

Microbial fuel cells (MFCs) with interpolymer cation exchange membranes

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Abstract

Interpolymer cation exchange membranes have been prepared from the system polyethylene/poly(styrene-co-divinylbenzene) [PE/poly(St-co-DVB)] by their sulfonation with a solution of chlorosulfonic acid in 1,2-dichloroethane. The membranes have been characterized electrochemically in mediator-less microbial fuel cell (MFC). MFC has worked on *Escherichia coli* bacteria with ferrocyanide as an oxidizer. Real-time voltage and current measurement gave us reliable results. Consequently, it was found that the amount of DVB in the copolymer is the main factor that determines the electrical efficiency of the membrane.

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Keywords: Microbial fuel cell; PE/poly(St-co-DVB) interpolymer; Cation exchange membranes; Renewable energy; Bioenergy

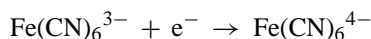
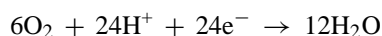
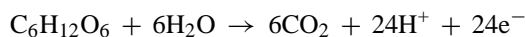
1. Introduction

In recent years the interest in renewable energy sources has been rapidly grown. Microbial fuel cells (MFC), like other members of fuel cell family, directly convert biochemical energy into electricity without the use of combustion. MFC works in mild conditions: room temperature, normal pressure, and neutral pH.

Microbial fuel cells use microorganisms as biocatalysts [1,2]. Microorganisms are capable of metabolizing food to provide them with energy. By breaking down the substrate material through a complex series of stages in respiratory chain microorganisms store the energy of substrate oxidation. In a typical mediator-less MFC, an anodic electrode potential is generated when the electrons from the oxidation of the substrate by microorganisms are available at the electrode (Fig. 1) [3]. In the cathode chamber the oxidant is reduced. MFCs with the use of mediators (thionine, methyl viologen,

2-hydroxy-1,4-napthoquinone, neutral red, methylene blue) work much more effectively. Mediators shuttle electrons between the bacterial cells and the electrode, but there are still difficulties in using mediators at a commercial scale.

The driving force of our MFC is redox reaction of glucose using an *Escherichia coli* as catalyst.



Several types of MFCs have been documented in the literature, but only on Nafion membranes [1–5]. DuPont developed the perfluorinated ion exchange membrane Nafion in the early 1960s during work with General Electric on a fuel cell. The major application of Nafion has been as a separating membrane in electrolytic cells used to produce chlorine and sodium hydroxide [6]. Other applications have included its use as a solid polymer electrolyte in fuel cells [7] and batteries [8]. The morphology of Nafion has been extensively studied

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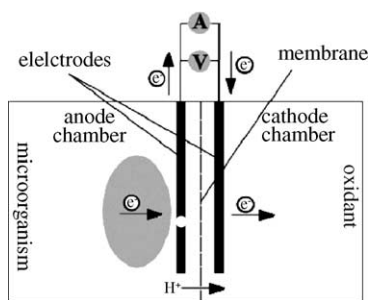


Fig. 1. Basic schematic diagram of a mediator-less microbial fuel cell.

using SAXS, and although it is agreed that ion clusters exist within Nafion [9].

Membranes obtained by chemical modification of the polyethylene/poly(styrene-co-divinylbenzene) interpolymer also have good ion exchange properties. These membranes are used for active transport of cation [10], for separation of water-pyridine mixtures by pervaporation [11] as well as for deacidification of aqueous solutions by means of diffusion dialysis [12,13], Donnan dialysis, and/or Poźniak dialysis [14].

Interpolymer cation exchange membranes from PE/poly(St-co-DVB) system have been synthesized and characterized electrochemically in mediator-less microbial fuel cell (MFC). Microbial fuel cells with interpolymer cation exchange membranes can be used in wastewater treatment facilities as preliminary reactors gaining power to maintain further apparatus in that plant. Highly efficient MFC technology may provide “green” and cheap source of energy.

2. Experimental

2.1. Membranes

2.1.1. Materials

The low-density polyethylene (granulate) was purchased from Blachownia, Poland. Its viscometrical average molecular weight was 33 kDa and the degree of crystallinity obtained by WAXS-ray analysis was 52 wt.%. Styrene and divinylbenzene were commercial products (Oświęcim, Poland). Chlorosulfonic acid, reagent grade, was supplied by Fluka, Switzerland, 1,2-dichloroethane and benzoyl peroxide were obtained from POCh, Poland.

2.1.2. Preparation of interpolymer PE/poly(St-co-DVB)

The interpolymerization was initiated with 1 wt.% benzoyl peroxide [15]. The two-phase reaction mixture contained 70 wt.% of PE (granular form) and 30 wt.% of liquid monomers: styrene and divinylbenzene. The proportion of DVB (crosslinking agent) in the monomer mixture was adjusted to obtain 1, 5, 10 and 20 wt.% of *m*- and *p*-isomers in the aromatic component of the product mixture. The reaction was carried out in a Werner-Pfleiderer mixer with a stirring rate

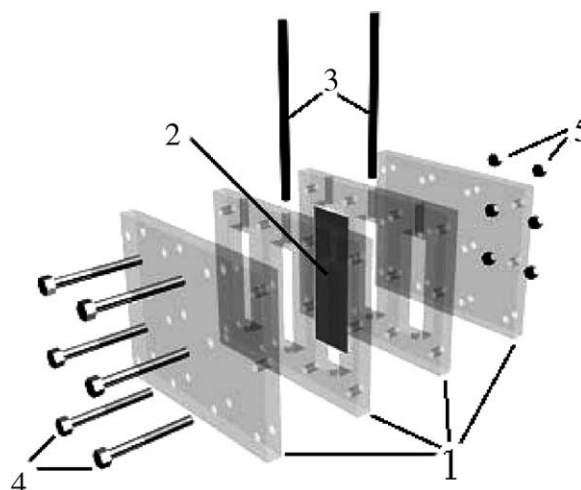


Fig. 2. Schematic diagram of the microbial fuel cell assembly: (1) cell body, (2) cation exchange membrane, (3) graphite electrodes, (4) zinc coated screws, and (5) zinc coated nuts.

of 0.25 and 0.75 s⁻¹ for both stirrers, respectively, at 80 °C for 210 min. The resulting interpolymer was then homogenized in an extruder with a screw 45 mm in diameter and a length/diameter ratio 20/1, equipped with a rod-forming die. The extruder temperatures were 180, 185, 195 and 200 °C in the I, II, III and IV barrel heating zones, respectively. The two-zone head temperatures were both 200 °C. The extrudate was granulated and then formed into a sheet form in a hydraulic press (pressure 10 MPa, temperature 150 °C, time 5 min).

2.1.3. Preparation of cation exchange membrane

The interpolymer PE/poly(St-co-DVB) was chlorosulfonated at room temperature with a 30 vol.% solution of chlorosulfonic acid in 1,2-dichloroethane for 4 h and then hydrolyzed with a 20 wt.% NaOH aqueous solution for 18 h. The cation exchange membranes in the sodium form were thus obtained.

2.1.4. Water content

The water content (P_w) of the final membrane was determined after equilibrating a sample of membrane in sodium

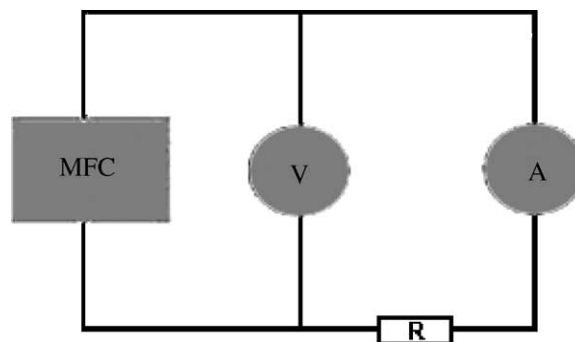


Fig. 3. Schematic diagram of a measuring system.

Table 1
Membranes characteristics

DWB content (wt.%)	Ion exchange capacity Z_c (mmol/g)	Water content P_w (g/g)	Molar concentration of ionic groups C_m (mmol/cm ³)
1	2.05	0.830	2.47
5	1.89	0.545	3.47
10	1.63	0.336	4.85
20	0.95	0.193	4.92

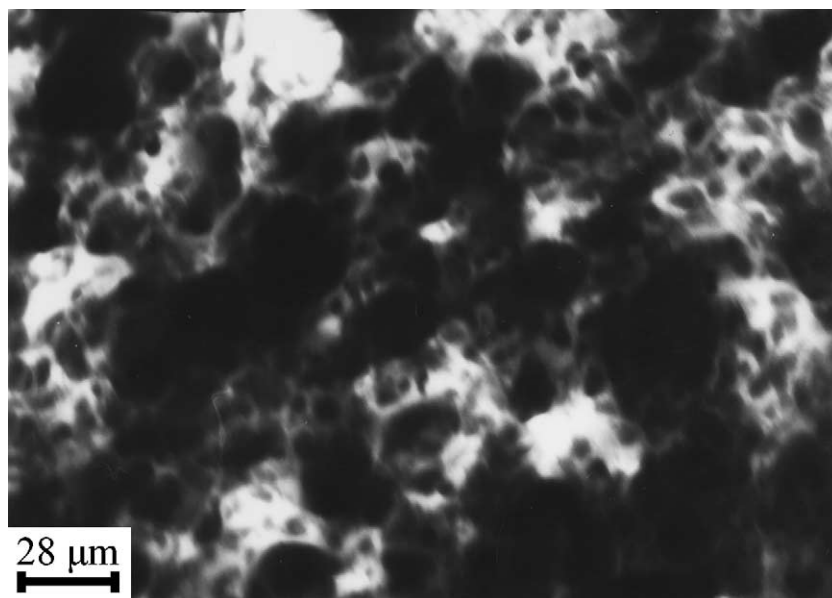


Fig. 4. Microdomains (1 wt.% DVB).

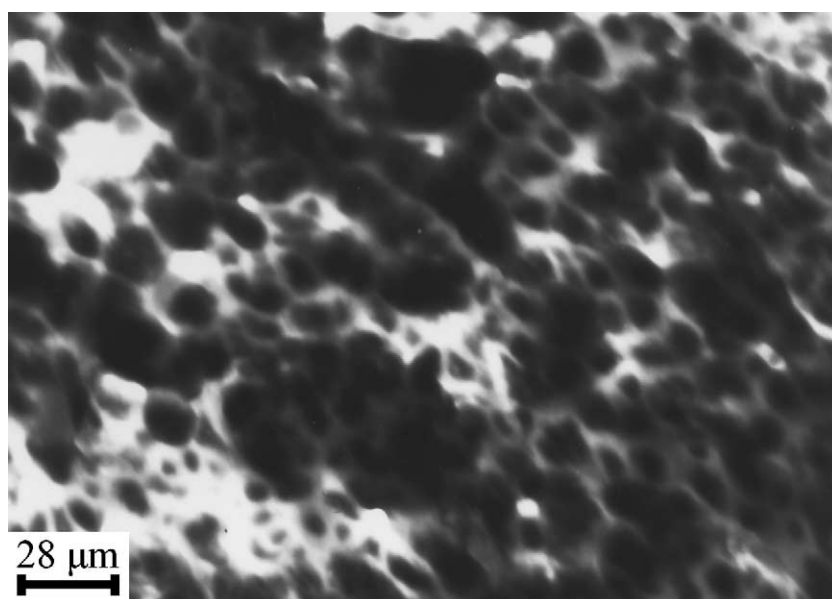


Fig. 5. Microdomains (5 wt.% DVB).

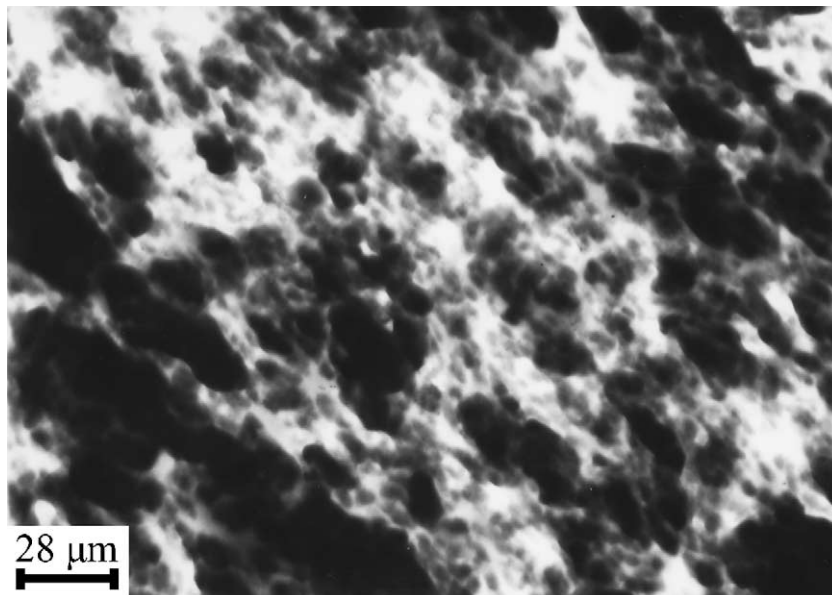


Fig. 6. Microdomains (10 wt.% DVB).

form with deionized water at room temperature. The membrane samples were removed from the water and weighed immediately after blotting the free surface water. Then, they were dried for over 4 h at 105 °C. The water content was deduced from the difference in weight between the wet and the dry membrane in unit gram H₂O/g dry membrane.

2.1.5. Cation exchange capacity and molar concentration of ionic groups

After dipping in pure water, a membrane sample was immersed for 1 day in a large volume of 1 M HCl solution to convert the membrane into H⁺ form. The membrane was then

washed free of excess HCl with distilled water and equilibrated in it to remove last traces of acid. The membrane was then equilibrated with 50 cm³ of 0.1 M NaCl solution for 24 h and its cation exchange capacity (Z_c) was determined from the increase in acidity, which in turn, was determined by acid titration.

The molar concentration of ionic groups (C_m) was determined from the ratio:

$$C_m = \frac{Z_c d_w}{P_w}$$

where d_w is the density of water (g/cm³).

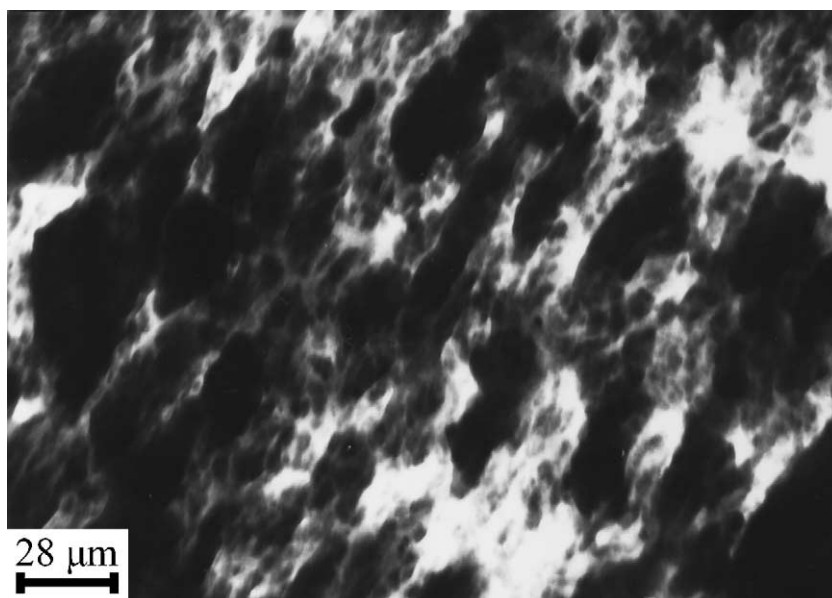


Fig. 7. Microdomains (20 wt.% DVB).

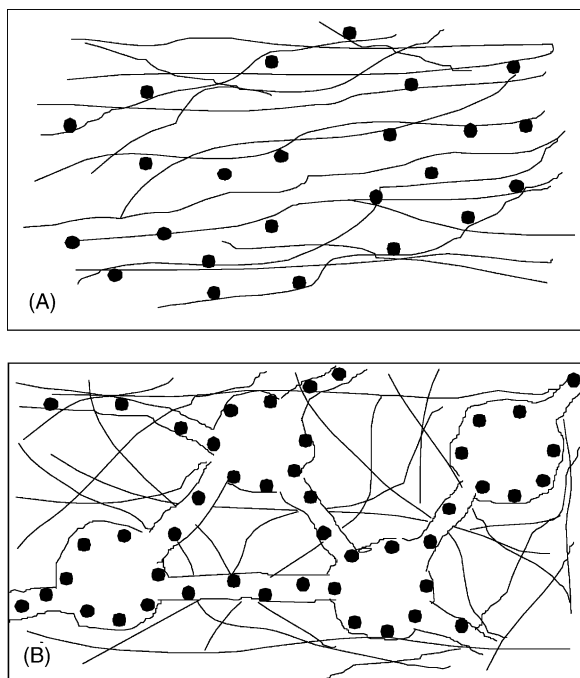


Fig. 8. Morphology of membranes ((●) $\text{SO}_3^- \text{Me}^+$ site): (A) PE/poly(St-co-DVB) with 1 and 5 wt.% of DVB; (B) PE/poly(St-co-DVB) with 10 and 20 wt.% DVB and Nafion.

2.1.6. Structure of membrane

Transmission electron microscope (Philips EM 301) was used to investigate the structure of the obtained membranes. Samples for microscopy examination were colored with uranyl acetate. Each sample was taken at $36,000\times$ magnification.

2.2. Construction of microbial fuel cells

Microbial fuel cell used in our experiments was made up of the cell body, cation exchange membranes, graphite electrodes and zinc coated screws (Fig. 2). The body cell was cut from poly(methyl methacrylate) and each electrode compartment has a volume of $65 \text{ mm} \times 20 \text{ mm} \times 10 \text{ mm}$. An active surface of cation exchange membrane sheet was equal to 13 cm^2 . Graphite electrodes was used both as anode and cathode rods, diameter – 5 mm – approximated working surface area $\sim 17 \text{ cm}^2$. Construction was squeezed by set of zinc-coated screws and sealed by vacuum grease put between the body cell plates.

2.3. Preparation of microorganism

E. coli (K12) was bought from Institute of Immunology and Experimental Therapy in Wrocław, Poland. It was maintained on a nutrient agar plate at 4°C . Each time the experimental culture was prepared by dissolving 1.5 g of broth bouillon and 1.8 g of glucose in 100 cm^3 of distilled water. At the end microorganism was added.

2.4. Potential and current measurements

Potential (V) and current (A) of the fuel cell were measured using a multimeters (Digital Multimeter M-3890D, Conrad Electronic, Germany) connected to the computer through the USB port. Data were recorded digitally using control software DMM ProfiLab v2.0, by Elektronik-Software. In Fig. 3 was shown diagram of a measuring system. Total resistance of a measuring system amounts approximately 830Ω (resistor (R) 330Ω and ammeter's internal resistance $\sim 500 \Omega$).

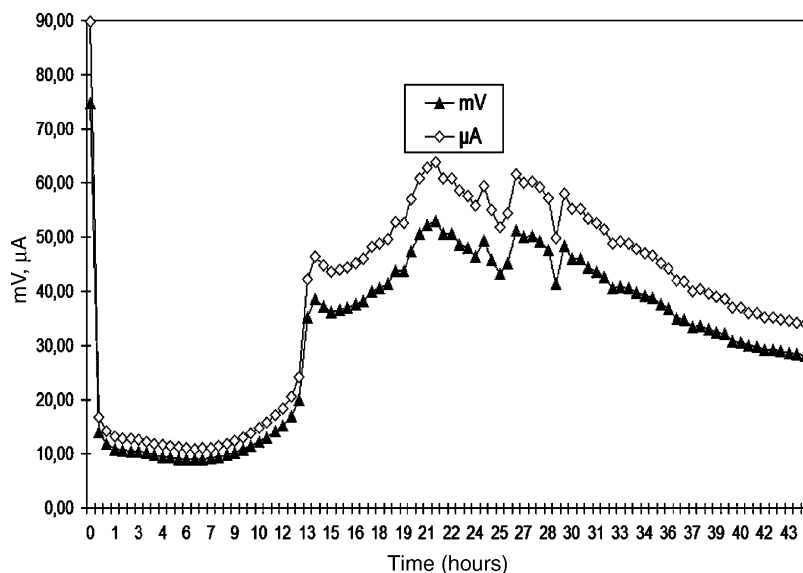


Fig. 9. Dependence of voltage and current on measurement time (membrane with 1 wt.% of DVB).

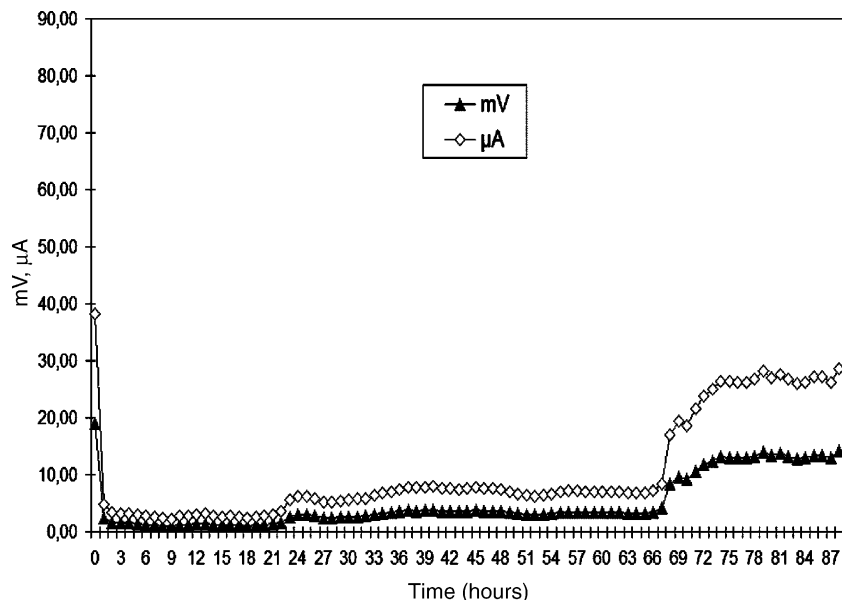


Fig. 10. Dependence of voltage and current on measurement time (membrane with 5 wt.% of DVB).

2.5. Procedure

Each cell chamber was disinfected with 70% ethanol and purged with distilled water. Before each measurement that operation was repeated at least two times. Next fresh prepared microorganisms were added into the anode chamber. The cathode chamber was filled with 20 mM of potassium ferrocyanide $K_3Fe(CN)_6$. Both microorganism mixture and potassium ferrocyanide solution was added in approximated amount of 12 cm^3 . Afterwards electrodes were put in chambers and connected to the monitoring system. The change in cell voltage and current was recorded digitally using a computer as a function of time immediately after connecting the resistor.

3. Results and discussion

The cation exchange membranes were prepared from the PE/poly(St-co-DVB) interpolymers by its shaping followed by chemical transformation [15]. It was assumed that the poly(St-co-DVB) in this interpolymers had properties similar to those of a poly(St-co-DVB) copolymer obtained by suspension copolymerization. It is well known that the amount of DVB in the copolymer is the main factor that determines the structure of ion exchange materials [16]. In this type of membrane, PE serve as the matrix and poly(St-co-DVB) with sulfonic groups as the crosslinked polyelectrolyte. The characteristics of the membranes are shown in Table 1.

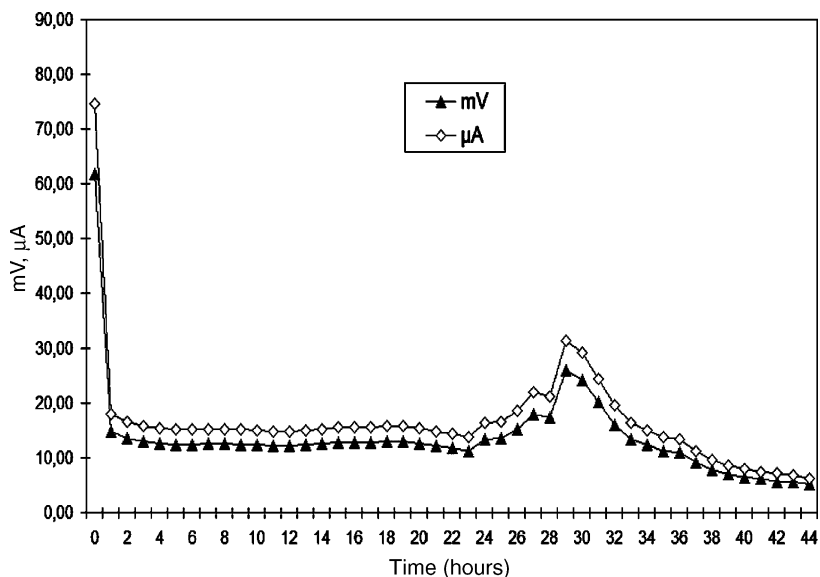


Fig. 11. Dependence of voltage and current on measurement time (membrane with 10 wt.% of DVB).

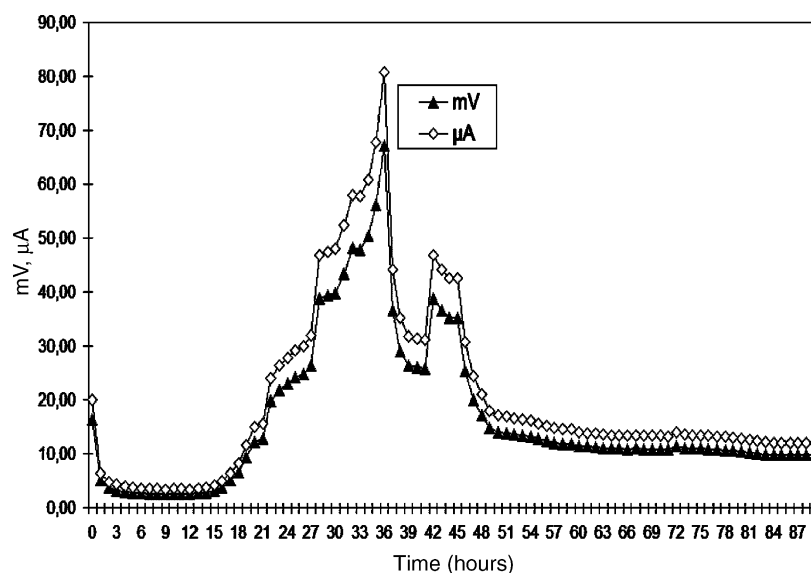


Fig. 12. Dependence of voltage and current on measurement time (membrane with 20 wt.% of DVB).

The ion exchange capacity and the water content of the membranes depend on the content of DVB; decrease when content of DVB increases. The higher content of crosslinking agent produces more chain entanglements and slower diffusion of sulfonic acid into the poly(St-co-DVB) (see Section 2.1.5). An increase of DVB content leads to the decrease of swelling of strong crosslinked polyelectrolyte domains (see Section 2.1.4). The charge density in the membrane is proportional to the molar concentration of ionic groups. The membranes with a DVB content of 10 and 20% have values of molar concentration of ionic group higher than with DVB content 1 and 5%.

The PE/poly(St-co-DVB) interpolymer is known to be a heterogeneous one: microdomains of poly(St-co-DVB) are distributed in the PE matrix. This can be seen on the electron micrographs shown in Figs. 4–7. Microdomains of poly(St-co-DVB) with ionic groups one can see as dark places. A relation between DVB content in membrane and its structure has been observed. After incorporating sulfonic groups into PE/poly(St-co-DVB) interpolymer with 1 and 5 wt.% of DVB, strong expansion of the polyelectrolyte domains might cause the polyelectrolyte network to become continuous (Figs. 4 and 5). With a DVB content of 10 and 20 wt.%, however, such an expansion is very small and polyelectrolyte domains are still isolated by the PE matrix; narrow channels are observed (Figs. 6 and 7). Structures of the interpolymer membranes containing 10 and 20 wt.% of DVB are similar to cluster structure of Nafion membrane [9] (Fig. 8).

A relationship between structure of interpolymer cation exchange membranes and their electrical properties has been determined. In Figs. 9–12 it is clearly visible that electrical properties of the cation exchange membranes are not changing linearly with increasing the crosslinking agent. Membrane with the least content of DVB (Fig. 9) passes the largest

amount of protons. After 10 h of *E. coli* incubation current and potential levels are growing rapidly to reach the highest values at about 21 h (~65 μA , ~50 mV). After 27 h, current and potential start to drop gently. Membrane with 5 wt.% content of DVB (Fig. 10) runs worst of all. After 22 h measured value starts to rise, just like in previous case. After next 40 h the state of equilibrium is established and after 66 h both current and potential violently grow. The highest value was obtained after 80 h (~30 μA , ~15 mV). The membrane containing 10 wt.% of DVB (Fig. 11) is the most homogeneous of all. Almost on the entire length of the graph the values stay on the same level, except from the period from 22 to 36 h. The highest peak is after 29 h (~30 μA , ~25 mV). The last graph – membrane with 20 wt.% of DVB (Fig. 12) – has more interesting course. The first changes in its pattern can be seen after 15 h. Then both current and potential steeply grow to reach the highest values after 36 h (~80 μA , ~67 mV). Afterwards in the next 16 h the current and potential drop to a stable level (~16 μA , ~14 mV).

Together with increasing the amount of DVB in membrane, the higher current and potential peaks are delaying (1 wt.% DVB (after 21 h), 5 wt.% DVB (after 24 h, concerning microbial growth phase only), 10 wt.% DVB (after 29 h), and 20 wt.% DVB (after 33 h)). Considering energy yield results from MFC with membranes containing 1 and 20 wt.% DVB are similar (concerning areas under graphs from 0 to 44 h).

4. Conclusions

In this paper, we develop a prototype microbial fuel cell using interpolymer cation exchange membranes from PE/poly(St-co-DVB) system with different amount of crosslinking agent. Consequently, it was found that the amount of

DVB in the copolymer is the main factor that determines the electrical efficiency of the membrane.

The best properties of membrane containing 20% of DVB result from either the highest concentration of ionic groups or cluster structure of the material. The high molar concentration implies the high charge density that in turns is mostly responsible for co-ion (ion with the same sign as fixed ionic groups of membrane) exclusion from the membrane phase. In consequence, the selectivity of ion exchange membrane is improved. Moreover, the cluster structure of membrane has a vital effect on transport properties of membrane.

The membrane with only 1% DVB is permeable to protons, which are transported through water phase (the higher water content) and expanded parts of polyelectrolyte domains. Thus, the weakly crosslinked membrane may be considered as continuous network of ion exchanged elements.

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