in fuel cells as electrolytes. They show high fuel cell performance, high ion conductivity, and long-term stability against oxidation by radical species which are generated during the fuel cell operation. Nafion can work in a fuel cell up to 60,000 h without significant decrease in the performance [1]. However, one of its disadvantages is its high cost. Therefore, sulfonated aromatic polymers are investigated as an alternative to perfluorosulfonic acid membranes in low-temperature fuel cells. The aromatic polymers include, in particular, sulfonated poly(1,4-phenylene oxide), poly (1,4-phenylene sulfide), poly(ether ether ketone), poly (ether ether sulfone), and poly(imide)s [2–10]. Proton

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exchange membranes based on sulfonated aromatic polymers are not sufficiently resistant against oxidation– they can only work in fuel cells approximately 500–4,000 h without a significant decrease in the performance. After that time, they lose mechanical strength and protonic conductivity [11] due to the reaction of benzene rings in polymer giving pseudoquinonic rigid structures [12]. The alternative to the membranes of polymers carrying sulfonic acid groups on benzene rings are the membranes carrying phosphonic acid groups on aliphatic chains. There are several papers describing the ion exchange membranes with phosphonic acid groups bound to aromatic ring polymers, such as poly(sulfone)s or poly(etherketone)s [13–17]. The membranes with phosphonic acid groups bound to aliphatic chains were prepared by grafting vinylphosphonic acid (VPA) onto poly(sulfone) [18] or via polymeranalogous Arbuzov reaction of halogenated side chain with triethylphosphite and subsequent hydrolysis [19]. Bozkurt prepared proton-conducting materials by copolymerization of VPA with 4-vinylimidazole [20]. Wu and Weiss [21] tried to prepare proton conductive materials by the copolymerization of diethylvinylphosphonate with styrene and by subsequent hydrolysis. The aim of this work was the synthesis of copolymers VPA with acrylonitrile (AN), preparation and characterization of membranes based on prepared copolymers, and testing their performance as an alterative polymer electrolyte in H_2/O_2 fuel cell.

2. Experimental

2.1. Materials

VPA (97%, Aldrich), AN (99%, Aldrich), dimethylsulfoxide (DMSO) (pure, Lach-Ner, Czech Republic), N,N´-dimethylformamide (DMF) (pure, Lach-Ner, Czech Republic), 2,2´-azobis(2-methylpropionitrile) (AIBN) (98%, Aldrich), hydrogen peroxide 30% (p.a. Lach-Ner, Czech Republic), iron sulfate annealed (p.a. Lachema, Czech Republic), hydrochloric acid (35% solution) (p.a. Lach-Ner), and Nafion 112 (Aldrich) were used as received.

2.2. Poly(vinylphosphonic acid-co-acrylonitrile) synthesis

Copolymers were synthesized by free radical solution polymerization of VPA and AN (total amount of monomers 30 g) in DMSO (70 g), using AIBN as an initiator (0.20 g). The amounts of vinylphoshonic acid and of AN were varied in different experiments from 40 (VPA10) to 60 wt% (VPA16), see Table 1. In all experiments, the polymerization temperature and time were 70°C and 5 h, respectively. The polymers were precipitated from the reaction mixtures into ethanol, filtered, and thoroughly washed with ethanol. They were dried at room temperature. Structural formula of copolymers is shown in Fig. 1.

2.3. Membrane preparation

All membranes were prepared as homogenous films from DMF solutions. Polymers were dissolved in DMF (10% solution) and cast on a glass plate. The solvent was evaporated at 70°C in an oven overnight. To remove the residual solvent, membranes were heated to 160°C for 30 min. Final membrane thickness after drying ranged from 150 to 200 μm.

2.4. Molecular weight determination

The weight-average molecular weights of polymers were determined by modular HPLC using pump HPP5001 (Laboratory Instruments, Prague, Czech Republic), column Labio GM1000, 8 × 500 mm (Labio Ltd., Czech Republic) and mobile phase DMAc + 0.5 wt% LiBr. The column was equipped with differential refractometer RIDK 101 (Laboratory Instruments, Prague, Czech Republic). The apparatus was calibrated with polystyrene standards (Merck, Germany). The molecular weights were calculated on polystyrene standards.

2.5. Thermogravimetric analysis

Thermogravimetric analysis (TGA) was performed using a Perkin-Elmer thermal analysis controller TAC 7/DX from 30 to 750°C at a heating rate of 10°C min^{-1} under a nitrogen atmosphere.

2.6. FTIR spectroscopy

The FTIR spectra of VPA membranes were recorded using a Perkin-Elmer Paragon 1000PC spectrometer using Specac MKII Golden Gate Single Reflection ATR System. All spectra were measured in the range 4,400–450 cm^{-1} with resolution 4 cm^{-1}.

2.7. Ion exchange capacity

The ion exchange capacity could not be measured by titration because membranes were not stable in alkaline environment and dissolved; therefore, the ion exchange capacity was calculated from phosphorus content in polymers found by elemental analysis.

Table 1
Vinylphosphonic acid copolymers: composition of polymerization mixtures and of resulting polymers

Polymer code	VPA monomer (mol)	AN monomer (mol)	P in polymer[a] (wt%)	N in polymer[a] (wt%)	VPA in polymer[b] (mol%)	AN in polymer[c] (mol%)	Sum of VPA and AN (mol%)
VPA10	0.0940	0.3398	5.17	19.67	9.75	85.62	95.37
VPA13	0.118	0.2835	6.49	17.95	12.57	81.23	93.80
VPA16	0.141	0.2263	7.81	16.69	15.53	77.77	93.30

[a] Elemental analysis.
[b] Based on P content.
[c] Based on N content.

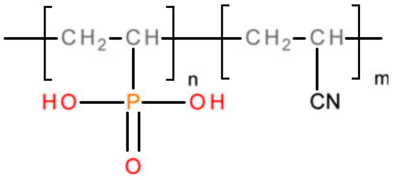

Fig. 1. Structural formula of poly(vinylphosphonic acid-co-acrylonitrile).

2.8. Water uptake

All membranes were dried at 160°C before measurement for a half-hour. After measuring the weights of dried membranes, the membranes were immersed into demineralized water at 25, 60, and 90°C, respectively, until reaching constant weight (24 h). Before measuring of hydrated membranes, water drops from membrane surface were removed by paper wipes. Water uptake (degree of swelling, DS) was calculated using Eq. (1):

$$\mathrm{DS} = \frac{m_{\mathrm{wet}} - m_{\mathrm{dry}}}{m_{\mathrm{dry}}} \times 100\% \tag{1}$$

where m_{wet} and m_{dry} are the weights of wet and dried membranes, respectively.

2.9. Oxidative stability

Oxidative stability of membranes was measured by Fenton reagent test. Fenton reagent consists of 3% aqueous solution of H_2O_2 containing 4 ppm anhydrous $FeSO_4$. A membrane thoroughly washed in water was dried, weighed, again swelled in water (48 h), and then immersed into Fenton reagent (0.5 g of the membrane into 25 g of the Fenton reagent) for 1 h at 70°C and again dried and weighed. The weight loss (WL) was calculated using Eq. (2):

$$\mathrm{WL} = \frac{m_0 - m_t}{m_0} \times 100\% \tag{2}$$

where m_0 and m_t are the weights of original and treated membranes, respectively.

2.10. Ionic conductivity measurement

The in-plane ionic conductivity of the membranes was determined in a tempered box in gas-tight cell in an environment of deionized water by means of electrochemical impedance spectroscopy in a four-electrode arrangement. A Solartron SI 1250 frequency response analyzer and Solartron SI 1287 electrochemical interface were used. The ionic conductivity σ was calculated from Eq. (3):

$$\sigma = \frac{l}{Rbd} \tag{3}$$

where l is the distance between reference electrodes (m), R is the ohmic resistance of membrane (Ω), b is the thickness of membrane (m), and d is the width of membrane (m).

2.11. Fuel cell test

Behavior of prepared membrane VPA16 in a laboratory single-fuel cell was following. The fuel cell with serpentine flow fields was operated with pure hydrogen and pure oxygen at 80°C with optional gas humidification at 60°C for both oxygen and hydrogen and at atmospheric pressure. The oxygen flow was set at 20 $\mathrm{cm^3\,min^{-1}}$ and the hydrogen flow at 30 $\mathrm{cm^3\,min^{-1}}$. Active area of the MEA was 2.5 × 2.5 $\mathrm{cm^2}$. Commercial gas diffusion electrodes ELAT LT140EWSI (E-TEK, USA) were used for this experiment. Electrodes were pressed to the membrane surfaces during cell assembly. Nafion 117 was tested in the fuel cell at the same conditions as a membrane VPA16, except the humidification which was done only for hydrogen at 60˚C.

3. Results and discussion

3.1. Polymer synthesis

The results of the polymerization reactions are summarized in Table 1. VPA copolymers: composition of polymerization mixtures and of resulting polymers. It can be seen that the concentration of VPA units in the polymer increases with increasing concentration of VPA monomer in the polymerization mixture (which is plausible), and that AN is incorporated into the polymer chain more readily than VPA. The sum of AN and VPA units in the polymer was not, however, 100%. A partial hydrolysis of AN groups in the polymer in the presence of VPA can be assumed—it is well known that nitrile groups are subject to hydrolysis in an acid environment [22]. The homopolymer of VPA is water soluble and therefore, it is of no interest for the membrane preparation.

3.2. Thermogravimetric analysis

TGA analysis of VPA membranes is shown in Fig. 2. All samples showed a high thermal stability. Initial weight loss (at temperatures up to 150˚C) evidently corresponded to moistures absorbed in these strongly hydrophilic polymers. Thermal degradation of phosphonic acid groups occurs at about 300˚C, and a subsequent weight loss can be attributed to the main chain degradation.

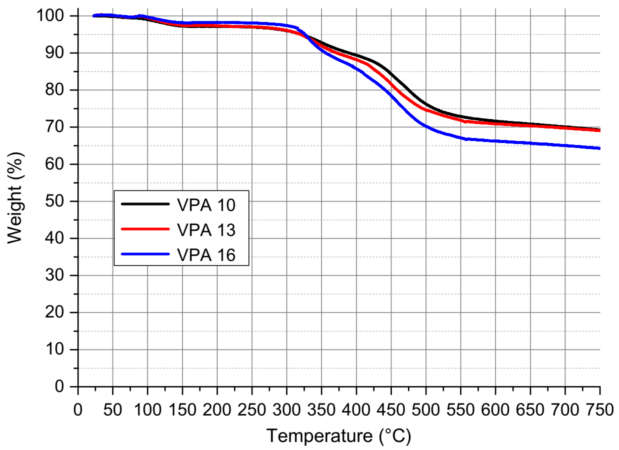

Fig. 2. TGA curves of membranes VPA10, VPA13, and VPA16.

3.3. Molecular weight determination

Molecular weight of prepared copolymers is summarized in Table 2. Molecular weight is high enough for the preparation of mechanically strong membranes, in all cases.

3.4. FTIR spectroscopy

The FTIR spectra of poly(vinylphosphonic acid-co-acrylonitrile) are shown in Fig. 3. The band at 1,150 cm^{-1} is induced by the (P=O) stretching, broad bands at 990 and 930 cm^{-1} by (P–O) stretching. The band at 2,245 cm^{-1} corresponds to valence vibrations of nitrile group and the bands at 2,940 and 2,870 cm^{-1} to symmetric and antisymmetric vibration of CH_2 groups, respectively, and the band at 1,447 cm^{-1} to the deformation vibrations of CH_2 groups. The band at 1,675 cm^{-1} (valence vibrations of a carbonyl group) indicates the presence of N,N´-dimethylformamide that was used as a solvent for membrane casting and was incompletely removed from the membrane.

3.5. Water uptake

Water uptake of prepared polymers from liquid water is summarized in Table 3. With increasing concentration of VPA units in the polymer the amount of absorbed water increased non-linearly. Polymer membranes with a high concentration of VPA units absorbed water enormously at elevated temperatures and their mechanical strength was inacceptable. Now, we attempt to cross-link the membranes to improve their mechanical properties at a water-swollen state.

3.6. Oxidative stability

The prepared membranes and Nafion 112 membrane were tested for oxidation stability in the Fenton test. Results of the test are shown in Table 4. Nafion 112 showed no weight decrease and no change in flexibility. VPA10 and VPA13, the two membranes with a low content of VPA polymeric units, showed no weight decrease but they became brittle. Membrane VPA16 lost 4.8% of its weight and became brittle.

3.7. Ionic conductivity

The ionic conductivities of prepared membranes at 35, 60, and 90˚C, respectively, are shown in Table 5. As expected, the ionic conductivities increased with temperature and with the content of VPA polymeric units in membrane. Ionic conductivity values at 90˚C

Table 2
Molecular weight of vinylphosphonic acid-co-acrylonitrile copolymers

Membrane code	M_n (g mol^{-1})	M_w (g mol^{-1})	Uniformity (1)	Conversion (%)
VPA10	22,900	93,200	4.07	61
VPA13	19,500	52,500	2.69	50
VPA16	19,500	49,000	2.51	40

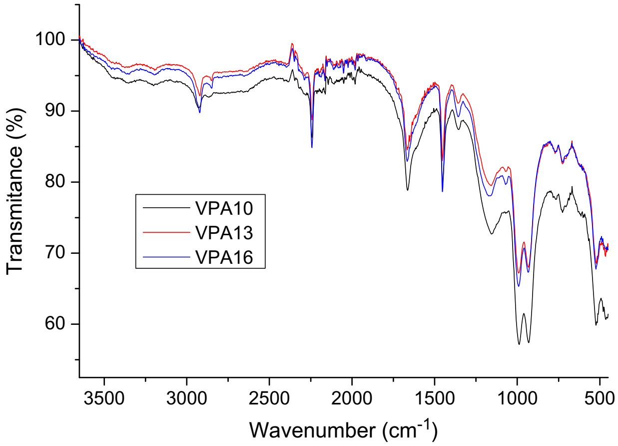

Fig. 3. FTIR spectra of poly(vinylphosphonic acid-co-acrylonitrile).

are influenced by high experimental errors which are due to an excessive membrane swelling in water, and the VPA16 membrane even disintegrated at 90˚C during the measurement.

3.8. Fuel cell test

Current–voltage and current–power curves of VPA16 membrane in a laboratory hydrogen-oxygen fuel cell are shown in Fig. 4. The curves of Nafion 117 membrane in the same fuel cell are not shown here, but the system with the Nafion membrane reached the maximum power performance of 242 mW cm^{-2} in contrast to that of 25 mW cm^{-2} obtained with the VPA16 membrane. The low efficiency of the cell with a VPA16 membrane may be caused by a high VPA 16 membrane water uptake. The water uptake of VPA16 membrane is 52 wt% at 25˚C and that of Nafion 117 is only 35 wt% [23]. The high water uptake means a more complicated water management. The humidification of only hydrogen stream was quite sufficient in the case of the cell with Nafion 117 membrane, but the same way of humidification was insufficient in the case of the cell with the VPA16 membrane. In this case, the oxygen stream also had to be humidified. On the other hand, the fuel cell open-circuit potential of 880 mV observed for VPA 16 membrane-based fuel cell indicates sufficiently low permeability of this polymer electrolyte for hydrogen.

Table 3
Water uptake (DS) of prepared membranes (in H^+ form)

Membrane code	VPA units in polymer (mol%)	IEC[a] (mmol g^{-1} dry sample)	DS 25˚C (%)	DS 60˚C (%)	DS 90˚C (%)
VPA10	9.75	3.34	30 ± 3	80 ± 9	130 ± 30
VPA13	12.57	4.19	38 ± 4	120 ± 15	>150
VPA16	15.53	5.04	52 ± 5	145 ± 25	>150

[a] Calculated from VPA units content in polymer.

Table 4
Weight loss and change of flexibility after 1 h in Fenton reagent at 70˚C

Membrane code	Weight loss after 1 h (%)	Change of flexibility
Nafion 112	0	No change
VPA10	0	Embrittlement
VPA13	0	Embrittlement
VPA16	4.8	Embrittlement

Table 5
Ionic conductivity of prepared membranes

Membrane code	IC 35°C (S m^{-1})	IC 60°C (S m^{-1})	IC 90°C (S m^{-1})
VPA10	0.22	0.26	2.54
VPA13	1.07	2.64	19.73
VPA16	5.15	7.11	NA[a]

[a] The mechanical strength did not allow the determination.

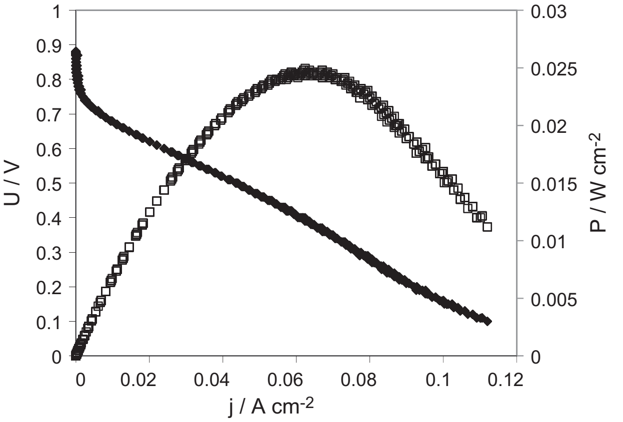

Fig. 4. Current density—voltage and power density curves for VPA16 membrane.

4. Conclusions

Poly(vinylphosphonic acid-co-acrylonitrile) can be prepared by a radical polymerization. The copolymer can be used for the preparation of ion exchange membranes. Copolymers with a high concentration of VPA polymer units have a high ionic conductivity, but they swell excessively in water. Hence, a composition of usable membranes must be a compromise between guaranteeing a good ionic conductivity and an acceptable swelling in water.

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