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Subject: Report concerning the project "Polymeric Membranes for Direct Methanol Fuel Cells" (Contract F61775-99-WE009)

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The work carried out within this project concentrated on two main problems

1. chemical modification of membranes made of Nafion 117
2. seeking of new proton conducting membranes

Modification of Nafion 117

The modification of membranes from Nafion 117 consisted mainly in the introduction of vinylphosphonic acid monomeric units [VPA: $CH_2=CHP(O)(OH)_2$] to the membrane structure by means of γ radiation at ambient temperature. The mean energy of quanta was 1.25 MeV and the power of radiation dose was in the 3-108 kGy range.

It was found that ~5-21 wt. % of the acid can be grafted on membranes immersed in aqueous solutions of VPA, depending on the radiation dose applied (Table 1). In the case of irradiating the membranes saturated with a VPA solution, the maximum grafting degree of the acid was ~3%.

As can be seen from Table 1, the grafting with VPA results in an increase in the maximum amount of water that can be imbedded by the membrane at room temperature from 16-20 wt. % for pristine Nafion 117 to 55-90 wt. %. The equilibrium amount of water, which is maintained by the membranes during storing in open air before grafting is ~5 wt. %, and that after grafting 7-12 wt. %.

It was found that it is possible to graft on Nafion 117 also 2-acrylamide-2-methylpropanesulfonic acid [AAMPSA: $CH_2=CHC(O)NHC(CH_3)SO_3H$].

Studies of the membranes with the DTG method show that at the heating rate of 5 °C/min a complete loss of water occurs at 112-114 °C, and the maximum evaporation rate takes place at 64-80 °C. Radiation grafting of VPA or AAMPSA on Nafion 117 causes a distinct increase in the ambient temperature conductivity of the membrane. At an equilibrium amount of water the modified membranes show ambient temperature conductivity values above 10^{-2} $S{\cdot}cm^{-1}$ (Table 1). The increase in the concentration of charge carriers and the increase in the amount of water in the membrane are probably the reasons for the increase in conductivity. The irradiation of Nafion 117 in the absence of organic acids does not cause essential changes both in the ability towards water absorption or in conductivity.

Table 1. Properties of the grafted copolymers of Nafion 117.

Additive	Dose kGy	% of grafting	Imbibition at 25 °C		σ, $S{\cdot}cm^{-1}$	
			maximum	equilibrium	20 °C	70 °C
-	-	-	16.0	5.0	4.0×10^{-3}	6.9×10^{-3}
	10.0	-	16.3	5.0	8.5×10^{-3}	4.0×10^{-3}
VPA	3.0	4.9[a]	56.6	6.9	2.5×10^{-2}	3.4×10^{-2}
	7.5	13.7[a]	59.4	8.2	3.2×10^{-2}	2.8×10^{-2}
4×10^{-3}	12.0	14.7[a]	64.4	7.8	1.1×10^{-2}	1.3×10^{-2}
	108.0	20.7[a]	90.4	12.1	1.8×10^{-2}	1.8×10^{-2}
	10.0	~3.0[b]	15.3		8.0×10^{-3}	4.9×10^{-3}
AAMPSA	10.0		23.7	11.4	1.5×10^{-2}	2.4×10^{-2}

a) membranes were immersed in 50 % solutions of VPA.

b) membranes imbedded with an equilibrium amount of a 50 % solution of VPA.

Application of modified membranes in fuel cells

The membranes obtained from the grafting of VPA or AAMPSA and Nafion117 are now tested in a Glob-Tech station adapted for operation in a system charged with methanol. Such a station permits the measurement of the cell current and voltage in the constant current, constant voltage and constant resistance modes, control of the cell and methanol temperature, as well as of the methanol and oxygen flows. A composite cathode containing 1 mg Pt/cm^2 and an anode containing 1 mg Pt and 0.5 mg Ru/cm^2 were used, which were produced according to an original procedure elaborated in our laboratory. The overall surface of the cell was 5 cm^2. The operation temperature varied from 30 to 130 °C. The methanol flow was 2.3-2.5 cm^3·min^{-1}, and that of oxygen ~0.55 cm^3·min^{-1}. The pressure of methanol varied from 0 to 2.6 atm, and that of oxygen in the range of 3-4 atm. A series of measurements for 4 membranes has been completed:

- unmodified Nafion 117 (**I**)
- Nafion 117 after irradiation with a dose of 10 kGy (**II**)
- Nafion 117 containing ~3 wt. % of VPA (**III**)
- Nafion 117 containing AAMPSA (**IV**)

In Tables 2 and 3 examples of standard results of the measurements are shown, and in Figures 1 and 2 the changes of cell power as a function of temperature changes at constant methanol concentration and at different methanol concentration at constant temperature (130 °C) are shown, respectively.

Despite that the number of experiments is not yet relatively large, it can be stated already that the introduction of a small amount of VPA or AAMPSA causes an increase in the power achieved under operation at atmospheric pressure of methanol (Fig. 1). Under these conditions, when applying unmodified Nafion 117, the maximum power values were ~50 mW·cm^{-2}, and that after modification ~100 mW·cm^{-2}.

At higher temperature the differences between the modified and unmodified membranes are difficult to observe. At 130 °C the maximum value of power for modified membranes was ~300 mW·cm^{-2}, and for unmodified ones ~275 mW·cm^{-2}.

At 135 °C the optimal methanol concentration was about 2 mol·dm^3. At higher concentrations a decrease in power occurs due to the insufficient moistening of the membrane and methanol cross-over. Under the conditions of high methanol concentration the membrane modified with VPA assures the achieving of considerably greater power than the unmodified one (Fig. 2).

Table 2. Parameters achieved in a methanol fuel cell for membrane **III**[a)]

Cell temperature °C	Methanol temperature °C	Oxygen temperature °C	Methanol pressure atm	Oxygen pressure atm	Maximum power $mW \cdot cm^{-2}$	OCV mV
30	67	37	0	3.0	21.2	650
49	78	86	0	3.0	52.4	750
69	81	97	0	3.0	97.7	783
89	121	99	0.5	3.0	182.5	681
96	119	104	0.5	3.0	190.2	795
100	124	110	0.5	3.0	212.7	806
106	131	114	1.0	3.5	202.5	790
109	132	119	1.0	3.5	210.6	772
114	134	124	1.5	3.5	187.3	702
119	137	129	1.5	3.5	190.2	704
126	139	127	2.0	3.5	180.1	714
130	136	119	2.0	3.5	197.8	774
131	139	127	2.6	4.0	173.4	738
134	133	119	2.5	4.5	202.1	812
90[b)]	124	99	0.5	3.0	106.1	705

[a)] A – 2.05 mg $Pt \cdot cm^{-2}$; K – 2.13 mg $Pt \cdot cm^{-2}$; $c_{met} = 2\ mol \cdot dm^{-3}$; [b)] $c_{met} = 0.5\ mol \cdot dm^{-3}$.

Table 3. Parameters achieved in a methanol fuel cell for membrane **III**[a)]

Maximum power $mW \cdot cm^{-2}$	OCV mV	c_{met} $mol \cdot dm^{-3}$
256.5	900	0.5
269.6	882	1.0
253.6	820	1.5
282.0	861	2.0
264.7	826	2.5
249.9	801	3.0
238.6	775	4.0
209.5	739	6.0
167.8	588	10.0

[a)] Temperature of cell 130 °C, of methanol 149 °C, of oxygen 120 °C; pressure of methanol 2 atm, of oxygen 3.5 atm.

We believe that consecutive attempts with membranes containing 5-20 wt. % of VPA will permit to achieve still more clear effects of an increase in the power of the cell.

Fig. 1. Maximum power density depending on the cell temperature for neat and modified Nafion 117 membranes.

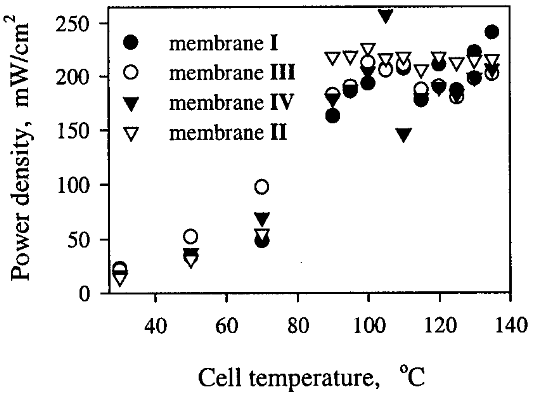
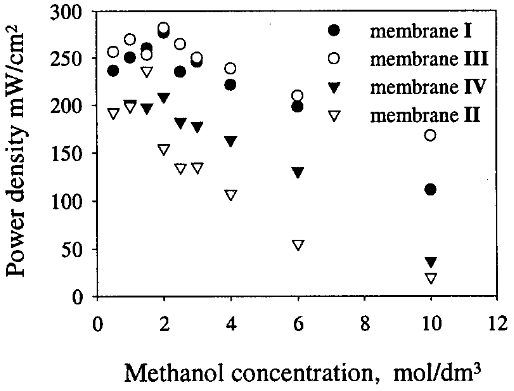
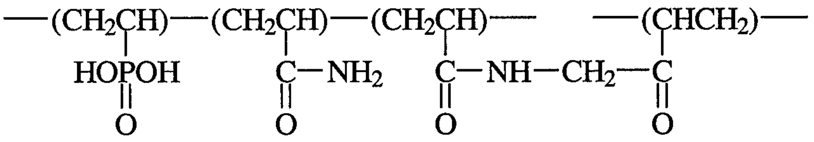


Fig. 2. Maximum power density depending on methanol concentration for neat and modified Nafion 117 membranes



Attempts have also been carried out to modify Nafion 117 by free radical copolymerization of VPA with acrylamide and bisacrylamide in a membrane saturated with water. The copolymerizations were carried out at 60 °C using potassium persulfate as initiator. It was found that under these conditions terpolymer T is formed of the following composition:



$$-(CH_2CH(P(=O)(OH)_2))-(CH_2CH(C(=O)NH_2))-(CH_2CH(C(=O)-NH-CH_2-C(=O)))- \quad -(CHCH_2)-$$

T VPA 37 wt. %
DAA 33 wt. %
AA 30 wt. %

After extraction it was found that in this way about 2 wt. % of the terpolymer could be permanently introduced into the Nafion 117 structure. It was found that this type of membranes imbed less water (~0.1 g/g) than a Nafion 117 membrane (~0.2 g/g), and their conductivity is comparable with the unmodified Nafion within the 20-80 °C temperature range. At 90 °C, contrary to membranes of Nafion 117, they do not lose rapidly water and maintain good conducting properties (Fig. 3).

Figure 3. Conductivity vs. inverse temperature for a membrane composed of Nafion 117 (82 wt. %) and the VFA, AA and DAA terpolymer (18 wt. %)

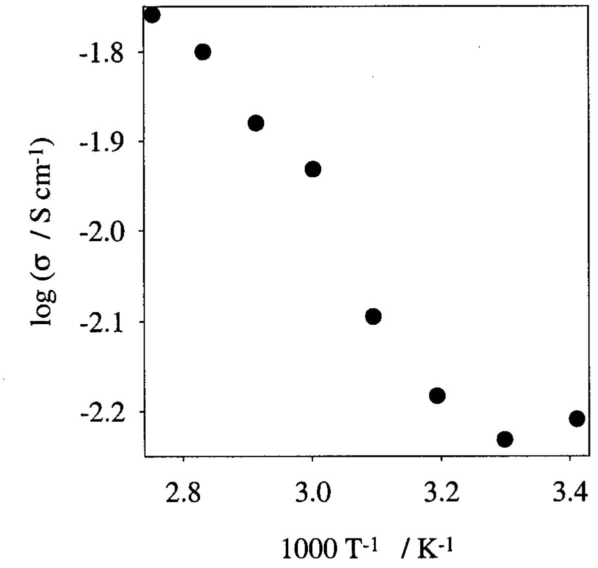
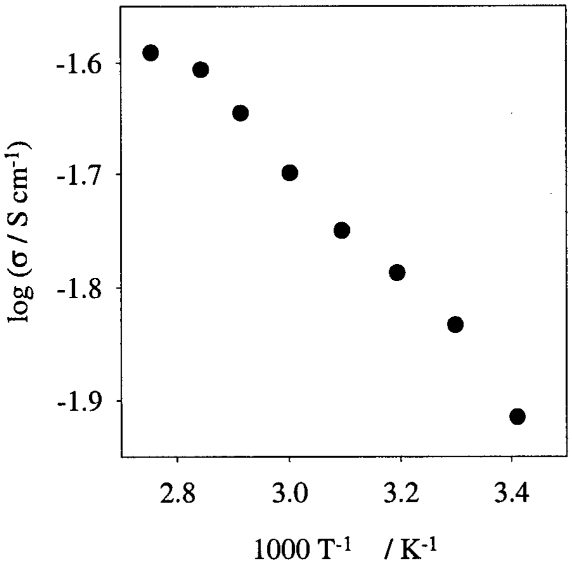


Fig. 4 Conductivity versus inverse temperature for membrane composed of Nafion 117 (71 wt %) and PBI (19 wt %) imbedded with phosphoric acid.



We studied also composites comprising Nafion 117 with 14-29 wt. % of polybenzimidazole (PBI), embedded with aqueous solutions of phosphoric acid. In such systems, already at ambient temperature conductivities exceeding 10^{-2} S·cm^{-1} are achieved (Table 4, Fig. 4) and the membranes do not lose water during storage at 90 °C. However, in these membranes separation of the PBI layer from the Nafion layer took place after about two weeks.

Table 4. Conductivity of some composite membranes

Polymer	Additive	Water sorption at 20 °C %	Conductivity σ / S·cm^{-1} 20 °C	60 °C	90 °C
PVdF (40)	R_1 (60)	48	1.9×10^{-3}	2.6×10^{-3}	2.7×10^{-3}
PVdF (40)	R_2 (60)	32	7.0×10^{-4}	9.2×10^{-4}	1.4×10^{-3}
PVdF (45)	T (55)	53	1.5×10^{-3}	9.8×10^{-4}	2.7×10^{-4}
PBI (40)	R_1 (60)	8	5.9×10^{-7}	6.0×10^{-6}	1.7×10^{-5}
PBI (62)	H_3PO_4 (37)	65	1.3×10^{-3}	1.7×10^{-3}	2.1×10^{-3}
PBI (57)	PVPA[b0] (43)	92	2.1×10^{-5}	1.3×10^{-4}	1.4×10^{-4}
Nafion	–	21	5.5×10^{-3}	6.3×10^{-3}	
Nafion (81.5)	T (18.5)	10	6.7×10^{-3}	1.2×10^{-2}	1.7×10^{-2}
Nafion (49)	PBI (8) / H_3PO_4 (43)	38	2.0×10^{-3}	5.5×10^{-3}	1.2×10^{-2}
Nafion (31.5)	PBI (8) / H_3PO_4 (43)		1.2×10^{-2}	2.0×10^{-2}	2.6×10^{-2}

a) Abbreviations are given in the text; b) PVPA – homopolymer of vinylphosphonic acid.

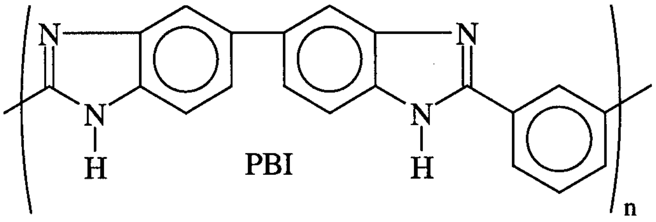
Conclusions

- When applying radiation grafting it is possible to introduce to the Nafion structure up to 20 wt. % of additional monomeric units containing acidic groups: $-P(O)(OH)_2$ or $-SO_3H$.
- This type of modification leads to an increase in water imbibition and conductivity of the membranes.
- Preliminary results of studies in a methanol fuel cell indicate the possibility of a considerable increase in power up to ~70 °C.
- The purpose of further work is to determine the optimum content of the additive and to check whether the modifications can be carried out by radical polymerization with the formation of a hydrogel in the pores of the membrane.

Other proton conducting membranes

Besides Nafion, also membranes were studied, in which the matrix was composed of:

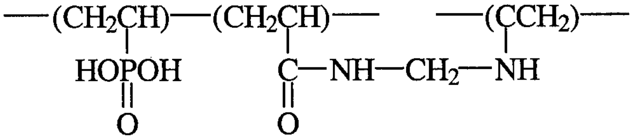
- poly(vinylidene fluoride) (PVdF – Aldrich 18,270-2)
- polybenzimidazole



(Aldrich 30,979-6)

PVdF is a neutral matrix not involved in the conductivity process, PBI is a strongly basic matrix capable of immobilizing proton acids, and Nafion 117 is a polyelectrolyte, which alone exhibits high proton conductivity.

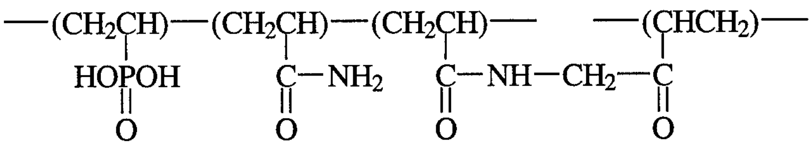
Vinylphosphonic acid (VPA) was used in the form of crosslinked copolymers (R_1, R_2) with N-methylenediacrylamide (DAA) or a terpolymer of these monomers with acrylamide (AA).



$$-(CH_2\underset{\underset{\underset{O}{\|}}{HO\overset{|}{P}OH}}{CH})-(CH_2\underset{\underset{\underset{O}{\|}}{\overset{|}{C}-NH-CH_2-NH}}{CH})- \qquad -(\underset{|}{C}CH_2)-$$

R_1 VPA 39 wt. %
DAA 61 wt. %

R_2 VPA 48 wt. %
DAA 52 wt. %



$$-(CH_2\underset{\substack{|\\ HO\underset{\underset{O}{\|}}{P}OH}}{C}H)-(CH_2\underset{\substack{|\\ \underset{\underset{O}{\|}}{C}-NH_2}}{C}H)-(CH_2\underset{\substack{|\\ \underset{\underset{O}{\|}}{C}-NH-CH_2-\underset{\underset{O}{\|}}{C}}}{C}H)- \quad -(\underset{|}{C}HCH_2)-$$

T VPA 37 wt. %
DAA 33 wt. %
AA 30 wt. %

The copolymers and terpolymer were obtained by free-radical polymerization at 60 °C in the presence of benzoyl peroxide. The precipitates were isolated from a solution in ethanol by extraction with boiling water in order to remove water-soluble fractions. Their content did not exceed 3 wt. % of the initial product.

The composite membranes with PVdF were obtained by casting from a solution in dimethylacetamide. In order to maintain good mechanical proprieties the PVdF content should be at least 40 wt. %. The membranes obtained were immersed in water at room temperature. After two days they achieved an equilibrium degree of swelling and at the same time they exhibited high flexibility.

Membrane **V** containing 40 wt. % of PVdF and 60 wt. % of R_1 absorbs 0.479 g of H_2O per 1 g of the membrane, which corresponds to ~7.4 moles of H_2O per 1 mole of VPA. Its ambient temperature conductivity is ~1.9×10^{-3} $S\cdot cm^{-1}$, and at 90 °C ~2.7×10^{-3} $S\cdot cm^{-1}$ (Table 2).

Membrane **VI** containing 40 wt. % of PVdF and 60 wt. % of R_2 absorbs 0.322 g of H_2O per 1 g of the membrane, which corresponds to ~4.1 moles of H_2O per 1 mole of VPA. Its ambient temperature conductivity is ~7×10^{-4} $S\cdot cm^{-1}$ and increases with a rise of temperature (Fig. 5) reaching at 90 °C the value of 1.4×10^{-3} $S\cdot cm^{-1}$.

Fig. 5. Conductivity versus reverse temperature for a membrane containing 40 wt. % of PVdF and 60 wt. % of R_2.

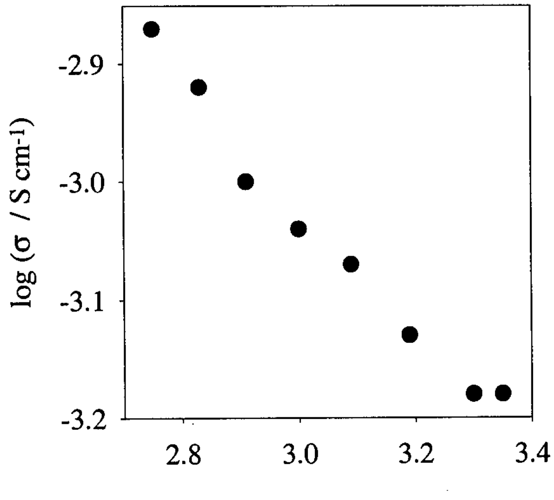
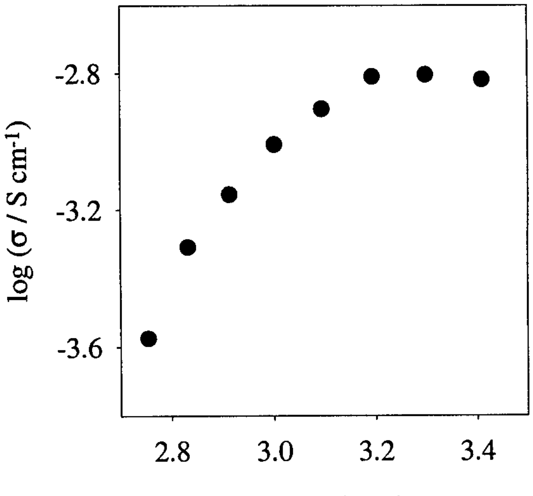


Fig. 6. Conductivity versus inverse temperature for a membrane containing 45 wt % PVdF and 55 wt % of the VPA-AA-BAA terpolymer.



Membrane **VII** containing 45 wt. % of PVdF and 55 wt. % of T absorbs 0.525 g of H_2O per 1 g of the membrane, which corresponds to ~8.6 moles of H_2O per 1 mole of VPA. This membrane shows ambient temperature conductivity of $\sim 1.5\times10^{-3}$ $S\cdot cm^{-1}$, but it decreases with a rise of temperature (Fig. 6).

From the data presented it appears that the ability to absorb water at ambient temperature increases with an increase in the amide component content, and at ambient temperature the conductivity depends to a greater degree on the water content than on the number of acidic groups. However, with a rise of temperature systems of small acid content easier lose water, which affect unfavorably their conducting properties.

In the case of analogous composites with PBI the attempts to obtain membranes of good mechanical properties did not succeed. These membranes absorb a smaller amount of water in the 0.2-0.3 g / g of membrane range, but their conductivity values do not differ essentially from those with PVdF (see Table 4).

Membranes of good mechanical properties were obtained by embedding membranes with PBI with aqueous solution of vinylphosphonic acid and then polymerizing the acid in a PBI matrix at ~100 °C. However, the conductivity of such membranes appeared to be low, about 2.1×10^{-5} $S\cdot cm^{-1}$ at ambient temperature and about 1.4×10^{-4} $S\cdot cm^{-1}$ at 90 °C. These values are 1-2 orders of magnitude smaller than those obtained for PBI composites wit H_3PO_4, which are tested in fuel cells (Table 4).

Membrane **VI** was tested in a fuel cell. As can be seen in Fig. 7, with an open cell the voltage achieved was ~770 mV, the maximum current density was ca. 3.4 $mA\cdot cm^{-2}$, and power density ca. 0.73 $mW\cdot cm^{-2}$. The power density value increased with an increase in the current density, achieving a plateau at ca. 2 $mA\cdot cm^{-2}$.

In order to increase the conductivity of this system, the content of membrane-forming substances was reduced to ca. 10 % by adding an additional acidic component in the form of a zeolite (Zeolon 100H). The composite obtained was hot pressed between cylinders. The thus formed membrane absorbs about 60 wt. % of H_2O at room temperature, and its conductivity at ambient temperature and at the cell operation temperature is similar and is equal to ca. 1.8×10^{-2} $S\cdot cm^{-1}$. Cells with such composites show an open circuit voltage of ~570 mV. The maximum current density was about 50 $mA\cdot cm^{-2}$, and the maximum power of ~1.4 $W\cdot cm^2$ is achieved at the current density of ~4 mA/cm^2.

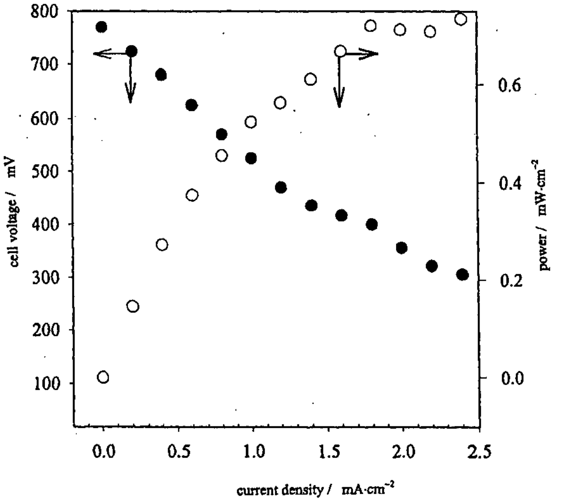


Fig. 7. Current – voltage characteristics of a methanol fuel cell with an electrolyte based on crosslinked poly(vinylphosphonic acid) (40 wt. % and containing 60 wt. % of the acidic agent. Cathode 1 mg Pt/cm^2 anode 1 mg Pt + 0.5 mg Ru/cm^2; temperature of cell performance 71 °C; methanol concentration 2 mol/dm^3; methanol pressure: atmospheric, oxygen pressure: 2 atm

Conclusions

- hydrogels obtained from the copolymerization of VPA are characterized by high ambient temperature conductivity values of $>10^{-2}$ S·cm^{-1}.
- they assure high values of power in a methanol fuel cell in combination with Nafion 117.
- when using a neutral matrix with PVdF the powers achieved are still not too high enough (~2-3 mW·cm^{-2}) to consider them for practical applications.

The procedure for the preparation of composite polyelectrolyte membranes described in this report has been worked out by us in a reproducible way and we are able to submit, on request, a membrane within a month.

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13. ABSTRACT (Maximum 200 words)

This report results from a contract tasking Warsaw University of Technology as follows: The contractor will investigate the potential to reduce the methanol crossover and enhance the performance of direct methanol fuel cells by developing two new types of polymeric electrolytes. The first type will be a modification of the traditional Nafion polymer electrolyte by grafting vinylphosphonic acid to the Nafion. The second type will be the use of vinylphosphonic acid with polybenzimidazole (PBI).

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