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Anion exchange membranes and binders based on polystyrene-*block*-poly (ethylene-*ran*-butylene)-*block*-polystyrene copolymer for alkaline water electrolysis

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ABSTRACT

The preparation of hydroxide ion-conductive membranes and catalyst binders starting from polystyrene-*block*-poly(ethylene-*ran*-butylene)-*block*-polystyrene (PSEBS) is described. Highly chloromethylated (CM) and soluble polymer was obtained by the reaction of PSEBS with dimethoxymethane (formaldehyde precursor), $ZnCl_2$ (catalyst), and phosphorus trichloride (chlorinating agent). The prepared CM polymer was used for casting of membranes and preparation of binders of catalytic particles. The membranes and binders were converted into quaternized form (PSEBS-CM-trimethylamine (TMA)) by immersion into an ethanolic solution of TMA. Ionic conductivity of PSEBS-CM-TMA was 56.1 mS cm^{-1} at 30°C and 79.2 mS cm^{-1} at 70°C, respectively. A laboratory water electrolyzer using a PSEBS-CM-TMA membrane and an anode with PSEBS-CM-TMA binder was operated permanently for 1 month without considerable deterioration of its performance. The anodes containing PSEBS-CM-TMA binder and $NiCo_2O_4$ catalyst greatly outperformed those containing the same amount of $NiCo_2O_4$ fixed to the anode by polytetrafluoroethylene.

Keywords: Polystyrene block copolymer; Alkaline water electrolysis; Anion exchange membrane; Anion exchange catalyst binder

1. Introduction

Anion exchange polymers are being investigated in alkaline membrane fuel cells and alkaline water electrolyzers as membranes separating the electrodes and polymer binders fixing discreet catalyst particles to the electrodes [1–6]. The main requirements for these polymers are high OH$^-$ ion conductivity (IC) and chemical and mechanical stabilities at elevated pH and temperatures. Preparation, structure, and stability of anion exchange membranes are discussed in a number of review articles [1,2,7,8].

Anion exchange membranes based on block copolymers are gaining importance. A hydrophobic polymer block gives the membrane good mechanical strength and stability while the ion exchange block controls the transport of hydroxide anions across the membrane. Block copolymers with hydrophobic and ion exchange blocks have domain microstructures [9]. The concentration of ion exchange groups in the ion exchange domains and thus the conductivity of the domains (if interconnected) may be extremely high, but the membrane water swelling and mechanical properties are controlled by hydrophobic blocks [10–15].

In the past, our group prepared and investigated anion exchange polymer for use in alkaline electrolysis: (a) We

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developed heterogeneous membranes by blending finely powdered anion exchange particles with molten polyolefins followed by compression moulding into the shape of a flat membrane [16]. The resulting membranes were mechanically and chemically resistant with a somewhat lower IC. This method of membrane preparation is easy and cost-effective; however, it may not be used for the development of catalyst binders. (b) We prepared membranes and binders based on TMA-quaternized poly(2,6-dimethyl-1,4-phenylene oxide) (qPPO) [17]. The application of qPPO in the electrolyzer anode leads to higher current densities than the application of a nonconductive polytetrafluoroethylene (PTFE) one at all electrolyte KOH concentrations. However, the performance of the electrolyzer declined after 400 h of operation at 50°C, probably due to the qPPO degradation via the backbone hydrolysis mechanism. (c) We prepared membranes and binders based on TMA-quaternized or 1,4-diazabicyclo[2.2.2]octane-quaternized polysulfone [18]. Though the membranes and binders showed immediately after their preparation satisfactory electrochemical properties, they became extremely brittle after a short time in concentrated KOH solutions at 60°C, and therefore, they were not suitable for application in electrolysis.

The aim of this work was the preparation of a CM polystyrene-*block*-poly(ethylene-*ran*-butylene)-*block*-polystyrene (PSEBS) without using harmful and carcinogenic chloroalkyl ethers with a subsequent preparation of a TMA-quaternized PSEBS derivative and TMA-quaternized PSEBS anion-conductive membranes and anionic binders. The prepared binders and membranes with convenient electrochemical properties were to be tested in laboratory water electrolyzers.

2. Experimental

2.1. Materials

PSEBS (Aldrich, USA, Milwaukee), M_w = 118,000 g mol^{-1} (data according to Aldrich, USA, Milwaukee), M_w = 193,900 g mol^{-1}, M_n = 178,100 g mol^{-1} (determination in this work by size exclusion chromatography in tetrahydrofuran on polystyrene standards) was used for this study. PSEBS contained 12 mol% styrene structural units, 67 mol% ethylene structural units, and 21 mol% butylene structural units [19]. Dimethoxymethane (DMOM) (≥99%, Aldrich, USA, Milwaukee), zinc chloride anhydrous (Lachema, Czech Republic), titanium tetrachloride (99.9%, Aldrich, USA, Milwaukee), phosphorus trichloride (99%, Aldrich, USA, Milwaukee), thionylchloride (99%, Fluka, Switzerland), tetrachlorosilane (99%, Aldrich, USA, Milwaukee), dimethyldichlorosilane (DMDCS) (Fluka, Switzerland, ≥99%), TMA (Aldrich, USA, Milwaukee, 31–35 wt.% solution in ethanol), chloroform, dichloromethane, toluene, tetrahydrofuran (all Lach-Ner, Czech Republic (p.a)), and ethanol (technical grade) were used as received.

2.2. PSEBS chloromethylation and membrane preparation

DMOM (0.138 mol), a chlorinating agent (0.0140 mol) (phosphorus trichloride, thionylchloride, tetrachlorosilane, or dichlorodimethylsilane) and a catalyst (0.0140 mol) ($ZnCl_2$ or $TiCl_4$) (Table 1), was added to a 100 g of 5 wt.% solution of PSEBS in chloroform which contained 0.0139 mol of styrene structural units. The mixture was stirred until catalyst was dissolved or dispersed (typically 1 h) and then heated to 60°C or 70°C for 48 h. The mixture gradually changed color from transparent to brownish. After 48 h, the mixture was diluted with chloroform (1:1 vol.) and precipitated into an excess of ethanol. Chloromethylated PSEBS (PSEBS-CM) was filtered off, washed with ethanol, and dried at room temperature.

Membranes were cast from a 5% PSEBS-CM solution in chloroform, dichloromethane, toluene, or tetrahydrofuran on a PTFE plate. The solvent was slowly evaporated at room temperature. Final drying (24 h) was done under vacuum at 60°C. A typical dry membrane thickness was 100 μm.

The PSEBS-CM membrane was immersed into an excess of solution of TMA in ethanol (48 h, room temperature). The product (PSEBS-CM-TMA) was then neutralized with 1M HCl (1 h), and then it was washed and kept in water. Formulas of PSEBS, PSEBS-CM, and PSEBS-CM-TMA are shown in Fig. 1.

2.3. Water uptake

All membrane samples were dried at 160°C for 30 min before measurement. Then the samples were immersed into demineralized water at 25°C. After 24 h, the samples were removed from water, wiped with tissue paper, and weighed. Water uptake was calculated using Eq. (1):

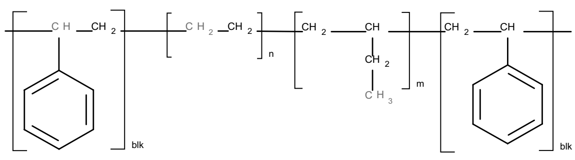
$$WU = \frac{m_{\text{wet}} - m_{\text{dry}}}{m_{\text{dry}}} \times 100(\%) \tag{1}$$

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

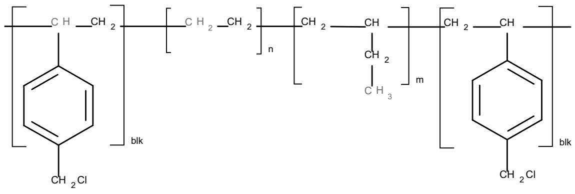
Table 1
Reaction mixtures, degree of PSEBS chloromethylation, and solubility of products. Polystyrene unit/formaldehyde precursor/catalyst/chlorinating agent molar ratio in the reaction: 1:9.9:1:1. Reaction temperature 60°C, reaction time 48 h

Sample	A^a	B^b	C^c	Conversion^d (%)	Solubility
PSEBS-CM1	DMOM	$ZnCl_2$	PCl_3	54	+
PSEBS-CM2	DMOM	$ZnCl_2$	$SOCl_2$	80	-
PSEBS-CM3	DMOM	$ZnCl_2$	$SiCl_4$	87	-
PSEBS-CM4	DMOM	$ZnCl_2$	DMDCS	66	-
PSEBS-CM5	DMOM	$TiCl_4$	PCl_3	6	+

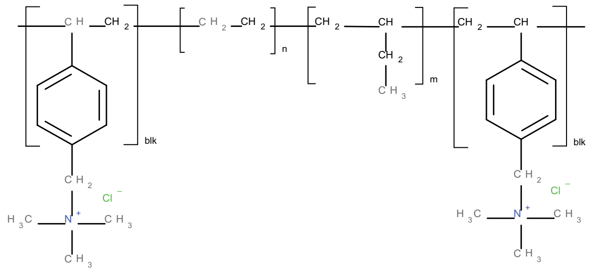
[a]Formaldehyde precursor; [b]Catalyst; [c]Chlorinating agent; [d]Proportion of styrene structural units bearing a CH_2Cl group in the product.



PSEBS



PSEBS-CM



PSEBS-CM-TMA

Fig. 1. Structural formula of PSEBS, PSEBS-CM, and quaternized PSEBS-CM-TMA.

2.4. Fourier-transform infrared spectroscopy, proton nuclear magnetic resonance spectroscopy and small-angle X-ray scattering

Fourier-transform infrared spectroscopy (FTIR) spectra of PSEBS, PSEBS-CM, and PSEBS-CM-TMA membranes were recorded using a PerkinElmer 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 of 4 cm^{-1}.

Proton nuclear magnetic resonance (^1H NMR) spectra were recorded with a Bruker Avance 300 DPX NMR spectrometer. Measurements were done at 330 K in a solution of $CDCl_3$. As an internal standard was used hexamethyldisiloxane.

Membranes were characterized by a pinhole camera Molecular Metrology SAXS System connected to a microfocused X-ray beam generator (Osmic MicroMax 002) working at 45 kV and 0.66 mA (30 W). Multiwire, gas-filled area detector was utilized, while its active area diameter was 20 cm (Gabriel design). To cover the q range of 0.005–1.1 $Å^{-1}$, two experimental setups (different sample-to-detector distances) were used ($q = (4\pi/\lambda)\sin\Theta$, where $\lambda = 1.54$ Å is the wavelength and 2Θ is the scattering angle). Glassy carbon standard was utilized to put the scattering intensities on absolute scale.

2.5. Ion exchange capacity and ionic conductivity

In this work, ion exchange capacity (IEC) was evaluated by potentiometry during the transition of the membrane sample from the OH^- to the Cl^- form. This approach was deeply described elsewhere [20]. Shortly, the potential response of a Ross combined glass electrode (Orion) was recorded during the experiment using a Keithley 6514 electrometer with high input impedance (200TX). The potential value of the glass electrode was converted into concentration of displaced OH^- ions in the solution by a calibration curve. This series of experiments was performed in 125 ml of 0.1 mol dm^{-3} NaCl solution in a gastight cell under argon atmosphere to avoid the effect of carbon dioxide. Decarbonized demineralized water was used in the experiments.

The in-plane IC of the membranes was determined in a tempered box in gastight 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 IC σ was calculated using Eq. (2):

$$\sigma = \frac{l}{Rbd} \tag{2}$$

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

2.6. Alkaline water electrolysis

A single-cell alkaline laboratory electrolyzer was used to test the performance under alkaline water electrolysis conditions. Ni foam electrodes (INCO Advanced Technology Materials, Dalian Co., Ltd, Dalian, China) with pore size 580 mm and geometric area of 1.9 × 1.9 cm^2 were used as a catalytic layer support. As an anode, electrocatalyst served $NiCo_2O_4$ spinel prepared by a direct thermal decomposition of the $Ni(NO_3)_2{\cdot}H_2O$ and $Co(NO_3)_2{\cdot}H_2O$ [21]. Catalytic ink was prepared by mixing 10 ml of chloroform ($CHCl_3$), 5% solution of PSEBS-CM in $CHCl_3$, and 0.192 g of catalyst powder. The ink was sprayed onto the surface of Ni foam using an airbrush. Ni foam was heated at 50°C to accelerate chloroform evaporation and thus to prevent penetration of the catalyst into the bulk of Ni support. The coated Ni foam was immersed into the solution of TMA in ethanol for 48 h to convert PSEBS-CM into PSEBS-CM-TMA. After removal from solution of TMA, the electrode was washed with demineralized water. The resulting anodes always contained 8 mg cm^{-2} of $NiCo_2O_4$ spinel electrocatalyst and 0.42, 0.88, or 2.67 mg cm^{-2} of PSEBS-CM-TMA, respectively. For comparison, an anode containing 8 mg cm^{-2} of $NiCo_2O_4$ and 2.67 mg $cm^{-2}$of PTFE was used. The cathode contained catalyst layer composed of 0.3 mg Pt cm^{-2} and 0.05 mg cm^{-2} of PTFE binder. Operational temperature was 70°C during load curve measurement or 50°C in a long-term experiment. As a separator of the anode and cathode compartment, heterogeneous anion-selective membrane [22,23] during load curve measurement or a PSEBS-CM-TMA membrane prepared within this work in a long-term experiment was used. The electrodes were attached directly to the membrane surface. The rear sides of the electrodes were washed with tested electrolyte solution. The scheme of the electrolysis process with the role of the anion-selective membrane can be seen in Fig. 2.

3. Results and discussion

3.1. PSEBS chloromethylation

One of the purposes of this work was the preparation of a soluble CM polystyrene block copolymer using safe and commercially available reagents. Nonvolatile and inorganic solvent soluble DMOM was always used as a formaldehyde precursor; $ZnCl_2$ and $TiCl_4$ were tested as a catalyst; and PCl_3, $SOCl_2$, $SiCl_4$, or DMDCS was used as chlorinating agent (Table 1). All reactions that were carried out at 70°C (and 48 h) lead to insoluble products. Insoluble products were also obtained with $SOCl_2$, $SiCl_4$, and DMDCS as chlorinating agents and with a $ZnCl_2$ catalyst in reactions carried out at 60°C [24]. A soluble and highly CM block copolymer was obtained by the reaction carried out with $ZnCl_2$ and PCl_3. The same reaction but catalyzed with $TiCl_4$ yielded low degree of conversion.

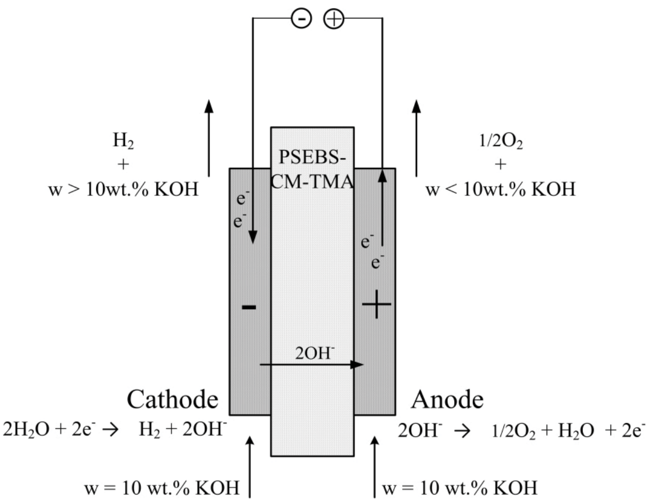


Fig. 2. The scheme of the alkaline water electrolysis in zero-gap arrangement for a case of 10wt.% KOH.

In the ^1H NMR spectra of CM products (Fig. 3), a new maximum (singlet) appears at 4.49 ppm (protons of CH_2Cl group) in addition to the signals of original PSEBS at 6.35–7.03 ppm (aromatic protons), 1.06–1.83 ppm (CH_2 protons), and 0.78–0.83 ppm (CH_3 protons).

While PSEBS FTIR (Fig. 4) spectrum contains peaks at 3,025, 3,059, 1,638, 699, and 747 cm^{-1} that belong to the vibrations of CH= bonds in a styrene ring and the peaks in region of 2,923–2,853 and 1,492–1,461 cm^{-1} refer to the vibrations of CH_2 groups in ethylene and butylene structural units and to those of CH groups in the main chain, in the spectrum of PSEBS-CM, there are two new peaks at 800 and 1,265 cm^{-1} that belong to the vibrations of CH_2Cl group on a styrene ring. The peak at 699 cm^{-1} decreased after reaction significantly, which confirms the chloromethylation of styrene ring.

3.2. Membrane casting and quaternization

PSEBS-CM membranes were prepared by casting from PSEBS-CM solution in chloroform, dichloromethane, toluene, or tetrahydrofurane followed by a slow evaporation of a solvent.

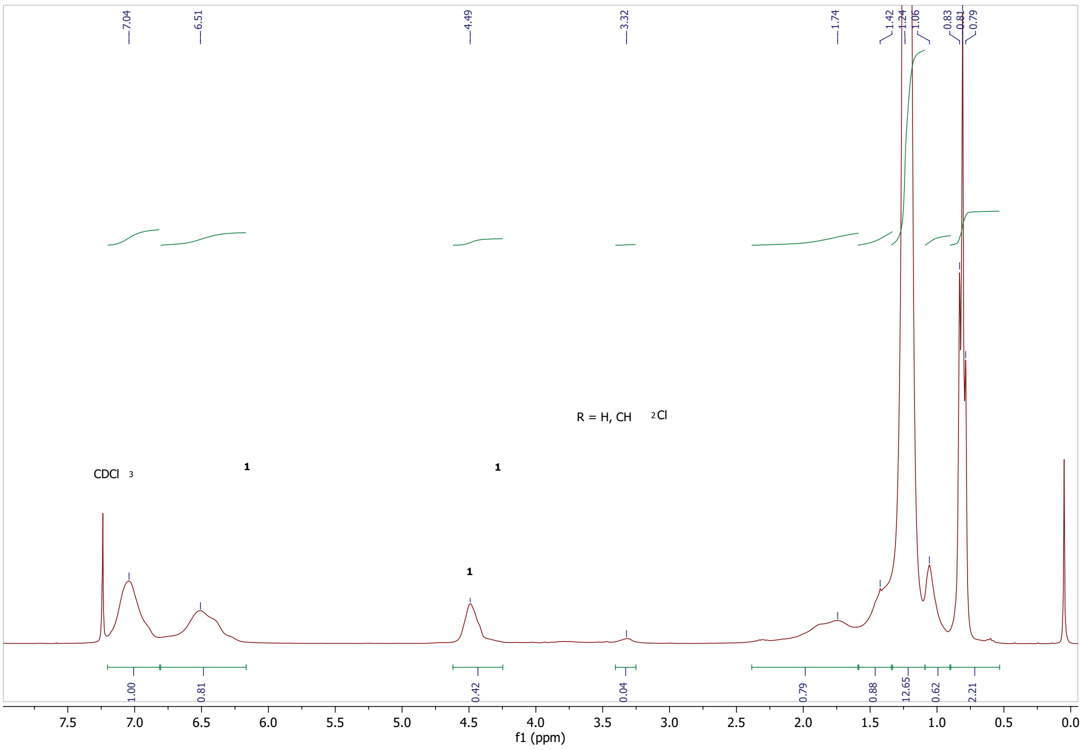


Fig. 3. ^1H NMR spectra of PSEBS-CM.

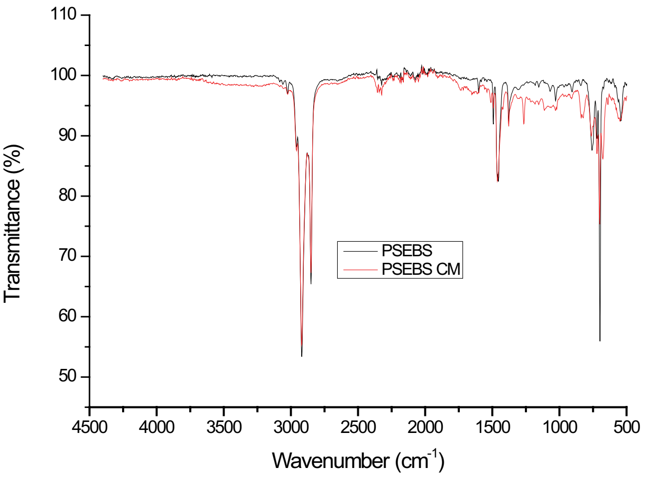


Fig. 4. FTIR spectra of PSEBS and PSEBS-CM.

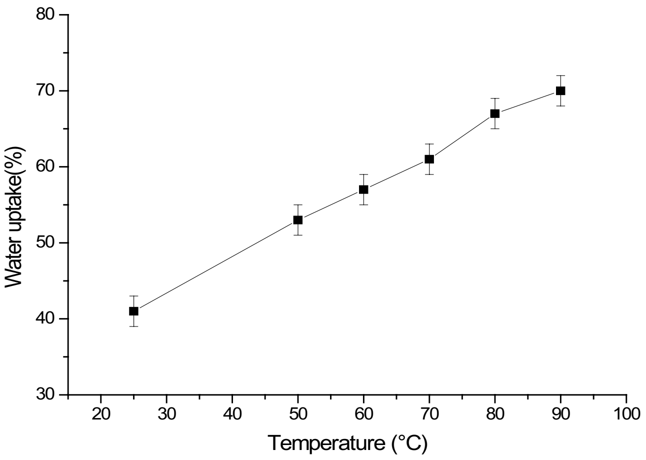


Fig. 5. Water uptake by a PSEBS-CM-TMA membrane (Cl$^-$ form, quaternization degree 52%) is dependent on temperature.

PSEBS-CM quaternization was carried out by the immersion of a PSEBS-CM membrane with a chloromethylation degree 54% into an excess of TMA solution for 48 h at room temperature. An elemental analysis (N and Cl contents) showed that practically all CH$_2$Cl groups were converted into CH$_2$N$^+$(CH$_3$)$_3$ groups. In the IR spectrum of PSEBS-CM-TMA, there appear new peaks at 3,393 cm^{-1} (adsorbed water or/and quaternary ammonium group), 1,261 cm^{-1} (CH$_2$ group in the vicinity of a quaternary ammonium group), and 2,365 cm^{-1} (quaternary ammonium group).

On the one hand, the membranes must sorb some water, which is a prerequisite for sufficient IC, but on the other hand, an excessive swelling (more than about 80%) leads to the problems with membrane shape stability and to the deterioration of membrane mechanical properties. The dependence of water uptake of a PSEBS-CM-TMA membrane on temperature is shown in Fig. 5.

3.3. PSEBS, PSEBS-CM, and PSEBS-CM-TMA solubilities

Original PSEBS and uncrosslinked PSEBS-CM (Table 1) are well soluble at room temperature in nonpolar or slightly polar solvents, such as cyclohexane, toluene, tetrahydrofuran, diethylether, tetrachloromethane, chloroform, and dichloromethane. They are insoluble in polar solvents such as dimethylsulfoxide, *N*-methylpyrrolidone, *N*,*N*-dimethylformamide, propylenecarbonate, triethylphosphate, and acetonitrile. On the other hand, no solvent was found to dissolve PSEBS-CM-TMA in the form of membrane or powder.

3.4. Small-angle X-ray scattering

PSEBS-CM membranes were cast from four different solvents (chloroform, toluene, dichloromethane, and tetrahydrofuran). The SAXS curves of all investigated membranes show a microphase separation and high absolute intensities of scattering (Fig. 6). The curves have two distinct maxima with the ratio of 2:1, which indicates a lamellar structure. Based on the positions of these maxima and using the Bragg law, long periods of 32–35 nm can be estimated in all investigated membranes. The curves of all investigated membranes are almost identical, and this means that the casting solvent did not affect the microstructure of PSEBS-CM membranes.

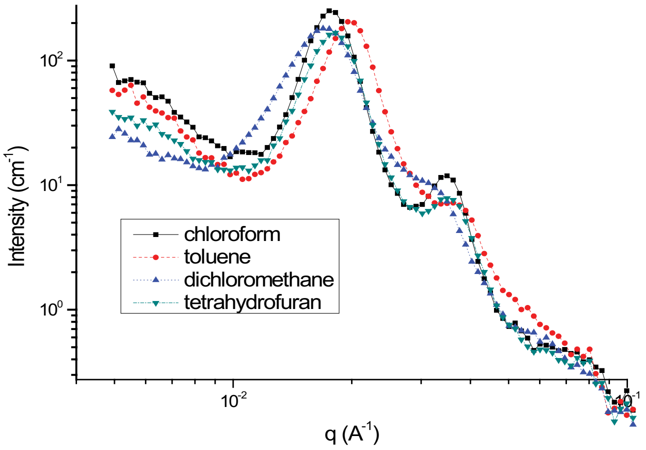


Fig. 6. SAXS curves of PSEBS-CM membranes cast from the solutions in chloroform, toluene, dichloromethane, and tetrahydrofuran, respectively.

3.5. Ion exchange capacity and ionic conductivity

The IEC of a PSEBS-CM-TMA membrane with a quaternization degree of 52% was found to be 0.75 ± 0.04 meq g^{-1} dry membrane. The majority of commercial and experimental anion exchange membranes have a significantly higher IECs [8]. However, all quaternary ammonium groups are located in quaternized polystyrene microdomains, and consequently, the IEC inside polystyrene microdomains (and thus inside conducting paths) is very high – about 2.7 meq g^{-1} (calculated from the degree of quaternization).

Therefore, the IC of this membrane is also rather high: 56 mS cm^{-1} at 30°C. Its dependence on temperature is shown in Table 2

Table 2
The dependence of IC on temperature of the PSEBS-CM-TMA membrane with a quaternization degree of 52%

Temperature (°C)	IC (S m^{-1})
30	5.61
50	7.48
70	7.92

3.6. Alkaline water electrolysis

PSEBS-CM-TMA was tested as a catalyst binder on the anode of an alkaline laboratory electrolyzer. Anodes with PSEBS-CM-TMA binder were compared with an anode with a standard PTFE binder and the anode comprising only Ni foam. The influence of the amount of PSEBS-CM-TMA in the catalytic layer (anodic) was also tested. Cathode catalytic layer was formed with Pt catalyst in PTFE binder and was the same in all experiments.

Performance of electrolyzers with different anode compositions is shown in Fig. 7. It is plotted as dependence of the current density obtained for particular anode composition at cell voltage 1.74 V depending on the concentration of the KOH liquid electrolyte. The value of the cell voltage 1.74 V was chosen because it corresponds to the 85% thermodynamic efficiency when compared with the thermoneutral voltage of water decomposition (1.48 V at 25°C).

It can be seen that the anodes modified by catalyst bonded by PSEBS-CM-TMA binder greatly outperform not only those containing bare Ni foam but also the Ni foam/ $NiCo_2O_4$ + PTFE binder. This is unambiguously due to the improved utilization of the $NiCo_2O_4$ catalyst allowing decrease in overpotential of the oxygen evolution reaction. The reason for better utilization of the catalyst when using the PSEBS-CM-TMA polymer binder instead of PTFE binder consists in the nature of both the materials. While the PTFE is the inert material which only can ensure the mechanical stability of the catalyst layer, the novel synthetized PSEBS-CM-TMA is able to ensure mechanical properties of the catalyst layer as well as the IC inside this layer. The later mentioned ability represents significant advantage to the inert PTFE binder. It significantly increases probability of the three-phase boundary occurrence in the catalytic layer. Three-phase boundary indicates part of the catalyst particle in contact with ionic conductor (electrolyte membrane), electron conductor (electrode), and reactant at the same time. The desired electrode reaction, i.e. oxygen evolution, can take place just on such places. The contact with reactant is easily achieved due to the presence of the liquid water in the system. The ionic contact represents more difficult point. The high concentration of the KOH in circulating water represents one possibility how to achieve a good ionic contact. On the other hand, this is connected with the lower flexibility of the water electrolyzer and higher safety risk. The other possibility lies in utilization of the anion-selective material as polymer binder. Such material should be able to ensure the ionic contact even in the environment of the diluted liquid electrolyte. In the present case, this role is fulfilled by PSEBS-CM-TMA.

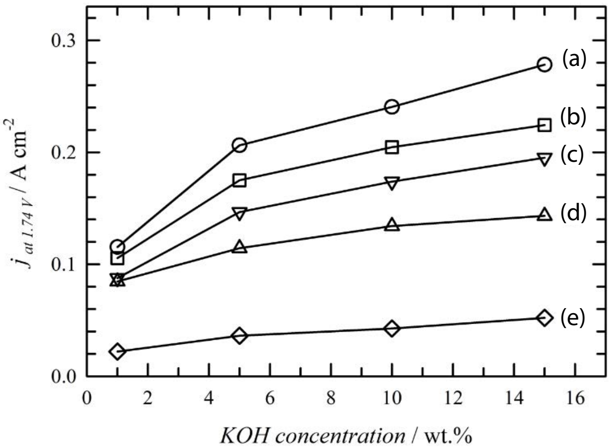


Fig. 7. Current density achieved by laboratory alkaline water electrolysis cell with different anodes. Cell voltage 1.74 V, 70°C, separator – heterogeneous anion-selective polymer membrane, cathode –0.3 mg Pt cm^{-2} + 0.05 mg PTFE cm^{-2}, liquid electrolyte – indicated on x axis. Anode – (a) 8 mg $NiCo_2O_4$ cm^{-2} + 0.42 mg PSEBS-CM-TMA cm^{-2}; (b) 8 mg $NiCo_2O_4$ cm^{-2} + 0.88 mg PSEBS-CM-TMA cm^{-2}; (c) 8 mg $NiCo_2O_4$ cm^{-2} + 2.67 mg PSEBS-CM-TMA cm^{-2}; (d) 8 mg $NiCo_2O_4$ cm^{-2} + 2.67 mg PTFE cm^{-2}; (e) bare Ni foam.

The second difference in the nature of both used polymer binders consists in an affinity to the water. The PTFE represents the hydrophobic material which repeals the molecules of water. This may result in the accumulation of the evolved oxygen in the catalytic layer structure and subsequent disturbance of the water molecule supply. The PSEBS-CM-TMA is, in contrast, the hydrophilic material which will ensure better access of the water to the catalyst.

The best results were achieved using anode with the smallest used amount of PSEBS-CM-TMA in the catalytic layer. It is due to the fact that a small amount of anion-selective polymer binder increases ionic contact of the catalyst particles but it does not interfere with the transport of electrons and reactants.

Fig. 8 shows full load curves of the alkaline water electrolysis dependent on electrolyte concentration. Anode catalyst layer contained optimal concentration of PSEBS-CM-TMA binder (Fig. 7). It can be seen that with increasing KOH concentration, the electrolyzer performance improves. This indicates that even an anion-selective binder is not able to ensure a perfect ionic contact between the electrodes and in the catalytic layer (though the improvement is great). For comparison, Fig. 8 shows the region of current densities achieved by commercial (nonmembrane) alkaline electrolyzers [25] which are usually operated with 25–30 wt.% aqueous KOH. This comparison shows that the electrolyzers with anion-selective binders outperform classical commercial electrolyzers at least on a laboratory scale.

Long-term stability of PSEBS-CM-TMA in an alkaline environment was tested in a laboratory electrolyzer where PSEBS-CM-TMA membrane was used as a separator of the anode and cathode compartments. Operation temperature was 50°C, and the electrolyte was 10 wt.% KOH. Fig. 9 shows time dependence of the cell voltage during the long-term alkaline water electrolysis experiment. In the first 80 h, the cell voltage increased from initial 1.76 to 1.84 V followed by

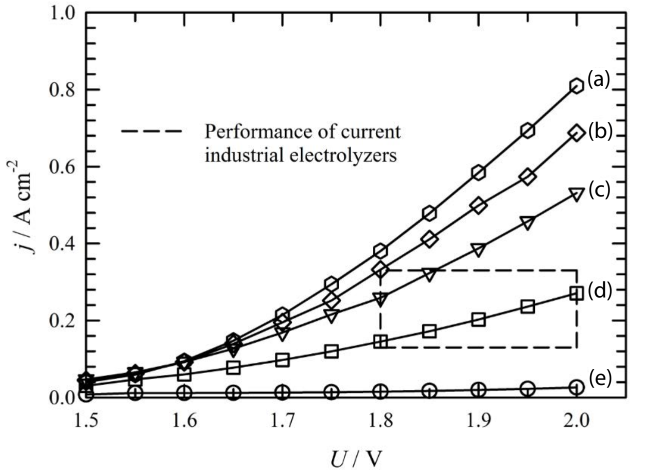


Fig. 8. Load curves of the alkaline water electrolysis. Anode – 8 mg $NiCo_2O_4$ cm^{-2} + 0.42 mg PSEBS-CM-TMA; cathode – 0.3 mg Pt cm^{-2} + 0.05 mg PTFE; 70°C. The values typical of industrial water electrolyzers are bordered by a dashed line. (a) 15 wt.% KOH, (b) 10 wt.% KOH, (c) 5 wt.% KOH, (d) 1 wt.% KOH, (e) deionized water.

the decrease back to 1.76 V in next 80 h. This is most probably connected with the establishment of the equilibria in the system including phenomena such as activation of the catalysts, flooding the catalytic layers, establishing dynamic equilibrium between liquid electrolyte and produced gases in the catalytic layers, equilibrating the temperature, etc. Nevertheless, with respect to the average value and standard deviation of the cell voltage (average value showed in the Fig. 9 as dashed line) reaching 1.78 ± 0.13 V, the maximum observed deflection is about 60 mV. It represents deviation of up to 4%, which can be considered with respect to its character as a stable system. The performance of the electrolyzer can thus be considered as stable even after more than 800 h of operation. This shows (a) a good stability of trimethyl benzyl ammonium groups on styrene block copolymers in alkaline environment and (b) a good mechanical stability of PSEBS-CM-TMA membrane.

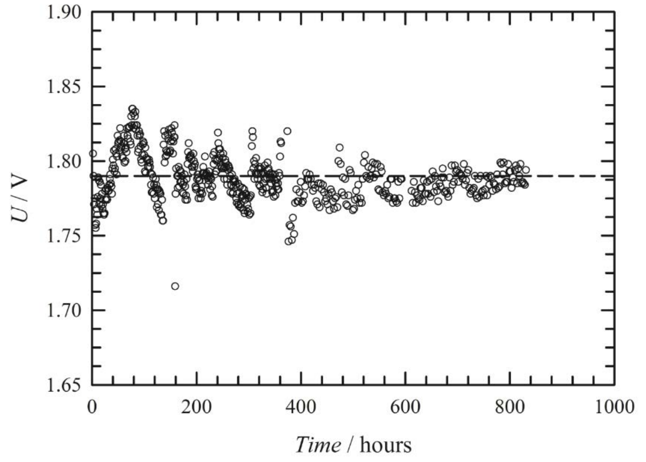


Fig. 9. Voltage vs. time. Current density 0.3 A cm^{-1}. Single-cell alkaline laboratory electrolyzer; PSEBS-CM-TMA membrane, anode and cathode: see captions to Fig. 7; 10 wt.% aqueous KOH electrolyte, 50°C.

4. Conclusions

Quaternized PSEBS-CM-TMA copolymer was successfully synthesized and tested in the form of anion-selective membrane as well as polymer binder of the catalytic layer. IEC was as high as 0.75 mmol g^{-1} dry membrane; however, the proper distribution of the functional groups allowed to achieve high IC of 5.6 S m^{-1} at 30°C. Application of the PSEBS-CM-TMA in the form of polymer binder of the catalyst layer resulted in significant decrease of the concentration of the circulating liquid electrolyte down to 1 wt.% KOH while keeping the performance of the alkaline water electrolysis cell comparable with the industrial units. Such decrease in the concentration of the liquid electrolyte results in improving safety and flexibility of the process. Under the conditions of the long-term alkaline water electrolysis, PSEBS-CM-TMA showed no signs of degradation in the range of 800 h, which documents high stability of the synthetized copolymer.

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