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Alkali doped poly (2,5-benzimidazole) membrane for alkaline water electrolysis: Characterization and performance

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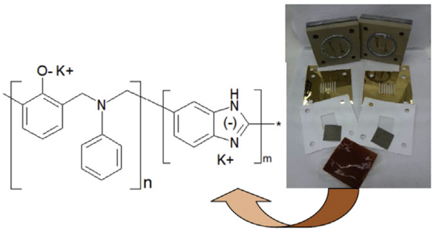
HIGHLIGHTS

- Linear and cross-linked KOH doped ABPBI membranes were prepared.
- Specific ionic conductivity at 22 °C was in the range between 7 and 25 $mS \cdot cm^{-1}$.
- Short term measurements show comparable performance with commercial Zirfon$^{(R)}$ diaphragm.
- Cross-linked ABPBI membrane shows better performance than linear one.

GRAPHICAL ABSTRACT



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ABSTRACT

The properties and performance of linear and cross-linked KOH doped ABPBI membranes as electrolyte/separator for zero gap alkaline water electrolysis cells are evaluated and compared with a commercial Zirfon® diaphragm. Stability in alkaline environment, swelling, thermal properties, water sorption, KOH uptake and conductivity of linear (L-ABPBI) and cross-linked (C-ABPBI) membranes doped with different concentrations of KOH are analyzed. Linear membranes show stability up to 3.0 $mol \cdot dm^{-3}$ KOH doping, while cross-linked membranes are stable up to 4.2 $mol \cdot dm^{-3}$ KOH doping. Both kinds of membranes exhibit good thermal stability and reasonable specific ionic conductivity at 22 °C in the range between 7 and 25 $mS \cdot cm^{-1}$, being slightly higher the conductivity of C-ABPBI membranes than that of L-ABPBI ones. In short-term electrolysis tests both L-ABPBI and C-ABPBI membranes show better performance than Zirfon diaphragm in the range from 50 to 70 °C. A current density of 335 $mA \cdot cm^{-2}$ at a cell voltage of 2.0 V is attained with C-ABPBI membranes doped in 3 $mol \cdot dm^{-3}$ KOH at 70 °C, a performance comparable with that of commercial units operating at temperatures ca. 80 °C and 30 wt% KOH (6.7 $mol \cdot dm^{-3}$) as electrolyte.

1. Introduction

Water electrolysis is an environmental friendly process for hydrogen production when electricity is generated from renewable sources. The technologies developed or under development include conventional liquid alkaline water electrolysis (LAWE), high-temperature steam electrolysis, proton exchange membrane and anion exchange membrane water electrolysis (PEMWE and AEMWE respectively). Among these, AEMWE and LAWE are the

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most inexpensive alternatives, owing to the fact that relatively cheap non-precious metals are employed as electrodes [1,2].

AEMWE employing a hydroxide conducting polymer membrane electrolyte/separator, with electrodes deposited directly onto the membrane surfaces (as the membrane electrode assembly, MEA, in fuel cell technology [3]), represents a highly promising approach, as it reduce the total ohmic resistance of the system. However, robust and mature LAWE technology is the current state of the art particularly in large-scale applications, while emerging technologies are tested and try to obtain wide acceptance as candidates to replace it. LAWE usually employ massive nickel-based two-dimensional electrodes, a porous diaphragm as electrode compartment separator, and a highly concentrated KOH solution, typically 6–7 $mol \cdot dm^{-3}$ as electrolyte, being the high concentration necessary to reduce the ohmic drop of the cell. Conventional industrial electrolyzers work at current densities comprised between 200 and 400 $mA \cdot cm^{-2}$ -with cell voltage between 1.7 and 2.2 V- this means electrical energy consumption between 4.2 and 5.2 $kWh \cdot Nm^{-3}$ of H_2, and voltage efficiency between 57 and 71%, corresponding to a theoretical electrical energy consumption of 2.95 $kWh \cdot Nm^{-3}$ of H_2.

In the last decade, a polysulfone matrix with ZrO_2 as inorganic filler [4], known as Zirfon®, has been successfully employed in free asbestos diaphragms for LAWE. More recently, new materials were studied, like tape casting manufactured membranes or screen printing films composed by inorganic fillers and organic binders in polyphenylene sulfide (PPS) felts [5]. A significant improvement is expected if a zero gap configuration is employed, in which the diaphragm is replaced by an anion exchange membrane (AEM) attached to the electrodes, as a first step towards a cell structure where electrocatalysts are deposited directly onto the membrane surfaces. The main challenge of this alternative is the lack of an anion selective membrane having satisfactory electrochemical properties, along with sufficient chemical stability under the strongly alkaline environment and elevated temperature employed.

Anion exchange membranes (AEMs) have been extensively studied as ionomer electrolyte in fuel cells, being classified in three categories according to Merle *et al.* [6]: heterogeneous membranes, interpenetrating polymer networks and homogeneous membranes, based on functional groups with fixed charges. The first ones are formed by a polymer matrix (based in an anion solvating polymer) and an aqueous alkaline hydroxide, typically potassium hydroxide. The combination of both materials maintains the mechanical properties of the polymer and the electrochemical properties and ionic conductivity of the hydroxide solution.

The first anion solvating polymers, discovered more than thirty years ago, were based on polyethylene oxide (PEO). However, PEO tends to crystallize, resulting in a depletion of the ionic conductivity [6].

Homogeneous membranes based in quaternary ammonium groups as fixed charges were extensively used in AEMs [7–9] exhibiting high thermal and chemical stability. Nevertheless, the ammonium group may undergo degradation due to the OH^- anions via direct nucleophilic displacement and/or Hofmann elimination [10], causing the conversion of the groups into tertiary or secondary amines, or even promoting the group's entire separation, reducing significantly the ion-exchange capacity and consequently the ionic conductivity of the AEM.

Among the anion solvating polymer membranes, those based on alkali doped PBI poly [2,2′-(*m*-phenylene)-5,5’-bibenzimidazole] and PBI modified structures, such as ABPBI poly (2,5-benzimidazole), seem to be a promissory alternative. PBI and ABPBI are characterized by their high oxidative and thermal stability, along with good mechanical properties. PBI and ABPBI membranes are neutral, but become acceptable proton conductors when doped with acids, mainly with H_3PO_4 (PA). For this reason, they were extensively evaluated as candidates for PEM fuel cells, particularly high temperature PEM fuel cells (HT-PEMFC) and direct methanol PEM fuel cells (DMPEMFC) [11]. Recently, PBI membranes doped in 2–3 $mol \cdot dm^{-3}$ KOH aqueous solutions, exhibiting ionic conductivities (IC) in the range between 0.005 $S \cdot cm^{-1}$ and 0.02 $S \cdot cm^{-1}$ at 25 °C, were proposed by Xing and Savadogo for alkaline fuel cells [12]. Moreover, alkali doped PBI membranes for alkaline direct methanol and ethanol fuel cell were proposed by other authors [13,14], though their stability was not evaluated by aging tests or long term measurements. More recently, cross-linked PBI membranes prepared for LAWE devices presented ionic conductivities of 0.09 and 0.06 $S \cdot cm^{-1}$ at room temperatures [15]. Cross-linked PBI membranes showed no ionic conductivity loss after 176 days of aging tests performed by immersion in 6 $mol \cdot dm^{-3}$ KOH aqueous solution at 85 °C, while linear PBI membranes became fragile when exposed to the same conditions. So far, the use of cross-linked polymer structures have long been known to improve the mechanical and chemical stabilities of PBI and ABPBI membranes, allowing to obtain a proton conductivity enhancement via the increase of acid doping concentrations that would cause detrimental effects in long term stability of linear PBI/ABPBI ones [16].

Kim et al. reported a method to prepare cross-linked co-polymeric membranes based on polybenzimidazole and benzoxazine (BZ) [17,18] showing high proton conductivity and long term durability for use in PEMFC at temperatures higher than 100 °C. Keeping in mind that ABPBI is advantageous over PBI in terms of its synthesis, because it can be polymerized from a single monomer, it seems interesting to study KOH doped linear and cross-linked ABPBI membranes, as candidates for alkaline water electrolysis systems. We assume that the preparation of C-ABPBI membranes employing Kim *et al.* method can be advantageous, because the co-polymerization proceeds through the reaction between the open ring of benzoxazine and the benzene ring of benzimidazole without affecting the imidazole groups engaged in KOH doping.

The aim of this work is to characterize the thermal and chemical stability, KOH and water uptake, and ionic conductivity of linear ABPBI (L-ABPBI) and cross-linked ABPBI (C-ABPBI) membranes doped with aqueous KOH, and to test them as candidates for application in the zero gap configuration of a LAWE process, and comparing their performance with a commercial Zirfon® diaphragm.

2. Experimental

2.1. Materials

ABPBI polymer, whose chemical structure is shown in Fig. 1, was prepared by condensation of 3,4-diaminobenzoic acid (DABA) monomer in polyphosphoric acid (PPA) following the procedure reported elsewhere [19]. The polymer obtained was neutralized with aqueous NaOH, and washed with water using a Soxhlet

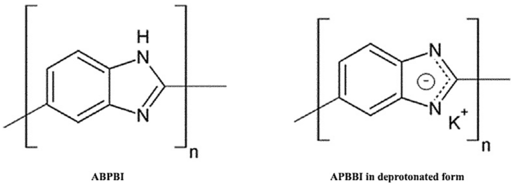

Fig. 1. Chemical structure of the ABPBI polymer.

apparatus. Finally, it was dried at 180 °C for 10 h and finely milled.

The molecular weight of ABPBI was determined from viscosity measurements of its solutions in 96 wt% H_2SO_4, using a Cannon – Fenske 150 viscosimeter. The value of the extrapolated intrinsic viscosity at 30 °C was 2.11 $dl \cdot g^{-1}$ and, resorting to the Mark–Houwink equation [20], the averaged molecular weight of the polymer was 17 040 $g \cdot mol^{-1}$. The degree of polymerization (DP) of the prepared ABPBI was approximately 210.

The BZ preparation was based on the procedure described by Kim *et al.* [17] to prepare cross-linked PBI (C-PBI), which allowed us to obtain linear benzoxazine chains in the co-polymer by blocking the para-position of the benzene ring. The method employed by Kim *et al.* was modified by the use of p-cresol as phenol derivative instead of 4-tert-butylphenol. Briefly, BZ monomer was obtained, as it is schematized in Fig. 2a, by mixing the 1:2:1 *M* ratio of p-cresol, paraformaldehyde and aniline, respectively. In a 100 mL round bottom flask, paraformaldehyde and aniline were mixed at 60 °C. Then, p-cresol was added to the mixture and the temperature was raised to 100 °C. After 60 min, the mixture was cooled and kept at 5 °C until further use.

3,4-diaminobenzoic acid, 97 wt% and polyphosphoric acid, 85 wt% (Aldrich), H_2SO_4, 96 wt% (Baker Analyzed), NaOH, KOH, ethanol, p-cresol, paraformaldehyde and aniline (Merck) all analytical grade, were used as received. Water was deionized and passed through a Millipore filter.

2.2. Membrane preparation

L-ABPBI membranes were casted from a solution of ABPBI polymer in ethanol/NaOH solvent, according to a procedure previously reported [21], followed by a heating step at 180 °C for 24 h and finally washed with water using a Soxhlet apparatus.

C-ABPBI membranes were prepared, as schematically showed in Fig. 2b, by mixing ethanol solutions of BZ monomer and ethanol/NaOH solutions of ABPBI, with a BZ:ABPBI weight ratio 35:65. After membrane formation, the benzoxazine polymerization and cross-linking process was induced by thermal treatment at 180 °C for 10 h. The high temperature promotes the oxazine ring opening and further reaction between the methylene group and benzene ring of benzoxazine monomer (oligomerization or polymerization) or ABPBI polymer (crosslinking). Finally, the cross-linked membranes were washed with water using a Soxhlet apparatus. The membrane thickness lied in the range from 90 to 120 μm, and was measured by means of a Mahr XL1-57B-15 dead load gauge. Prior to their use, linear and cross-linked ABPBI membranes were alkali doped by immersion in KOH aqueous solutions at room temperature during seven days.

2.3. Stability in alkaline environment, swelling and thermal properties

Stability of the ABPBI membranes in an alkaline environment was evaluated after immersion of membrane samples during 7 days in 50 mL aqueous KOH solutions with different concentrations, 1.9–4.2 $mol \cdot dm^{-3}$, at room temperature and at 70 °C.

The membrane swelling was calculated based in the measured thickness, length and width before and after doping of the dry membrane.

Thermal properties of the ABPBI samples were investigated by means of thermogravimetry analysis (TGA). A Setsys Evolution equipment (Setaram, France) was used, and the measurement was performed under air at a flow rate of 20 $cm^3 \cdot min^{-1}$, with a Pt vessel as sample holder. The temperature range was varied between 20 and 900 °C, with a heating rate of 10 $K \cdot min^{-1}$. In order to investigate the nature of the volatile products generated, the TGA chamber was connected to a mass spectrometer Omnistar™ (Pfeiffer Vakuum, Germany) by means of a stainless steel capillary tube.

2.4. KOH doping level and water sorption

The water and KOH content of the membranes were determined using the method described by Aili *et al.* [15]. After 7 days of immersion in pure water and KOH solutions of concentrations up to 5.5 $mol \cdot dm^{-3}$, the surface of membrane samples were carefully wiped off with tissue paper and weighted to obtain the wet weight of the sample (w_s). Then, they were dried at 120 °C for 16 h in vacuum and weighted again to get the weight of membrane plus KOH (w_d). The water content (w_w) was determined as $w_w = w_s - w_d$.

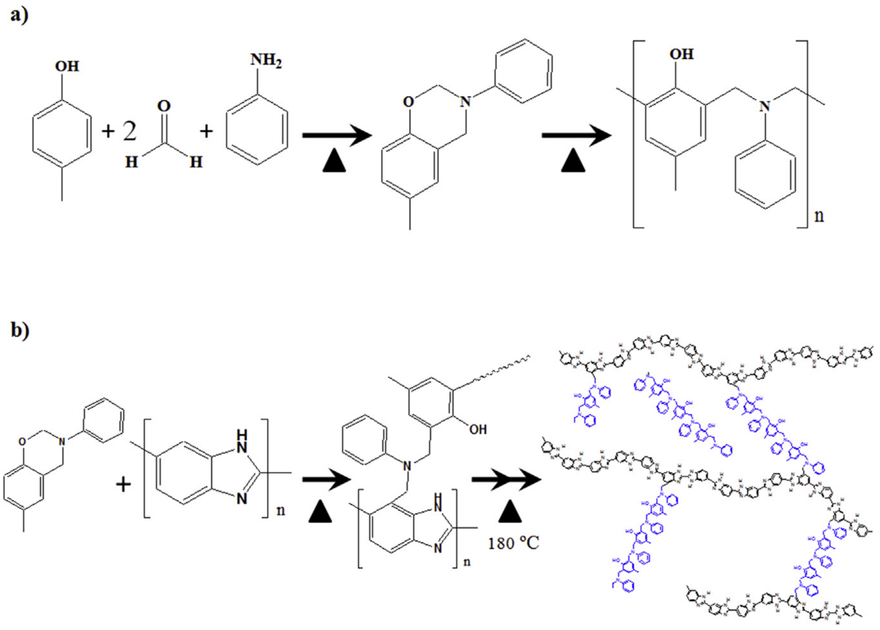

Fig. 2. a) Benzoxazine monomer synthesis reaction. b) Preparation of C-ABPBI membranes.

Later, the samples were washed with water using a Soxhlet apparatus to eliminate the KOH and weighted after being dried for 8 h at 120 °C in vacuum to determine the dry weight (w_0). The KOH, or alkali content (w_a) was obtained as $w_a = w_d - w_0$. The mass percentage of ABPBI, water and KOH were subsequently calculated on the wet weight of the membrane basis. Alternatively, the water and KOH uptake was expressed as the weight of water and KOH (in grams) uptake by gram of dry polymer, $m_w = w_w/w_0$ and $m_a = w_a/w_0$ respectively.

2.5. Ionic conductivity

The specific ionic conductivities (σ) of the ABPBI membranes were determined in a two electrode arrangement cell, using a LCR bridge Hameg HM 8118 (Germany) with a perturbing signal of maximal amplitude 50 mV at 500 Hz. The disk-shaped membrane sample was taken out of the equilibrating solution of KOH, and the excess of KOH solution was carefully removed from the surface with tissue paper. The membrane was then sandwiched between two plastic blocks with channels of 5 mm in diameter, filled with mercury. Mercury plays a multiple role in this arrangement: it prevents any contact of the membrane sample with the atmosphere so, the membrane sample remains in equilibrium with the solution used for its doping; it provides very good electrical contact and, owing to the high overvoltage of the hydrogen evolution reaction, which is about 0.8 V for mercury, successfully eliminates any water splitting reaction and hence prevents any electrochemical reaction to occur in measurable extend. Two platinum wires immersed in the mercury electrodes served as electric signal feeders. The specific ionic conductivity was calculated as:

$$\sigma = \frac{\delta}{RA} \tag{1}$$

where δ is the thickness of the membrane, measured by means of a Mahr XL1-57B-15 dead load gauge, R is the experimentally determined ohmic resistance of the membrane, by considering a constant resistance value at the fixed frequency selected and A represents the active surface area of the sample (0.1963 cm^2).

2.6. Alkaline water electrolysis

A zero gap configuration single cell water electrolyzer, schematized in Fig. 3a, was used to test the ABPBI membranes and Zirfon® diaphragm performance under LAWE conditions. Two Ni foam electrodes with geometric area 3.61 cm^2 were attached directly to the ABPBI membrane surfaces. When the Zirfon separator was tested, two Teflon separators where added in order to set a 1 mm gap between the Ni foam electrodes and the Zirfon diaphragm. An active electrode geometric surface area of 4.40 cm^2 was attained in this arrangement. Gold plated Ni sheets were used as current feeders as well as electrolyte distributors. The cell was inserted in a system, schematized in Fig. 3b. KOH solution was recirculated from a reservoir tank by a MasterFlex peristaltic pump equipped with dual head. Alkaline water electrolysis at short term was performed by using a cell voltage range from 1.5 to 2.0 V. Operational temperatures of 50 °C and 70 °C were used.

3. Results and discussion

3.1. Chemical stability, swelling, and thermal properties

L-ABPBI membranes doped in KOH solutions with concentrations higher than 3.0 $mol\cdot dm^{-3}$ became fragile and unhandable, while C-ABPBI membranes exhibited the same behavior at KOH concentration higher than 4.2 $mol\cdot dm^{-3}$.

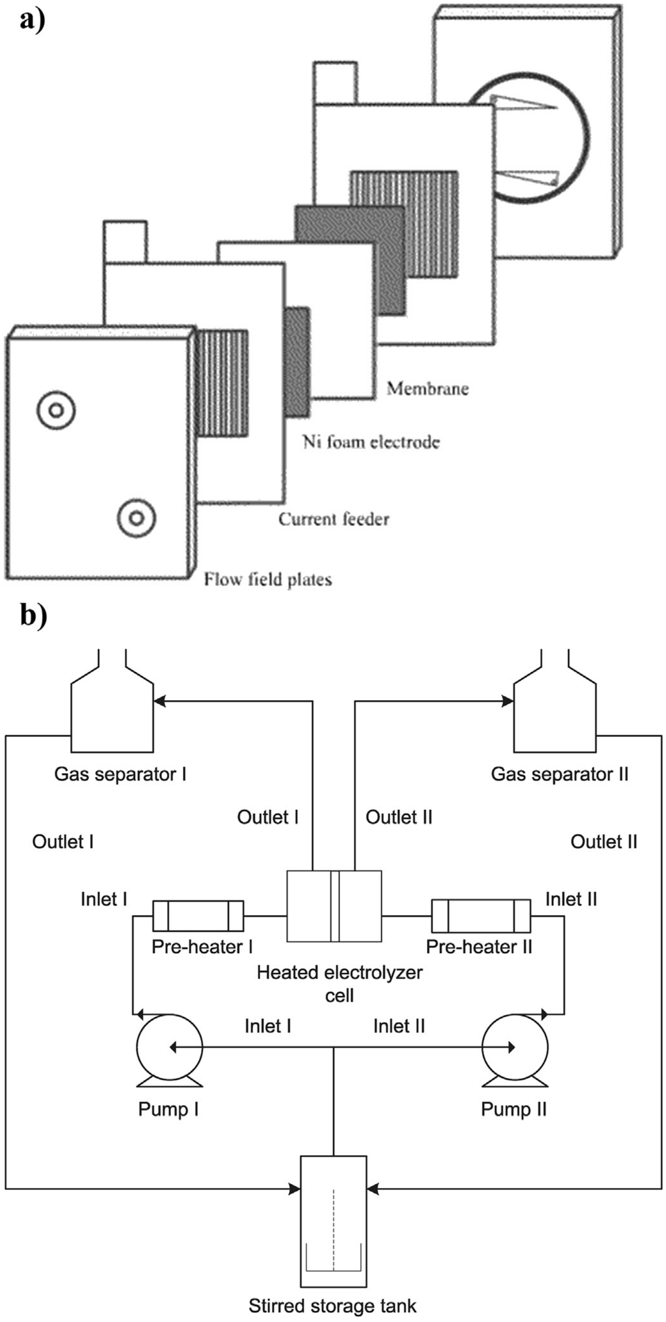

Fig. 3. a) Scheme of the alkaline water electrolysis cell consisting on Ni foam electrodes attached to the membrane surface, current feeders and flow feed plates. b) Scheme of the laboratory alkaline water electrolyzer setup.

The properties of KOH doped membranes (otherwise specified) were measured only in the range of KOH concentrations in which ABPBI membranes were stable, this means, between 1.9 and 3.0 $mol\cdot dm^{-3}$ for L-ABPBI, and between 1.9 and 4.2 $mol\cdot dm^{-3}$ for C-ABPBI.

Table 1 shows the swelling results in L-ABPBI and C-ABPBI membranes after 7 days of immersion in KOH solutions.

It can be seen that there is no difference between the swelling behavior of L-ABPBI and C-ABPBI in the concentration range between 1.9 and 3.0 $mol\cdot dm^{-3}$ KOH. The swelling in both type of membranes doped in 3.0 $mol\cdot dm^{-3}$ KOH is not higher than that of

Table 1
Swelling behavior of KOH doped linear and cross-linked ABPBI membranes.

	L-ABPBI			C-ABPBI		
c_{KOH} mol·dm^{-3}	Volume swelling/%	Thickness swelling/%	Length swelling/%	Volume swelling/%	Thickness swelling/%	Length swelling/%
1.9	50	10	17	50	10	17
3.0	50	10	17	50	10	17
4.2	Fragile			58	10	20

membranes doped in 1.9 mol·dm^{-3} KOH. Moreover, the length of C-ABPBI membranes doped in 4.2 mol·dm^{-3} KOH are comparable with the same membranes doped in 3.0 mol·dm^{-3} KOH. Aili *et al.* [15] published data on the swelling of linear PBI obtaining a 64% volume increase, comparable with the values obtained in this work for L-ABPBI and C-ABPBI. The length and thickness grow are moderate in both L-ABPBI and C-ABPBI membranes. This is a positive characteristic, taking into account that an excessive or uneven swelling could have a negative impact in the mechanical stability.

Fig. 4a shows the thermograms and derivative thermogravimetry curves (DTG) of L-ABPBI and C-ABPBI membranes doped in 3.0 mol·dm^{-3} KOH in air flow. The thermogram profiles of both membranes show loss of weight at two temperature ranges. At low temperature they have a similar behavior presenting a DTG peak below 100 °C. At high temperature, C-ABPBI membrane shows an earlier mass loss than the L-ABPBI one. In the DTG profile the onset peak for C-ABPBI membrane is observed at 300 °C, 100 °C lower than for the L-ABPBI one. In order to understand the process experimented by the membranes, an evolved gas analysis by mass spectrometry (MS) was performed during the TG measurements. Fig. 4b and c shows the normalized mass signal corresponding to *m*/*z*: 18 (H_2O) and *m*/*z*: 44 (CO_2), respectively, attributed to desorption and decomposition processes from/of the membrane. According to this, the DTG peaks close to 100 °C would correspond to the elimination of water sorbed from the membrane and the peaks at temperatures higher than 300 °C -related with CO_2 and H_2O evolution mass signal- could be attributed mainly to thermal decomposition of the membrane. Although C-ABPBI suffers thermal degradation at lower temperature than L-ABPBI, it is worth mentioning that both membranes show degradation process far from operation temperature.

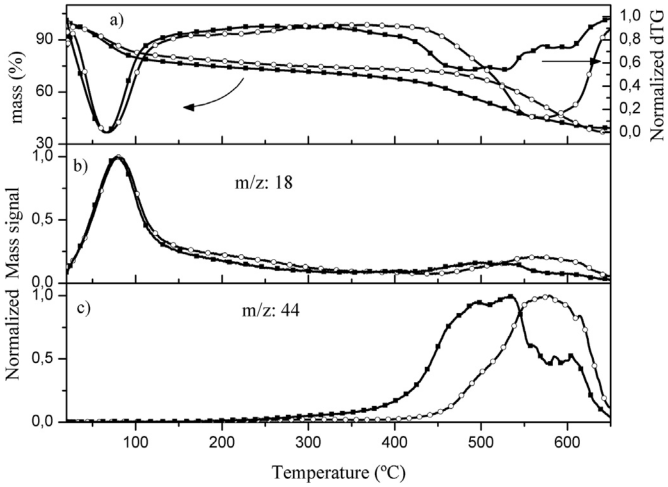

Fig. 4. a) Thermograms and its normalized derivatives DTG, b) *m*/*z*: 18, c) *m*/*z*: 44 normalized mass signal profiles for (-○-) L-ABPBI and (-■-) C-ABPBI in air flow.

3.2. Water sorption and KOH doping level

Table 2 shows water and KOH sorption in L-ABPBI and C-ABPBI membranes as a function of the KOH concentration used for doping. Table 2 also summarizes the swelling measurements.

The water content of un-doped L-ABPBI membrane is 21.5 wt% ($m_w = 0.27$). There are no reported values of water sorption in un-doped L-ABPBI membranes to compare with, and our results are higher than that measured by Aili *et al.* [15] in un-doped linear PBI (15 wt % water sorption). This difference is probably due to the hydrophobic nature of the phenyl ring in the PBI repeating unit, being this phenyl ring not present in the ABPBI molecule [22].

The water content of un-doped C-ABPBI membranes is 14.3 wt% ($m_w = 0.17$), in coincidence with Wannek *et al.* who measured 1.0 water molecules per polymer repeating unit ($m_w = 0.16$), in pristine cross-linked ABPBI (Fumatech) [23]. The decrement of water uptake in C-ABPBI membranes compared with L-ABPBI ones is probably due to the cross-linked nature of C-ABPBI and additionally to the presence of a hydrophobic benzene ring in the benzoxazine cross linker repeating unit.

In both types of membranes, the water content increases with the concentration of doping solution. The water uptake is moderate, between 33.8 wt% and 51.0 wt%, in membranes doped in the range of 1.9–4.0 mol·dm^{-3} KOH (m_w between 0.68 and 2.31), being lower in C-ABPBI membranes than in L-ABPBI ones. This is a positive issue, because water is needed to assure ion transport, but an excessive water uptake generally comes up with a loss of mechanical properties when the membranes become overhydrated.

Table 2, show the increase of the KOH membrane content with the concentration of the doping solution. As it can be seen in Table 2, the KOH uptake expressed as m_a of L-ABPBI doped in the range 1.9 M–4.2 M KOH lies between 0.34 and 1.22, being this values higher than that reported for L-PBI for membranes doped in the same range (m_a between 0.1 and 0.3) [15]. The same behavior was observed in PA doped membranes: higher PA content was found in L-ABPBI membranes compared with L-PBI ones doped in the same PA concentration [24].

The values reported by Luo *et al.* for L-ABPBI [25], are between 0.9 and 1.1 KOH moles per polymeric repeating unit (m_a between 0.4 and 0.5), inside the range of our results. The KOH uptake values for C-ABPBI are slightly higher than that of L-ABPBI membranes at the same doped concentration. Nevertheless, the differences are not significant, showing that the alkali content is apparently independent of ABPBI membrane type, in agreement with the tendency observed for alkali doped L-PBI and C-PBI membranes [15]. The same behavior is reported by Kim *et al.* in PA doped membranes: the PA content grows slightly in C-PBI membranes prepared with BZ cross-linker compared with L-PBI ones doped in the same PA solution [17].

3.3. Ionic conductivity (IC)

The dependence of ionic conductivity of L-ABPBI and C-ABPBI on KOH concentration in the doping solution, at 22 °C, are shown in Table 3; in which conductivity data from literature were also

Table 2
Sorption of KOH/water and swelling of KOH doped linear and cross-linked ABPBI membranes.

	L-ABPBI						C-ABPBI					
c_{KOH} mol·dm^{-3}	H_2O wt.%	KOH wt.%	Pol. wt.%	m_w	m_a	Vol. sw.%	H_2O wt.%	KOH wt.%	Pol. wt.%	m_w	m_a	Vol. sw.%
0	21.5	0.0	78.5	0.27	0.0	–	14.3	0.0	85.7	0.17	0.0	–
1.9	37.8	15.9	46.3	0.82	0.34	50	33.8	16.8	49.4	0.68	0.34	50
3.0	48.4	20.7	30.9	1.57	0.67	50	44.1	22.1	33.8	1.30	0.65	50
4.2	51.0	26.9	22.1	2.31	1.22	Fragile	43.1	26.6	30.3	1.42	0.88	58

Table 3
Conductivity and calculated KOH content inside doped linear and cross-linked ABPBI membranes at 22 °C. Conductivity data from literature for KOH doped linear and cross-lined PBI membranes at room temperature are also included.

	L-ABPBI		C-ABPBI		L-PBI [15]	L-PBI [15]	C-PBI [15]
c_{KOH} mol·dm^{-3}	$c^m{}_{KOH}$ mol·dm^{-3}	σ/S·cm^{-1}	$c^m{}_{KOH}$ mol·dm^{-3}	σ/S·cm^{-1}	σ/S·cm^{-1}		
0							
1.9	6.6	0.007 ± 0.001	7.5	0.008 ± 0.001	<0.005		
3.0	6.7	0.017 ± 0.001	7.5	0.018 ± 0.001	0.02		
4.2	7.8	Fragile	8.7	0.025 ± 0.001	0.04		
6.0		Fragile		Fragile	0.09	0.09[a]	0.06[a]

[a] Temperature 80 °C.

included. As it can be seen, the membranes studied exhibit ionic conductivities in the range from 0.007 S·cm^{-1} to 0.025 S·cm^{-1}, being slightly higher in C-ABPBI than in L-ABPBI ones. The measured ICs are similar to that measured in L-PBI by Xing and Savadogo [12], who obtain the highest value in membranes doped in 6 M KOH. Aili *et al.* [15] showed IC values higher than ours, but measured at 80 °C and 6 M KOH doping solution. Taking into account that in anion solvating polymers ionic conductivity is strongly related with the hydroxide salt concentration [6], it would be interesting to relate our ICs results with the KOH concentration inside the membrane after its doping in KOH solutions. In order to make this analysis, we calculate the KOH concentrations inside the membranes ($c^m{}_{KOH}$) from the water and KOH uptake showed in Table 2, and results were included in Table 3.

The calculated KOH concentrations inside the membranes lie between 6.6 and 8.7 mol·dm^{-3} KOH, being slightly higher in C-ABPBI membranes than in L-ABPBI ones, suggesting that a direct correlation between the ionic conductivity and the hydroxide salt concentration exists.

In order to further understand the conductivity behavior of KOH-ABPBI membranes, the specific ionic conductivity was corrected by the free space inside the membrane. The hypothesis is that the anion transport mechanism is the same as in an aqueous KOH solution with a volume equal to the free volume inside the membrane, i.e. the membrane volume less the volume occupied by the polymer itself (estimated as the inverse of its density).

According to this assumption, we define a relative IC (σ_r) as:

$$\sigma_r = \sigma \cdot V \tag{2}$$

$$V = V_w/(V_w + V_0) \tag{3}$$

where V is the fraction of volume occupied by the KOH solution, V_w is the volume of water (in cm^3) sorbed per gram of dry polymer and V_0 is the inverse of the ABPBI density ($\rho_{ABPBI} = 1.5$ g·cm^{-3}) [22].

The IC dependence of L-ABPBI and C-ABPBI for the calculated KOH concentration inside the membranes is shown in Fig. 5, along with the relative IC calculated with (2) and based in reported data of aqueous KOH solutions at 25 °C [26].

As can be seen in Fig. 5, the measured IC values are very far from the relative conductivities of KOH aqueous solution, showing that the assumption that the conductivity mechanism inside the membrane is similar to that of a KOH aqueous solution is not valid, being probably influenced by the physicochemical interactions between the KOH and the polymer.

Aili *et al.* [15], based in fundamental acid-base chemistry calculations, point out that, when polybenzimidazole polymers are doped in a strong aqueous base like KOH, they deprotonate to form a potassium polymeric salt as illustrated in Fig. 1. According to this, at KOH concentration higher than 0.6 mol·dm^{-3} inside the membrane, ABPBI is almost completely in the potassium salt form, formed by combination between K$^+$ ions and –NH– moieties in the ABPBI matrix, according to the reaction:

$$-NH- + K^+ + OH^- = -NK- + H_2O \tag{4}$$

In the case of C-ABPBI membranes, the benzoxazine molecule has a –OH moiety, that can also form a K salt at KOH concentrations even lower than 0.6 mol dm^{-3} inside the membrane, taking into

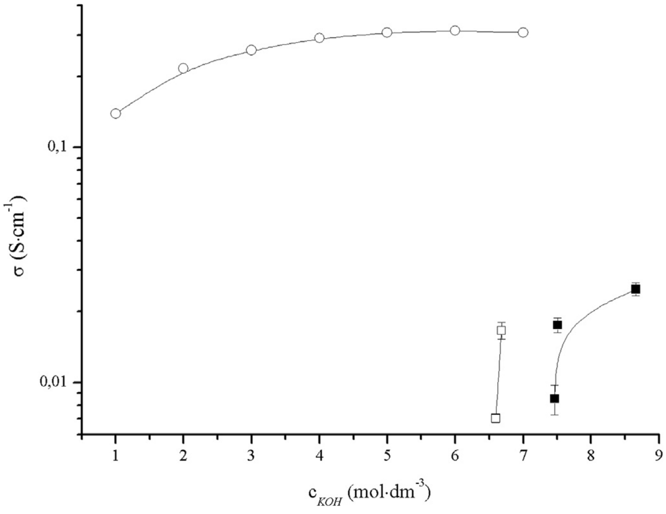

Fig. 5. Dependence of ionic conductivity of (□) L-ABPBI and (■) C-ABPBI vs. KOH concentration inside the membrane, at 22 °C. (○) Dependence of the relative ionic conductivity of KOH aqueous solutions at 25 °C with the concentration of the KOH aqueous solution [26].

account that phenol has *pKa* = 10.

Once the –NH- and –OH moieties are in the deprotonated form, forming the corresponding potassium salts, K^+ and OH^- inside the membrane either remain as free ions, or OH^- forms a hydrogen bond with –N= in the polybezimidazole backbone (as postulated by Hou *et al.* [27]) or with N atoms of benzoxazine in C-ABPBI copolymer, with K^+ as counter ion.

It is known that the ion transport mechanism in AEM involves mainly Grotthuss (the hydroxide is transported along a chain of water molecules through H bonds) and, next to Grotthuss, diffusion is supposed to be important [6]. Obviously, K^+ ions are not involved in Grotthuss mechanism, but they are involved in diffusion transport. According to this, at very low KOH concentrations in doping solution, only K^+ ions contribute to conductivity, and as a result the conductivity is very low, as it was observed by Aili *et al.* in L-PBI membranes [15]. The IC increases considerably after doping in higher KOH concentrations, owing to the increment of OH^- concentration inside the membrane. Nevertheless, we consider that at the doping grade range studied in this work the conductivity is mainly due to the presence of free OH^- ions inside the membrane, and this explain the linearity of the dependence of IC vs. KOH concentration in doping solution.

The interaction between benzoxazine and KOH could explain that KOH sorption of C-ABPBI membranes is higher than that of L-ABPBI ones, doped at the some KOH concentration.

3.4. Alkaline water electrolysis

In order to explore the feasibility of ABPBI/KOH membranes under conditions of LAWE, they were tested in a laboratory single-cell electrolyzer with a zero gap configuration, fed with KOH aqueous solutions in the range from 1.9 to 3.0 mol·dm^{-3}. The electrolysis load curves obtained for L-ABPBI and C-ABPBI membranes compared with those for Zirfon for the two KOH concentrations and two temperatures are shown in the Figs. 6 and 7.

The results show that the performance of both L-ABPBI and C-ABPBI membranes doped with KOH is comparable to the commercial Zirfon membrane in LAWE. Comparing L-ABPBI and C-ABPBI membranes no significant differences in load curves was observed. This is partially in agreement with the observations from section 3.3. The IC seems to be dependent with the concentration of KOH inside the membrane rather with the material *per se*. Therefore, the IC value can fluctuate slightly under the dynamic conditions of the alkaline water electrolysis, affecting thus the shape of the load curve. Compared to other LAWE devices reported in literature, such as that of Aili *et al.* [15] that obtained current densities of 150 mA·cm^{-2} for L-PBI and 200 mA·cm^{-2} for C-PBI membranes at a cell voltage of 2 V, our results are similar or even higher, despite the fact that lower KOH concentrations and lower temperatures were used.

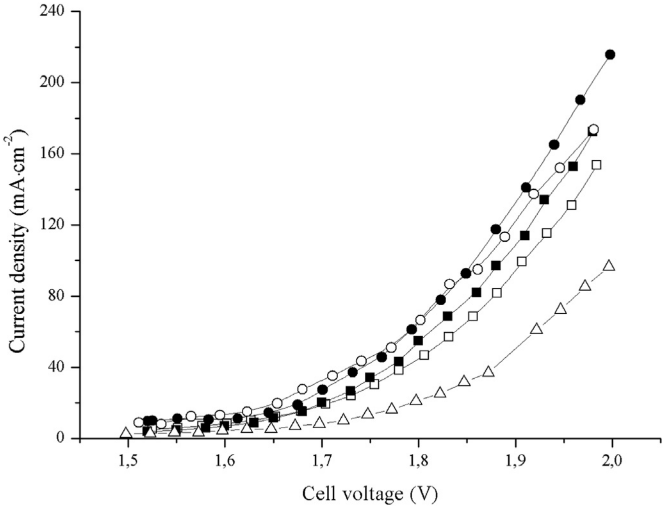

Fig. 6. LAWE load curves for ABPBI membranes and Zirfon diaphragm in 1.9 mol·dm^{-3} KOH, at two different temperatures: (□) L-ABPBI at 50 °C; (■) C-ABPBI at 50 °C; (○) L-ABPBI at 70 °C; (●) C-ABPBI at 70 °C and (△) Zirfon at 50 °C.

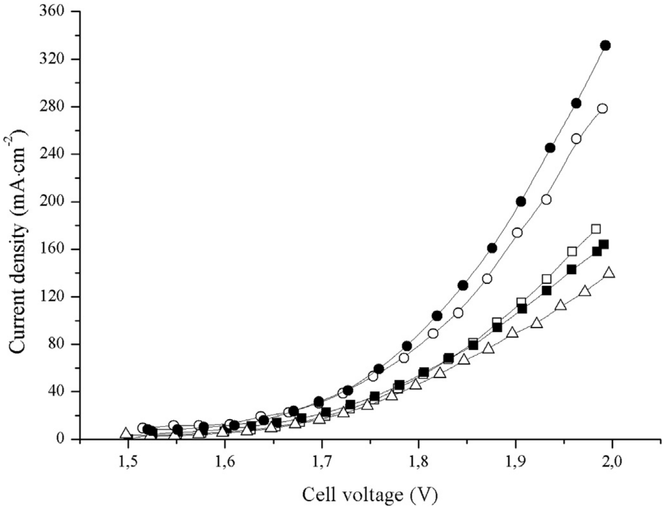

Fig. 7. LAWE load curves for ABPBI membranes and Zirfon diaphragm in 3.0 mol·dm^{-3} KOH at concentrations, at two different temperatures: (□) L-ABPBI at 50 °C; (■) C-ABPBI at 50 °C; (○) L-ABPBI at 70 °C; (●) C-ABPBI at 70 °C and (△) Zirfon at 50 °C.

The performance of the electrolyzer using the C-ABPBI operating at 3.0 mol•dm^{-3} KOH membrane at 70 °C is comparable or exceeds that of the industrial LAWE units, as can be seen in Table 4. Up to date, the higher performances reported for an electrolyzer are the ones developed by Hydrogenics, providing a current density of 375 mA·cm^{-2} at a cell voltage of 1.74 V. In the case of IHT and Oronzio de Nora the performance is comparable with our results obtained with C-ABPBI membrane at 70 °C. On the other end of the spectra, reported data of electrolyzer developed by Uralkhimmash indicate a current density of 200 mA·cm^{-2} at a cell voltage of 2.3 V [28,29]. However, it should be pointed out that these industrial units employ electrolyte solutions containing typically 30 wt% KOH (6.7 mol·dm^{-3}) at temperatures of 80–90 °C. It is well known that both of these parameters have positive effect on the performance of the alkaline water electrolysis, which was also observed for ABPBI membranes (Fig. 7). Further improvement can be expected in a zero gap LAWE system if high performance electrocatalysts were employed, like Ni based alloy or mesoporous Ni electrodeposited over Ni substrates in the cathode side or spinel coatings as electrocatalysts in the anode side, in spite of the massive Ni electrodes used in this work. These observations thus represent the possibility of further improvement of the LAWE performance.

The calculated electrical energy consumption was 4.8 kWh·Nm^{-3} of H_2, with voltage efficiency of 62%, corresponding to a theoretical electrical energy consumption of 2.95 kWh·Nm^{-3} of H_2. These values and that of some commercial LAWE units were included in Table 4.

The fact that the performance of the LAWE with ABPBI membranes was comparable with industrial units under milder conditions could have a strong impact in terms of cost, easy operation and less material corrosion. Moreover, operating the electrolysis cell at lower KOH concentrations is a major advantage with respect

Table 4
Performance of laboratory electrolysis cell tested with different anion exchange membranes. Performance of industrial LAWE is also reported [28].

Electrolyzer	Membrane	c_{KOH} mol·dm^{-3}	T/°C	Cell voltage/V	Current density/mA·cm^{-2}	Energy requirement/Kwh· N m^{-3}	Effs./%
This work	Zirfon®	1.9	50	2.0	100	4.8	62
This work	L-ABPBI	1.9	50	2.0	155	4.8	62
This work	C-ABPBI	1.9	50	2.0	180	4.8	62
This work	L-ABPBI	1.9	70	2.0	180	4.8	62
This work	C-ABPBI	1.9	70	2.0	220	4.8	62
This work	Zirfon®	3.0	50	2.0	140	4.8	62
This work	L-ABPBI	3.0	50	2.0	180	4.8	62
This work	C-ABPBI	3.0	50	2.0	160	4.8	62
This work	L-ABPBI	3.0	70	2.0	280	4.8	62
This work	C-ABPBI	3.0	70	2.0	335	4.8	62
Hydrogenics [28,29]		6.7	80–90	1.74	375	4.2	71
Oronzio de Nora [28,29]		6.7	80–90	1.75	150	4.2	70
IHT [28,29]		6.7	80–90	1.9	200	4.5	65
Teletype [28,29]		6.7	80–90	2.16	300	5.2	57
Uralkhimmash [28,29]		6.7	80–90	2.3	200	5.5	54

to the long-term stability of the membrane, taking into account that Aili *et al.* [30] observed that L-PBI is stable up to 200 days in aqueous 5 wt% KOH at 88 °C, but it degrades by hydrolysis at higher KOH concentrations.

Hence, this allows enhancing the flexibility and safety of the system, i.e. vital parameters when thinking in utilizing an electrolyzer as a part of distributed energy provided from renewable sources.

4. Conclusions

KOH-doped linear and cross-linked ABPBI membranes were prepared which are stable in KOH concentrations up to 3.0 and 4.2 mol·dm^{-3} respectively.

Both L-ABPBI and C-ABPBI showed a similar, moderate and even swelling behavior, and good thermo-oxidative stability, with an onset decomposition temperature around 300–400 °C.

The water content of the membrane was enough to assure anion transport, without being excessive as to have a negative effect in the mechanical properties due to an excessive swelling.

Conductivity was slightly higher in C-ABPBI membranes compared with L-ABPBI ones, in accordance with the tendency observed in the KOH concentration inside both kinds of membranes, calculated from sorption data.

Short-term performance for both, L-ABPBI and C-ABPBI, is better than that of a commercial Zirfon diaphragm at the conditions evaluated. The best performance was attained by C-ABPBI operating at 3.0 mol·dm^{-3} KOH at 70 °C, being comparable to that of industrial units, that typically operate at concentrations of 6–7 mol·dm^{-3} KOH and 80–90 °C.

Being able to operate electrolysis cells at lower KOH concentrations is a major advantage with respect to the long-term stability of the membrane material.

In this study the membrane durability issue has not been addressed. Further work is in progress in order to study the degradation behavior of KOH-doped ABPBI membranes under LAWE conditions.

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References

[1] M. Wang, Z. Wang, X. Gong, Z. Guo, The intensification technologies to water electrolysis for hydrogen production: A review, Renew. Sustain. Energy Rev. 29 (2014) 573–588.
[2] K. Zeng, D. Zhang, Recent progress in alkaline water electrolysis for hydrogen production and applications, Prog. Energy Combust. Sci. 36 (2010) 307–326.
[3] D. Pletcher, X. Li, Prospects for alkaline zero gap water electrolysers for hydrogen production, Int. J. Hydrogen Energy 36 (2011) 15089–15104.
[4] P.H. Vermeiren, W. Adriansens, J.P. Moreels, R. Leysen, Evaluation of the Zirfon® separator for use in alkaline water electrolysis and Ni-H_2 batteries, Int. J. Hydrogen Energy 23 (1998) 321–324.
[5] U.F. Vogt, M. Gorbar, M. Schlupp, G. Kaup, A. Bonk, A. Hermosilla, A. Züttel, Membranes development for alkaline water electrolysis, in: 4th European PEFC & H2 Forum, 2013 (Luzern, Switzerland).
[6] G. Merle, M. Wessling, K. Nijmeier, Anion exchange membrane for fuel cells: A review, J. Membr. Sci. 377 (2011) 1–35.
[7] G. Abuin, P. Nonjola, E. Franceschini, F. Izraelevitch, M. Mathe, H. Corti, Characterization of an anionic-exchange membranes for direct methanol alkaline fuel cells, Int. J. Hydrogen Energy 35 (2010) 5849–5854.
[8] J. Hnát, M. Paidar, J. Schauer, J. Zitka, K. Bouzek, Polymer anion selective membranes for electrolytic splitting of water. Part I: stability of ion-exchange groups and impact of the polymer binder, J. Appl. Electrochem 41 (2011) 1043–1052.
[9] J. Hnát, M. Paidar, J. Schauer, J. Zitka, K. Bouzek, Polymer anion-selective membranes for electrolytic splitting of water. Part II: Enhancement of ionic conductivity and performance under conditions of alkaline water electrolysis, J. Appl. Electrochem 42 (2012) 545–554.
[10] Klaus-Dieter Kreuer (Ed.), Fuel Cells: Selected Entries from the Encyclopedia of Sustainability Science and Technology, 2013.
[11] L.A. Diaz, G.C. Abuin, H.R. Corti, Methanol sorption and permeability in Nafion and acid-doped PBI and ABPBI membranes, J. Membr. Sci. 411–412 (2012) 35–44.
[12] B. Xing, O. Savadogo, Hydrogen/oxygen polymer electrolyte membrane fuel cells (PEMFCs) based on alkaline-doped polybenzimidazole (PBI), Electrochem. Commun. 2 (2000) 697–702.
[13] H. Hou, G. Sun, R. He, Z. Wu, B. Sun, Alkali doped polybenzimidazole membrane for high performance alkaline direct ethanol fuel cell, J. Power Sources 182 (2008) 95–99.
[14] A.D. Modestov, M.R. Tarasevich, A. Leykin, V. Filimonov, MEA for alkaline direct ethanol fuel cell with alkali doped PBI membrane and non-platinum electrodes, J. Power Sources 188 (2009) 502–506.
[15] D. Aili, M.K. Hansen, R.F. Renzaho, Q. Li, E. Christensen, J.O. Jensen, N.J. Bjerrum, Heterogeneous anion conducting membranes based on linear and cross-linked KOH doped polybenzimidazole for alkaline water electrolysis, J. Membr. Sci. 447 (2013) 424–432.
[16] S.-K. Kim, T.-H. Kim, T. Ko, J.-C. Lee, Cross-linked poly (2,5-benzimidazole) consisting of wholly aromatic groups for high-temperature PEM fuel cell applications, J. Membr. Sci. 373 (2011) 80–88.
[17] S.-K. Kim, S.-W. Choi, W.S. Jeon, J.O. Park, T. Ko, H. Chang, J. Lee, Cross-linked benzoxazine–benzimidazole copolymer electrolyte membranes for fuel cells at elevated temperature, Macromolecules 45 (2012) 1438–1446.
[18] S.-K. Kim, T. Ko, S.-W. Choi, J.O. Park, K.-H. Kim, C. Pak, H. Chang, J.-C. Lee, Durable cross-linked copolymer membranes based on poly (benzoxazine) and poly (2,5 -benzimidazole) for use in fuel cells at elevated temperature, J. Mater. Chem. 22 (2012) 7194–7205.
[19] J.A. Asensio, S. Borrós, P. Gómez-Romero, Proton-conducting polymers based on benzimidazoles and sulfonated benzimidazoles, J. Polym. Sci. A Polym. Chem. 40 (2002) 3703–3710.
[20] J.A. Asensio, S. Borrós, P. Gómez-Romero, Polymer electrolyte fuel cells based on phosphoric acid-impregnated poly(2,5-benzimidazole) membranes,

J. Electrochem. Soc. 151 (2004) A304–A310.

[21] F.A. Viva, M.M. Bruno, H.R. Corti, L.A. Diaz, M.A. Lozano, Método de preparación de membrana polimérica de intercambio de protones, INPI-ARG: P 2011-01-02615 (20/07/2011).

[22] S. Li, J.R. Fried, J. Colebrook, J. Burkhardt, Molecular simulations of neat, hydrated, and phosphoric acid-doped polybenzimidazoles. Part 1: Poly (2,2′-m-phenylene-5,50-bibenzimidazole) (PBI), poly(2,5-benzimidazole) (ABPBI), and poly(p-phenylene benzobisimidazole) (PBDI), Polymer 51 (2010) 5640–5648.

[23] C. Wannek, W. Lehnert, J. Mergel, Membrane electrode assemblies for high-temperature polymer electrolyte fuel cells based on poly(2,5-benzimidazole) membranes with phosphoric acid impregnation via the catalyst layers, J. Power Sources 192 (2009) 258–266.

[24] L.A. Diaz, G.A. Abuin, H.R. Corti, Water and phosphoric acid uptake of poly[2,5-benzimidazole] (ABPBI) membranes prepared by low and high temperature casting, J. Power Sources 188 (2009) 45–50.

[25] H. Luo, G. Vaivars, B. Agboola, S. Mu, M. Mathe, Anion exchange membrane based on alkali doped poly (2,5-benzimidazole) for fuel cell, Solid State Ion. 208 (2012) 52–55.

[26] X. Zhu, H. Yang, Y. Cao, X. Ai, Preparation and electrochemical characterization of the alkaline polymer gel electrolyte polymerized from acrylic acid and KOH solution, Electrochim. Acta 49 (2004) 2533–2539.

[27] H. Hou, S. Wang, Q. Jiang, W. Jin, L. Jiang, G. Sun, Durability study of KOH doped polybenzimidazole membrane for air-breathing alkaline direct ethanol fuel cell, J. Power Sources 196 (2011) 3244–3248.

[28] J.O. Jensen, S.H Jensen, N. Tophøj, Pre-investigation of water electrolysis, PSO-F&U 2006-1–6287, Draft 04-02-2008.

[29] L. Bertuccioli, A. Chan, D. Hart, F. Lehner, B. Madden, E. Standen, Study on Development of Water Electrolysis in the EU, Energy Ltd for the Fuel Cells and Hydrogen Joint Undertaking, February 2014.

[30] D. Aili, K. Jankova, Q. Li, N. Bjerrum, J.O. Jensen, The stability of poly(2,2′-(m-phenylene)-5,5’-bibenzimidazole) membranes in aqueous potassium hydroxide, J. Membr. Sci. 492 (2015) 422–429.