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ORIGINAL PAPER

Polymer anion selective membranes for electrolytic splitting of water. Part I: stability of ion-exchange groups and impact of the polymer binder

**Jaromír Hnát · Martin Paidar · Jan Schauer ·
Jan Žitka · Karel Bouzek**

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Abstract In this study, the chemical stability of three types of the anion-exchange functional groups in an alkaline environment was tested. The following groups were selected for the test: trimethylbenzylammonium, methyl pyridinium, and tributhylbenzylphosphonium. A KOH solution with various concentrations and temperatures was used as the environment. The trimethylbenzylammonium group showed the highest stability of the materials tested under conditions relevant to water electrolysis. In the next step, four types of polymeric binders, including ethylene-*co*-methacrylic acid, linear polyethylene, linear polyethylene blended with poly(ethylene-*co*-vinylalcohol), and low-density polyethylene, were selected to determine their impact on the resulting electrochemical properties of a heterogeneous membrane. This study reveals the morphology of the membrane, ion-exchange capacity, ionic conductivity, and performance in alkaline water electrolysis conducted on a laboratory scale. The material showing the most promising properties was selected for further optimization and testing.

Keywords Water electrolysis · Alkaline environment · Polymer electrolyte · Anion-exchange group · Stability

1 Introduction

Water electrolysis is a well-established industrial technology for hydrogen production. Nevertheless, so far it has only gained limited acceptance for large-scale applications. This is for economic reasons, mainly due to the significant electrical energy demands of this process. The reversible decomposition voltage of water is 1.23 V at 25 °C. This corresponds to theoretical electrical energy consumption of 2.95 kWh Nm^{-3} of H_2. Present alkaline technology with an actual cell voltage of about 1.9 V and corresponding energy consumption of 4.7–4.8 kWh Nm^{-3} falls considerably behind the ideal values [1]. The application of water electrolysis for industrial hydrogen production is thus limited to cases where electrical energy production is extremely cheap. In addition, if non-renewable electricity generation is used, it results in higher CO_2 emissions related to hydrogen production compared to natural gas steam reforming. Due to these economic and environmental aspects, nowadays hydrogen is mainly produced from fossil fuels [2].

The non-competitiveness of the technology of water electrolysis has resulted in numerous research laboratories focusing on further developing this technology. Moreover, they are motivated by the increasing number of installations of renewable sources of electrical energy in the distribution grid. A typical example is the rapid increase in installed solar photovoltaic (PV) power plants. With an estimate installed capacity between 14.3 and 16.5 GW for the year 2010, PV is expected to experience 100% growth comparing to the year 2009 [3]. Unfortunately, the majority of these sources are unreliable due to their strong dependence on weather conditions. This has resulted in an intensive search for a suitable technology for efficient and reliable buffering of the time fluctuations of these sources of energy production [4].

J. Hnát · M. Paidar · K. Bouzek (✉)
Department of Inorganic Technology, Institute of Chemical Technology Prague, Technická 5, 166 28 Prague 6, Czech Republic
e-mail: bouzekk@vscht.cz

J. Schauer · J. Žitka
Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic, Heyrovsky Sq. 2, 162 06 Prague, Czech Republic

Hydrogen is preferred as an energy vector for several reasons [5]:

(i) harmless products during its conversion at the point of use;
(ii) it can be produced using many energy sources, with renewable energy being the most attractive;
(iii) it works with fuel cells;
(iv) it is ubiquitous, i.e., no continent or nation is excluded as a producer, trader, or user of hydrogen.

The current challenges for the widespread utilization of water electrolysis are: to reduce the energy demands, decrease investment, and maintenance costs, and to ensure sufficient reliability, durability, flexibility, and safety [6].

Three principal process versions of electrolytic decomposition of water have been or are being developed:

(i) High-temperature steam electrolysis, which is a promising technology, available in the medium term, as it involves less electrical energy consumption compared to conventional low-temperature water electrolysis [1, 7];
(ii) Proton exchange membrane electrolysis is a near-term technology, which offers the advantages of higher efficiency over the alkaline system and good corrosion stability and flexibility over steam water electrolysis, however, the installation costs are higher than those of the alkaline system;
(iii) Alkaline water electrolysis (AWE) which is the most advanced and the lowest in capital costs [1].

So far, the only commercially utilized technology on an industrial scale is alkaline technology. The main reason is that no precious metals are needed for the electrodes' construction. Furthermore, other components of current cells are typically made of relatively cheap materials (Ni is the main construction material, asbestos for the diaphragm), resulting in a robust construction and a reliable cell. However, as already mentioned, this comes at the expense of cell efficiency. A KOH aqueous solution (up to 30 wt% KOH) is typically used as an electrolyte. A significant improvement in the behavior of the alkaline system can be expected if the asbestos diaphragm is replaced by an anion-selective polymer electrolyte. Currently, the main obstacle is the absence of an alkaline polymer electrolyte possessing satisfactory electrochemical properties together with sufficient chemical stability under conditions of AWE. The chemical instability of this type of material is mainly due to the displacement of ammonium functional groups by OH^- anions via direct nucleophilic displacement or Hofmann elimination which mainly becomes important at elevated temperatures, typically above 80 °C [8].

Hofmann elimination belongs to the class of bimolecular elimination reactions (E2) because two reactants are involved in the transition state. The E2 reaction involves the elimination of a β-hydrogen by a hydroxide ion and the removal of a tertiary amine, see Fig. 1a. An olefin, an amine, and water are the products of this reaction. The most common side reaction competing with elimination is a displacement reaction at the α-C atom. However, if none of the groups on a hetero atom bears a β-hydrogen, the nucleophilic substitution S_n2 is the only possible reaction, see Fig. 1b [9–11]. The two different mechanisms of S_n2 displacement of the trialkylammonium groups by hydroxide anions can occur simultaneously. In the first case, OH^- anions attack α-C bonded to the benzene ring. In such a case, the entire nitrogen functional group is separated from the molecule. In the second case, one of the α-C bounded to the nitrogen is attacked by OH^- anion. Here methanol is separated from the molecule by the formation of tertiary amines. The tertiary amine group still shows the ability to exchange ions only its strength is significantly reduced. The extent of these reactions generally depends on the substrate structure and on the stability of the leaving group as well as on the temperature [8, 9]. With increasing temperature, the first degradation mechanism becomes significantly more important. This is documented by Zagorodni et al. [12], who did not observe any reduction of the ion-exchange capacity (IEC) for trimethylbenzylammonium groups during their experiments performed in 3 M KOH at 80 °C. Such a reduction would be detected in the case of the first reaction mechanism shown in Fig. 1b, corresponding to the loss of the whole nitrogen group. Under the conditions used in this study, the second mechanism is clearly predominant. The authors reported [12] that only part of the tertiary amines formed by this degradation mechanism was further degraded in the second step by the formation of secondary amines.

A slightly different aspect has to be considered with regard to the heterocyclic compound. In this case, the main degradation reaction is again nucleophilic, but it takes place through the nucleophilic ring-opening reaction including replacement of the hydrogen by an OH group. This is followed by closing the ring and dehydrogenation of the alcohol group. For details of the mechanism, see Fig. 1c [12]. The product of this reaction loses its ion-exchange ability.

The stability of an anion-selective membrane in an alkaline environment is given by the stability of the weakest link. In this case, these are the incorporated, positively charged functional groups. As fixed charges in anion-selective membranes, the following groups can be used: $–NH_3^+$, $–RNH_2^+$, $–R_3N^+$, $=R_2N^+$, $–R_3P^+$, $–R_2S^+$. Among the different kinds of functional groups, the quaternary ammonium group possesses considerably higher thermal and chemical stability than quaternary phosphonium and tertiary sulfonium groups [9].

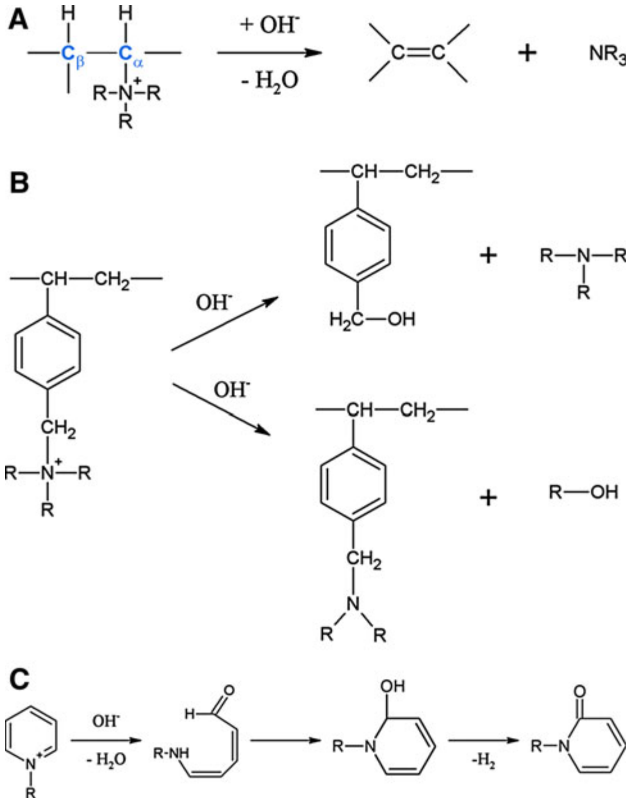

Fig. 1 Mechanisms of the degradation of the quaternary ammonium groups by **a** E2 elimination mechanism, **b** S_n2 mechanism, and **c** S_n2 mechanism on the aromatic ring

Up to now, promising alkaline membranes have been evaluated mainly from the point of their use in alkaline membrane fuel cells. Membranes have been prepared as a homogeneous type based on copolymers, with the quaternized positively charged comonomers [13]. Kang et al. [14] prepared a membrane using polysiloxane, i.e., material with excellent flexibility and thus an ideal material for ion conductor polymer backbone. The functionalized polysiloxane contains tertiary amino side groups. Another approach was chosen by Wang et al. [15] who prepared an anion-selective membrane based on functional poly (ether-imide). Aromatic polyimides are a well-established, high performance material with high-thermal stability combined with chemical resistance and excellent mechanical properties. However, the stability of the membrane was clearly limited by the stability of the quaternary ammonium groups. At room temperature, membranes based on this material were stable up to 8 mol dm^{-3} KOH solution. At a temperature of 80 °C, stability was limited only up to 1 mol dm^{-3} KOH solution. Lu et al. [16] used polysulphone modified by quaternary ammonium groups for membrane preparation. The resulting membrane in the OH^- cycle was thermally stable up to 120 °C. The membrane obtained shows high ionic conductivity and excellent mechanical stability. However, the preparation of membranes of this kind is quite complicated and expensive because it is based on the mixing of monomer, casting, and polymerization at a relatively high temperature. Furthermore, some reactants are very expensive materials, resulting in a dramatic increase in the cost of membrane manufacture [17]. Moreover, the preparation of a homogeneous type of anion-selective membranes typically involves several chemical reactions, like chloromethylation, quatenization, and alkalization, where the first two named are two key reactions that determine ionic conductivity. However, chloromethylation especially, is not easily controllable, and the number and yield of chloromethyl groups attached to the polymer could be very low [18].

As a class, homogeneous membranes are typically characterized by good electrochemical properties. On the other hand, they are more sensitive to chemical attack and are usually less chemically stable. Heterogeneous membranes represent an alternative. Their electrochemical performance is typically lower because of the presence of a no-conducting polymer phase in the membrane structure. However, heterogeneous membranes are more robust. The presence of an inert polymer binder improves the mechanical strength of a membrane and at the same time it protects the ion-selective phase from chemical attack by the surrounding solution [19]. The aim of this work is to test the stability of selected, suitable anion-exchange groups representing the main candidates for application in the AWE process. Materials either known for their stability in an alkaline environment or as yet untested were selected for this purpose. Consequently, the impact of suitable polymer binders on the performance of a membrane based on a selected ion-selective resin containing functional groups evaluated as the most stable one will be tested [20].

2 Experimental

2.1 Membrane preparation

Anion-selective particles (66 wt%) were blended with a binder polymer (34 wt%) in a Brabender Plasti-corder PLE 651 until the mixture became optically homogeneous and the torque value constant. The blend was press-molded between two poly(ethylene terephthalate) films to form a flat film at 10 MPa. The blending and molding temperatures of linear polyethylene, low-density polyethylene and poly(ethylene-*co*-methacrylic acid) were 150 °C, those of the mixture of linear polyethylene and poly(vinyl alcohol-*co*-ethylene) were 180 °C. The resulting membranes were typically 0.30 mm thick.

2.2 Stability in an alkaline environment

The heterogeneous membrane samples consisting of linear polyethylene polymer binder and polymer resin particles with three different functional groups in the OH^- form (0.5 g) were immersed in an aqueous solution of potassium hydroxide (50 mL) (concentration 0–10 mol dm^{-3}) at a controlled temperature for 7 days in a closed vial. The IEC value of the membrane sample before and after treatment was compared.

2.3 Ion-exchange capacity

The IEC, or more exactly in this particular case, the apparent IEC of the membrane, which is relevant to the conductivity of the membrane in the OH^- cycle, was evaluated by potentiometry during transient of the membrane sample from the OH^- to the Cl^- cycle. Apparent ion-exchange capacity corresponds in this case to the content of the ion exchange sites able to exchange OH^- ions. It is related to the fact that the basic ion exchange groups are substantially ionized only at pH lower than pK of the functional groups. Only quaternary ammonium salts are ionized independently of the environment pH [21]. It is thus clear that in OH^- cycle not all functional groups are ionized and thus able of ionic exchange. IEC value obtained is thus lower than the value determined for the same membrane materials using exchange of ions different from OH^-. The potential response of a Ross combined glass electrode (Orion) was recorded during the experiment by a Keithley 6514 electrometer with high input impedance (200 TΩ). The potential value of the glass electrode was converted to the concentration of displaced OH^- ions in the solution by mean of a calibration curve. This series of experiments was performed in 125 mL of 0.1 mol dm^{-3} NaCl solution in a gas-tight cell under argon atmosphere to avoid the effect of carbon dioxide. Decarbonized demineralized water was used in the experiments.

2.4 Ionic conductivity (IC)

The in-plane ionic conductivity of the membranes was determined in a tempered box in gas-tight cell in an environment of deionized water (i.e., 100% relative humidity) by means of electrochemical impedance spectroscopy (EIS) in a four-electrode arrangement. A Solartron SI 1250 Frequency Response Analyzer and Solartron SI 1287 Electrochemical Interface were used to accomplish this task.

2.5 Alkaline water electrolysis

A single alkaline laboratory electrolyzer was used to test the membranes' performance under AWE conditions. It is made of two plexiglas blocks. Membrane-electrode assembly consisting of the Ni foam electrodes with an active area of 2 × 2 cm^2 attached from both sides directly to the membrane surface is squeezed between these blocks. The rear side of the electrodes was washed by a 10-wt% KOH solution representing ionically conductive phase, source of water and providing removal of the evolved gaseous phase. All experiments were performed at the room temperature. A schematic sketch of the test rig is shown in Fig. 2. The performance of the cell was tested within a cell voltage range of 1.5 to 2.5 V.

2.6 Membrane morphology

The morphology of the prepared anion-selective membranes was investigated using a Hitachi scanning electron microscope (SEM) S4700. Samples of the membranes were dried in a desiccator over molecular sieves. To obtain cross-section images, a dry sample was immersed in liquid nitrogen and broken. Samples were coated by vacuum sputtering with a Au/Pd layer approximately 20 nm thick.

2.7 Materials

Linear polyethylene (ExxonMobil, EXACT 0210), a polymer blend obtained by mixing EXACT 0210 (60 wt%) with poly(vinyl alcohol-*co*-ethylene) (40 wt%) (Aldrich, ethylene content 44 mol.%), poly(ethylene-*co*-

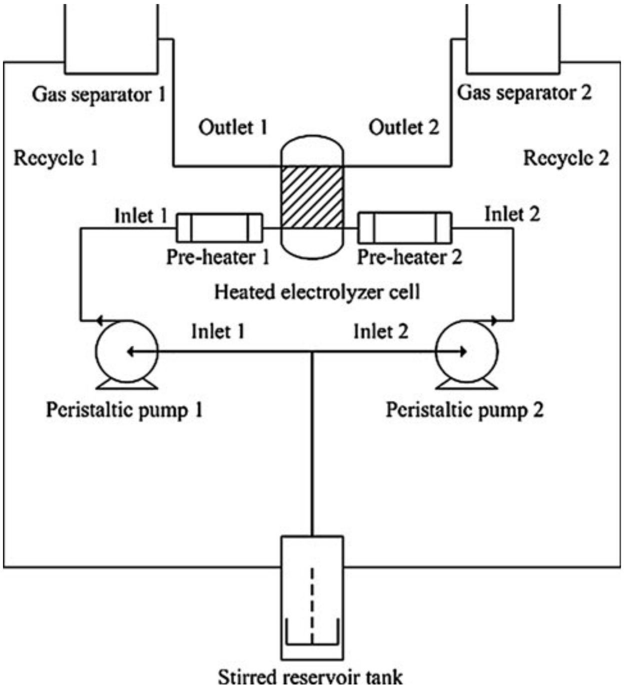

Fig. 2 Scheme of the laboratory alkaline water electrolyzer setup

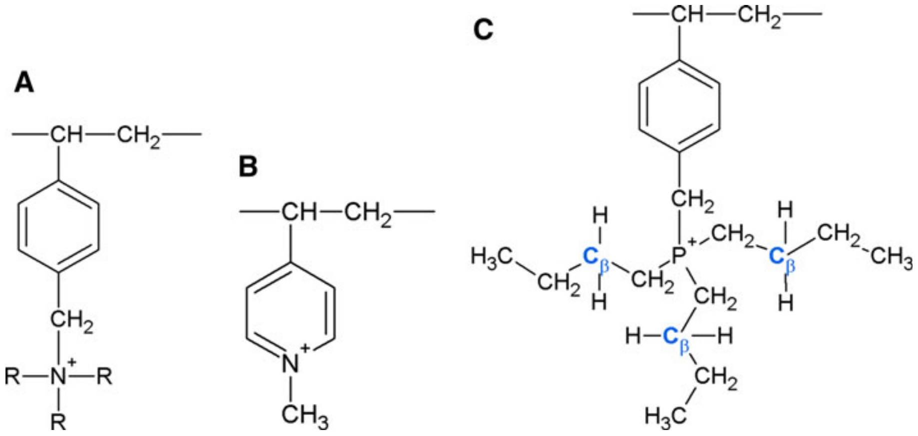

Fig. 3 Structures of the functional groups tested. **a** trimethylbenzylammonium, **b** methyl pyridinium, and **c** tributylbenzylphosphonium

methacrylic acid) (Surlyn® 9150, 15% of methacrylic acid units, DuPont), and low-density polyethylene (ExxonMobil, LDPE 605BA) were used as matrix polymers. A Lewatit MonoPlus M500 anion-exchanger (styrene-divinylbenzene matrix, gel, trimethylbenzylammonium functional groups; Bayer), Reillex™ HPQ anion-exchanger (methylchloride quaternary salt of cross-linked poly(4-vinylpyridine); Aldrich), and an anion-exchanger with tributylbenzylphosphonium functional groups were ground in a ball mill and sieved to obtain small particles 10–30 µm in size.

The anion-exchanger with tributylbenzylphosphonium groups was obtained by the reaction of chloromethylated styrene-divinylbenzene resin (50 g) (Aldrich, 4 mmol g^{-1} of chloromethyl groups) with tributylphosphine (50 g) (Aldrich) in 165 g of dimethylformamide and 85 g *N*-methylpyrrolidone. The mixture was kept at 150 °C for 1 h. After cooling down to room temperature it was poured into 1 L of acetone, filtered, washed several times with acetone, and dried.

3 Results and discussion

3.1 Stability in an alkaline environment

The stability of the ion-selective resins with trimethylbenzylammonium, methyl pyridinium and tributylbenzylphosphonium groups was tested. Trimethylbenzylammonium is representative of a compound with quaternary nitrogen surrounded by aliphatic hydrocarbons and one aromatic ring, see Fig. 3a. In the case of this structure, no β-hydrogen is available, i.e., Hofmann elimination cannot occur [9]. Methyl pyridinium is a representative of compounds in which quaternary nitrogen is part of the aromatic ring, see Fig. 3b. Therefore, Hofmann elimination does not take place in this particular case even though a β-hydrogen is available in the polymer structure [12]. Tributylbenzylphosphonium is a representative of a compound with quaternary phosphorus. Here, phosphorus is sterically protected from the aggressive environment. However, β-hydrogen is available in this structure, see Fig. 3c.

The stability of these groups was evaluated at 50 and 70 °C, i.e., at lowest temperatures relevant to the water electrolysis process, in potassium hydroxide solutions of various concentrations. The ion-selective materials were bonded in linear polyethylene by the method used for the membrane preparation and described in the experimental section of this work in order to facilitate handling of the material. Preliminary testing has confirmed that this particular binding polymer allows sufficient contact between the ion-selective particles and the surrounding solutions. Degradation of the functional groups was indicated by a decrease in the IEC, see Fig. 4.

Tributylbenzylphosphonium groups showed very poor stability even at low potassium hydroxide concentration. Methylpyridinium groups had poor stability at an elevated potassium hydroxide concentration. Only trimethylbenzylammonium groups were identified as relatively stable under the conditions studied. In all cases, the decrease in IEC was faster at higher temperatures, see Fig. 4. These observations correspond to the literature data [9, 11].

Degradation was most extensive in the case of the tributylbenzylphosphonium. This was due to the presence of β-hydrogen in the functional group structure, see Fig. 3c. Another general aspect is the lower stability of the phosphonium ion in comparison to the ammonium ion [9].

As already indicated, in the case of the methyl pyridinium group, a slightly different mechanism of the S_n2 reaction takes place [12]. This is due to the presence of quaternary nitrogen as a part of the aromatic ring. In such a case, the degradation product is not ionically active. Unfortunately, the degradation of the functional groups was faster compared to the trimethybenzylammonium groups and thus a rapid decrease in the IEC value over time was observed.

The slow decrease in IEC observed in the case of trimethylbenzylammonium corresponds to the S_n2

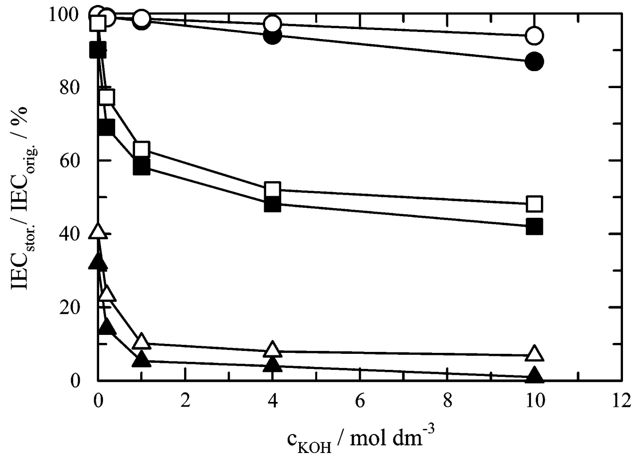

Fig. 4 Decrease in IEC in different concentrations of potassium hydroxide after 7-day storage; sample with: *open circle* trimethylbenzylammonium, *open square* methypyridinium, and *open triangle* tributhylbenzylfosfonium functional groups; temperature: *empty symbols* 50 °C, *full symbols* 70 °C

degradation reaction yielding benzyldimethylamin as the main product. Benzyldimethylamine belongs to the weakly basic groups, still showing the ability of ion exchange. The reason for the relatively slow kinetics of the degradation reaction lies in the strong basicity of the functional group in combination with the structure of the elimination product.

Due to these results, all subsequent electrochemical and morphological characterizations were carried out with membranes based on the trimethylbenzylammonium groups fixed on the polystyrene-*co*-divinylbenzene.

3.2 Morphology

The functionality of the membrane is closely related to its structure determined not only by the ion-selective particles but also by the properties of the polymeric binder. All membranes compared here comprised 66 wt% of anion-selective particles selected in the previous chapter and 34 wt% of a binder polymer. Highly flexible linear polyethylene, low-density polyethylene with a small amount of branching in the chain, a mixture of linear polyethylene and poly(ethylene-*co*-vinyl alcohol) and poly(ethylene-*co*-methacrylic acid) were used as polymer binders. The last two mentioned polymer binders were tested with a view to improve the electrochemical properties of the resulting membrane by introducing –OH^- or –COOH groups to the polymer binder.

SEM of the membrane cross sections are shown in Fig. 5a–d. The ethylene-*co*-methacrylic acid polymer binder (Fig. 5a) manifested extremely good compatibility with the anion-selective particles, resulting in the complete encapsulation of the ion-selective resin particles by the non-conducting polymer binder. This arrangement prevents the formation of interconnection channels between the individual functionalized particles. Consequently, the resulting material is typically non-conductive and shows practically no IEC.

With linear polyethylene (Fig. 5b), the mixture of linear polyethylene and poly(ethylene-*co*-vinyl alcohol) (Fig. 5c) and low-density polyethylene (Fig. 5d), the situation is different. All polymers allow direct contact among the anion-selective particles. From the pictures of cross sections of the dried membranes, it is difficult to predict the behavior of the individual materials, but a closer look reveals that linear polyethylene binder displays less adhesion to the particles of the ion-selective resin, thus promoting their interconnection, including the channels between the particles filled by the liquid. For the remaining two materials, no evident differences are visible in the SEM pictures.

Another important aspect of heterogeneous membrane materials having a strong impact on their electrochemical properties is the polymer skin layer covering their surface. This is a result of the production procedure based on compression molding of the membrane from a mixture of melted matrix polymer and ion-selective resin particles. The composition of the skin layer is generally different from that of the membrane core [22–24]. It typically consists exclusively of a polymer binder. The skin layer is already well apparent in the SEM pictures of the cross section of the membranes, with the exception of the ethylene-*co*-methacrylic acid matrix where the complete encapsulation of anion-selective particles by the polymer binder does not permit the clear identification of the membrane skin. In the case of linear polyethylene, a thin layer of binder polymer randomly penetrated by anion-selective particles can be discerned. A similar structure was observed for linear polyethylene + poly(ethylene-*co*-vinyl alcohol). With low-density polyethylene, the skin layer seems to be thin but compact with almost no penetration by functionalized resin particles.

More detailed information is revealed in Fig. 6, which shows the surfaces of the membranes with three different binder polymers. Among the materials presented, only the membrane based on a linear polyethylene matrix shows a significant number of cracks and ruptures of the skin layer, see Fig. 6a. Thus, it is clear that this material alone provides a sufficient number of ion conduction pathways to the ion-selective phase in the membrane bulk. From this point of view, the remaining materials offer only limited possibilities. It is to be expected that this will have a negative impact on the electrochemical properties of the membrane. The membrane based on an ethylene-*co*-methacrylic acid matrix is not presented here, because in this particular case no skin defects at all are observed (see the previous two paragraphs).

3.3 Ion-exchange capacity of the membrane

As already mentioned, due to the method used for determination of IEC it may be concluded that it corresponds

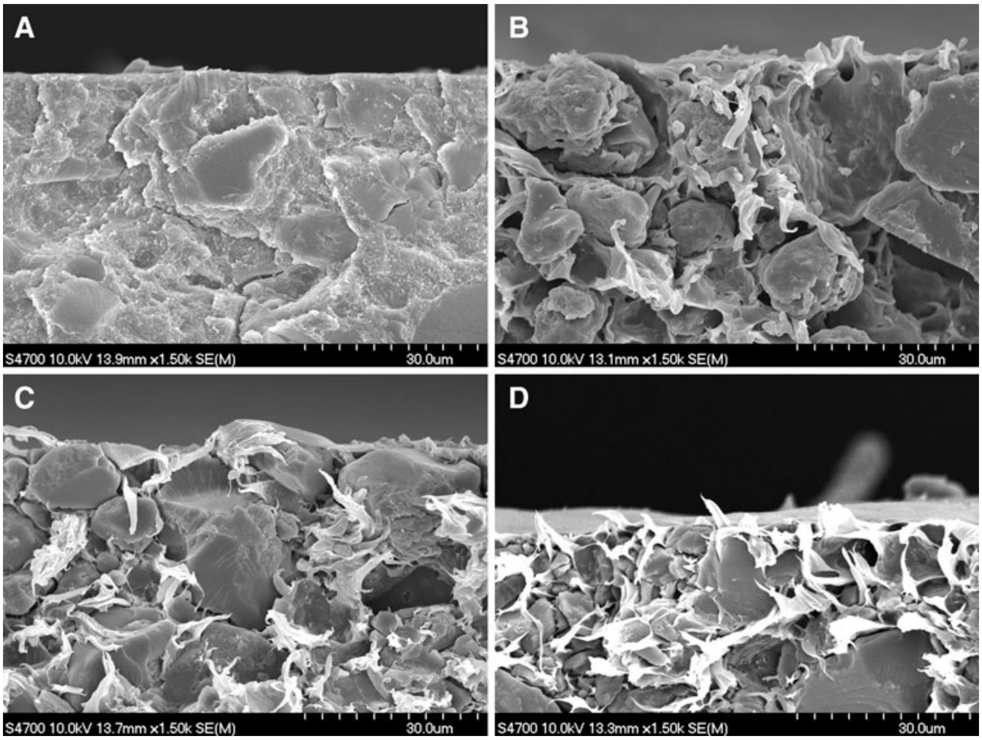

Fig. 5 SEM images of the cross section of the membrane. Polymer binder used: **a** ethylene-*co*-methacrylic acid, **b** linear polyethylene, **c** linear polyethylene + poly(ethylene-*co*-vinyl alcohol), and **d** low-density polyethylene

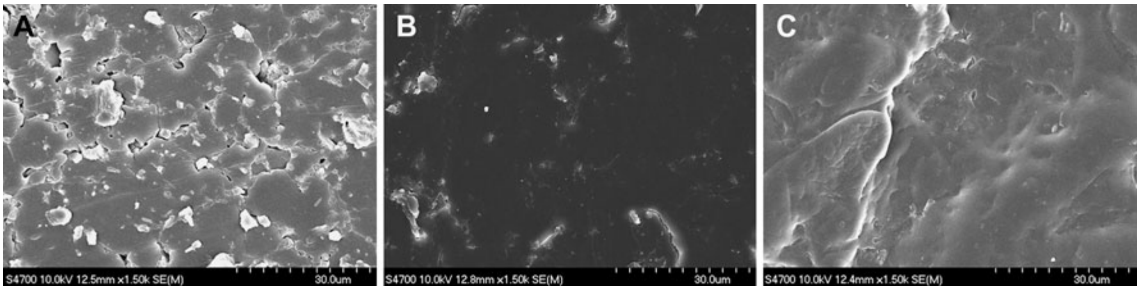

Fig. 6 SEM images of the surface skin layer of the membranes tested. Polymer binder used: **a** linear polyethylene, **b** linear polyethylene + poly(ethylene-*co*-vinyl alcohol), and **c** low-density polyethylene

more exactly to the *apparent* capacity of the membrane. This corresponds to the fact that only the OH^- ions exchanged by the membrane sample are determined. This value is directly relevant to the potential application of the membrane in the process of AWE, because this process is based on the transport of the OH^- ions across the membrane. Other ions do not directly contribute to the process. Therefore, it is the *apparent* capacity of the membrane that is the information of interest. The results of these experiments are summarized in Fig. 7.

The highest IEC value was obtained for the membrane with a linear polyethylene polymer matrix which attained a value of 1.6 mmol $g_{\mathrm{dry\ memb}}^{-1}$. This value is comparable [25] or even higher than IEC of the membranes reported in literature [15, 25, 26]. The second highest value of IEC was determined for the membrane whose matrix consisted of a mixture of linear polyethylene and poly(ethylene-*co*-vinyl alcohol). In this case, the IEC value was determined as 0.82 mmol $g_{\mathrm{dry\ memb}}^{-1}$. This membrane was followed by the sample with a low-density polyethylene polymer binder (0.69 mmol $g_{\mathrm{dry\ memb}}^{-1}$). In the case of the ethylene-*co*-methacrylic acid polymer matrix, a very low IEC (0.03 mmol $g_{\mathrm{dry\ memb}}^{-1}$) was determined.

These results are in agreement with expectations based on membrane morphology. The membrane with an ethylene-*co*-methacrylic acid polymer binder showed no

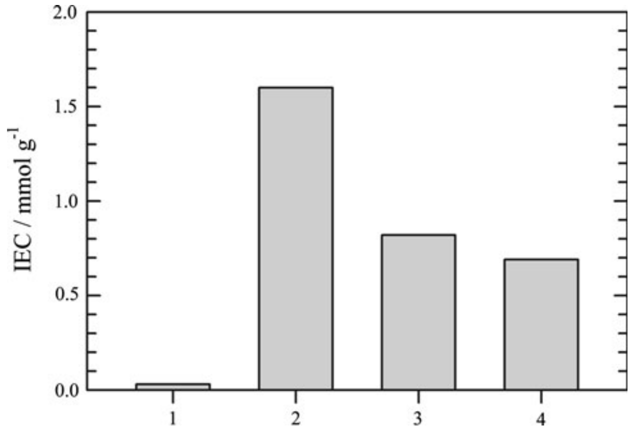

Fig. 7 Values for the ion-exchange capacity of the membrane containing 66 wt% of polymer resin containing trimethylbenzylammonium functional groups bonded in 34 wt% of: (1) ethylene-*co*-methacrylic acid, (2) linear polyethylene, (3) linear polyethylene + poly(ethylene-*co*-vinyl alcohol), and (4) low-density polyethylene polymer matrix

percolation of particles of the ion-selective resin and thus did not manifest any ion exchange with the surroundings. Additionally, the perfect encapsulation of the ion-selective particles by the matrix polymer did not allow their swelling and thus any dissociation of the functional groups.

In the case of the linear polyethylene matrix, good contact between the ion-selective particles was observed, including formation of the channels filled with the water solution. Moreover, the skin layer structure showed the most defects of the materials studied. As a consequence, good particle swelling as well as OH^- ion displacement can take place. This produced the highest IEC of the membranes studied.

In the case of the two remaining polymer binders, i.e., the mixture of linear polyethylene and poly(ethylene-*co*-vinyl alcohol) and low-density polyethylene, the IEC of the membrane is significantly reduced. The reason is the compact skin layer limiting membrane swelling as well as the exchange of ions between the membrane and the surroundings. Additionally, the structure of the membrane offers less conduction pathways, as discussed previously.

3.4 Ionic conductivity

The dependence of ionic conductivity on the temperature of the membranes based on the three different polymer binders is illustrated in Fig. 8. Since membrane based on the ethylene-*co*-methacrylic acid polymer binder did not show any conductivity, it is not included in this figure. It is obvious that results follow a similar trend to that of the IEC of the membrane. Thus, a similar explanation for the behavior observed also applies in this particular case.

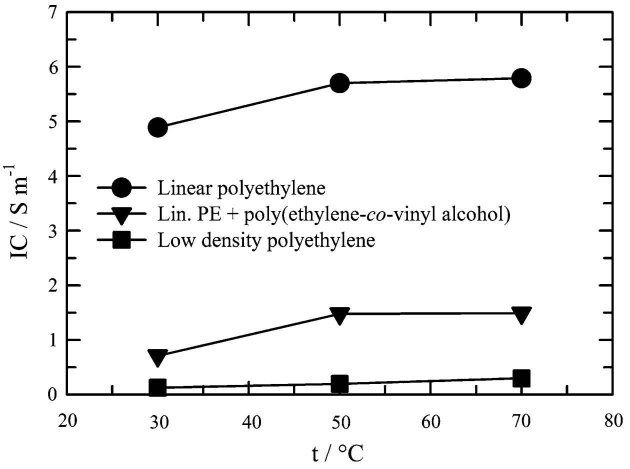

Fig. 8 Dependence of ionic conductivity on temperature for three different polymer binders tested. The polymer binders are indicated in the *inset*

It mainly concerns the membrane based on the ethylene-*co*-methacrylic acid polymer binder, where no conductivity was determined.

The highest conductivity was observed for the membrane based on a linear polyethylene polymer binder. The lowest conductivity was found for the membrane based on low-density polyethylene; the membrane based on a mixture of linear polyethylene and poly(ethylene-*co*-vinyl alcohol) polymer matrix displays a conductivity value falling within the boundaries delimited by the remaining two materials. So far this dependence follows the trends indicated by the IEC values. One interesting aspect is that the conductivity difference is significantly more important than the difference in the apparent IEC of the membrane. The reason is that, in contrast to the IEC representing the equilibrium value, the conductivity of the membrane is connected with the kinetics of ion transfer. The higher the number of defects in the skin layers together with the higher the occurrence of channels in the interior of the membrane based on the linear polyethylene matrix, the faster the kinetics of the ion transport.

In the case of linear polyethylene and mixture of the linear polyethylene with poly(ethylene-*co*-vinyl alcohol) polymer binders, a temperature increase up to 50 °C resulted in the anticipated enhancement of the ionic conductivity. In the case of the membrane with a low-density polyethylene polymer matrix, the ionic conductivity increase was insignificant. A further temperature increase up to 70 °C did not induce any significant conductivity increase in any of the membrane samples studied. The reason for this behavior is clearly on the one hand the decreasing viscosity of the pore fluid flow and thus increasing mobility of the ions in the membrane. Another explanation lies in the mechanical properties of the membrane. With increasing temperature, the mechanical

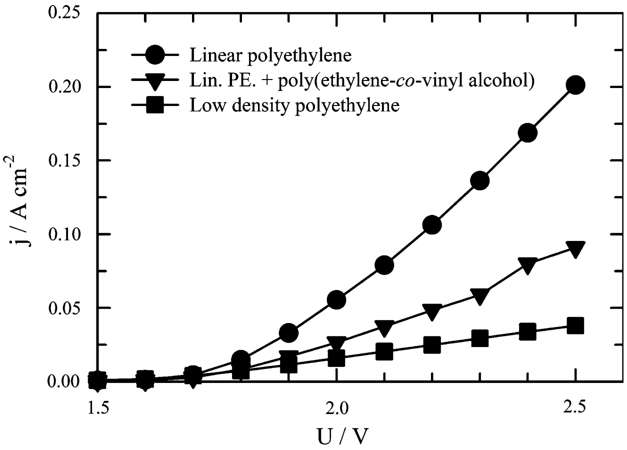

Fig. 9 Dependence of the current density measured on cell voltage. Measurement was made at laboratory temperature with Ni foam used as both anode and cathode (geometrical area of 4 cm^2) in 10 wt% of KOH solution. The polymer binders are indicated in the *inset*

strength of the two polymer components decreases and thus allows augmented membrane swelling positively contributing to its conductivity. Excessive swelling is, however, prevented by the cross-linked polymer backbone of the ion-selective resin.

IC values of anion selective heterogeneous membrane prepared within the framework of this study are higher or comparable with the IC of the homogeneous membranes reported in literature [15, 18, 25, 26].

3.5 Alkaline water electrolysis

Final testing of the prepared membranes was performed under conditions of AWE in a laboratory cell. Figure 9 documents the dependence of the current density attained on the cell voltage. In all cases, the current density values are significantly lower than the working current densities used in industrial electrolyzers units which typically achieve 0.2 A cm^{-2} at a cell voltage of 1.9 V [27]. It is, however, important to bear in mind the fact that industrial cells are operated with a KOH solution of a concentration up to three times higher and at temperatures of 80 °C [27]. It is, therefore, clear that improved electrolyte conductivity together with electrode reaction kinetics results in enhanced cell performance. However, the aim of this experiment was to compare the newly prepared membranes from the point of view of their performance.

Figure 9 reveals that the best result was achieved for the membrane with linear polyethylene used as a binder polymer, followed by the mixture of linear polyethylene and poly(ethylene-*co*-vinyl alcohol). The lowest current density values were achieved for the membrane whose polymer matrix consisted of low-density polyethylene. These results correspond to the results of the conductivity experiments. The explanation is once again the membrane morphology, as discussed in previous chapters. No functional groups degradation was indicated for the experimental conditions used within this study by determining membrane sample IEC prior and after electrolysis test. This is in agreement with the literature data [9, 12] reporting for these particular functional groups temperature stability limit at approx. 80 °C.

4 Conclusion

The stability of three types of anion-selective functional groups was tested. A decrease was observed with an increasing concentration of potassium hydroxide in aqueous solution and with increasing temperature. The trimethybenzylammonium group was found to be the most stable of those tested. This is due to the absence of β-hydrogen in the chain and to the general superior stability of nitrogen functional groups compared to phosphorous or sulphurous groups. This type of ion-selective resin manifests acceptable stability up to a temperature of 70 °C even at high potassium hydroxide concentrations.

The heterogeneous membrane morphology and electrochemical properties were proven to be strongly interconnected. This confirms the important role of the polymer binder. Linear polyethylene was found to provide a membrane with the best transport properties. This is due to the good interconnection of the ion-selective resin particles. Additionally, this material provides a skin layer covering surfaces of the membrane with a relatively high number of defects, providing ion-conducting pathways. The performance of the membranes in a laboratory cell confirmed the results of the previous experiments.

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