Spectroscopic Study of Reinforced Cross-Linked Polymeric Membranes for Fuel Cell Application

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ABSTRACT: Acid-doped reinforced polymer electrolyte membranes for high-temperature polymer electrolyte membrane fuel cell applications (HT PEMFCs) are presented and spectroscopically studied. Fully aromatic polyethers are employed bearing main chain pyridine units as the proton accepting sites, which have two different substitution patterns of the pyridine units, namely, 2,5- or 2,6-pyridine. This fact enables control of the solubility and of the acid doping ability of the polymeric membranes. Reinforcement is accomplished via incorporation of a PTFE woven fabric during the casting procedure for fabrication of the membranes. High acid uptake of the reinforced membranes was maintained for the 2,6-pyridine-based copolymers with high pyridine unit content. Studies of the swelling behavior of these reinforced membranes revealed that they expand mainly along the z-axis, which helps to avoid extensive damage in case of humidity or temperature changes during the fuel cell operation. Additionally, spectroscopic techniques are employed, namely, X-ray photoelectron spectroscopy, X-ray photoelectron spectroscopy with depth profile, near-edge X-ray absorption fine structure, and reflection electron energy loss spectroscopy, for the in-depth study of the two copolymer membranes doped with phosphoric acid. Through these spectroscopic evaluations, modifications in the membranes’ chemical structure, orientation, composition, and electronic structure after the reinforcement and doping processes were elaborated and unveiled.

1. INTRODUCTION

Environmentally friendly energy sources are of major scientific and societal demand for the sake of the world’s health, growth, and sustainability. Fuel cells are an integral part of the technological portfolio for the transition to a sustainable society, offering the potential to convert chemical energy to electricity more efficiently when compared to conventional engines and to reduce waste streams and emissions, with water and heat being the main by-products of their utilization. Within the fuel cell family, polymer electrolyte membrane fuel cells (PEMFCs) stand out due to their applicability in both portable and stationary applications, their versatile combination with heat utilization units, and furthermore the simplification of the supporting balance of plant systems.1 The operating temperature of the proton exchange membrane fuel cell system depends almost entirely on the ability of the electrolyte to endure high temperatures, hence focusing the research efforts on developing versatile and robust materials.2

To date, the most studied membrane for high-temperature PEM fuel cells is polybenzimidazole (PBI).3−6 Aromatic polyethers containing pyridine groups have emerged as promising alternatives to PBIs because of their inherent good thermal, mechanical, and oxidative stability and their ability to retain excellent properties after doping with phosphoric acid.7,8 One shortcoming that hinders the on–off switching and...
subsequently the long-term operation at high temperatures is the membrane contraction and expansion as the operation temperature and the relative humidity are changing. During the fuel cell operation at temperatures above 160 °C and due to the humidity changes, the membrane is dehydrated and the phosphoric acid is converted to pyrophosphoric acid.9,10 This causes contraction of the swelled membrane, pinhole and crack formation, and finally detrimental failure of the MEA (membrane electrode assembly).

One way to overcome such phenomena is to create membranes that are able to swell only in the z-axis with minimum or no dimensional changes along their x-y axes.11,12 Such reinforced membranes are developed in this work in order to control and reduce their swelling after doping. By using reinforced membranes, we increase durability, avoiding the expansion and contraction of the phosphoric acid doped membranes in the x-y plane, which subsequently should enhance the long-term performance of the fuel cell system.

The membranes developed in this work include two fully aromatic polyester sulfone copolymers13,14 having different pyridine unit substitution patterns along the polymeric backbones and different pyridine contents. Their PTFE reinforced analogues have been doped with phosphoric acid and were examined in terms of their acid doping level and their swelling behavior. The doped and the reinforced doped membranes have been extensively analyzed using in-depth spectroscopic techniques. X-ray photoelectron spectroscopy (XPS), X-ray photoelectron spectroscopy with depth profile, near-edge X-ray absorption fine structure (NEXAFS), and reflection electron energy loss spectroscopy (REELS) are applied to further investigate modifications in the membranes’ structure, orientation, composition, and electronic structure after the reinforcement and doping processes.

2. RESULTS AND DISCUSSION

2.1. Reinforced Membranes. Two sets of polymer electrolytes are studied in this work in order to understand the differences in the acid doping ability of polymer electrolytes having diphenyl-pyridine units with different structural characteristics (2,5- versus 2,6-connectivity) and in order to explore the possibility to ultimately stabilize the doped membranes using both the PTFE-based reinforcement net and side double bond cross-linking. In the first case, a linear polymer with the structure of LP is used, shown in Figure 1a, which contains the 2,5-diphenyl-pyridine in 60 mol % in order to maintain the solubility of the material while preserving a sufficiently high Tg value. Higher pyridine contents are not effective for this type of polymer due to insolvency problems.15 In order to overcome this bottleneck of low solubility at higher 2,5-diphenyl-pyridine contents of copolymer LP,15 we employed another type of aromatic copolymer, the CP having 2,6-diphenyl-pyridine moieties, that enable higher pyridine content and at the same time higher solubility. Furthermore, this type of CP copolymer can be combined with cross-linkable side double bonds in Figure 1b. As shown in Table 1, the 2,6-pyridine insertion along the main polymer backbone indeed leads to much higher doping levels than the LP type copolymers, but at the same time, plasticization of the doped membranes is observed. Therefore, the introduction of cross-linkable side double bonds was chosen as a pathway to avoid plasticization phenomena.13 The effect of cross-linking on the doping and swelling behavior of the phosphoric acid doped membranes has been studied previously, and different behaviors have been reported depending on the exact polymeric structure. The herein studied cross-linkable copolymer CP showed a reduced expansion during doping (entry DCP of Table 1) but not a zero expansion as anticipated. Thus, the CP membrane was reinforced (RDCP membranes) with the intention of reducing the swelling process after doping and, consequently, helping its long-term performance in the fuel cell at higher temperatures. During HT PEMFC operation, the membrane is dehydrated, converting the phosphoric acid into pyrophosphoric acid, which causes contraction of the membrane and unavoidably crack formation.

Table 1. Membrane Characteristics after the Doping or the Reinforcement-Doping Processes

| samplea | doping temperature (°C)/doping time (h) | DL (wt %)b | ΔTh%c | Δx%d or Δy%d |
|---------|-----------------------------------------|-------------|--------|-------------|
| LP      | 120/48                                  | 240         | 67     | 30          |
| DLP     | 80/72                                   | 50          | 20     | 0           |
| RDLP1   | 100/110                                 | 150         | 73     | 0           |
| RDLP2   | 100/110                                 | 150         | 73     | 0           |
| CP      | 80/12                                   | 250         | 25     | 20          |
| DCP     | 100/12                                  | 350         | 35     | 30          |
| RCP     | 100/110                                 | 250         | 70     | 0           |
| RDCP1   | 120/12                                  | 275         | 90     | 0           |
| RDCP2   | 100/110                                 | 200         | 60     | 0           |

aLP = linear polymer, DLP = doped linear polymer, RDLP = reinforced doped linear polymer, CP = cross-linkable copolymer, DCP = doped cross-linkable copolymer, RCP = reinforced cross-linkable polymer, RDCP = reinforced doped cross-linkable polymer, R(LP/CP) = reinforced blend of LP and CP. bDoping level wt %. cΔTh%: percentage change of thickness after doping. dΔx% or Δy%: percentage change of the x- or y-dimension, respectively.
In this direction, reinforcement can increase the durability and eliminate the expansion and contraction of the doped membranes.

For benchmarking, both types of copolymers, LP and CP, were used for the preparation of reinforced membranes as shown in Table 1. However, as mentioned in the Experimental Section (Section 4.3), the achieved doping levels of the LP reinforced membranes, namely, RDLCP, were insufficient to reach the required conductivity for the operation of a fuel cell. Thus, we focused our spectroscopic studies on the reinforced cross-linked membranes (RDCP).

For the reinforced membranes of copolymers RDCP, the doping procedure also results in the cross-linking of the side double bonds. More specifically, the cross-linking proceeds via a cationic-like polymerization in which the phosphoric acid acts as cationic initiator for the opening of the double bonds at high doping temperatures ranging from 80 to 120 °C. Further proof of the successful cross-linking of the reinforced and doped membranes RDCP arises from the insolvibility of the membranes in all organic solvents even after prolonged heating at elevated temperatures. In contrast, reinforced membranes of the LP type, after doping and undoping in boiling water, are almost fully soluble in solvents like DMAc, NMP, or DMF. A systematic investigation of the influence of the doping conditions on the cross-linking extent and the resulting solubility of the cross-linked membranes has been reported in our previous work. Thus, in the herein work, experimental conditions are refined to secure an extended cross-linking of the membranes during doping in H3PO4 85 wt %.

A study of the swelling behavior of all the membranes was performed, and the results in terms of the dimension changes after doping in H3PO4 85 wt % are presented in the two last columns of Table 1. The membranes obtained from the copolymers swell after doping showing a change in the x−y dimensions in the range of 20−50% as the acid uptake is increased at 200−270 wt %. The change in the out-of-plane z-axis is normally about 30%. However, when the reinforced membranes are doped, an almost stabilized situation is obtained in the in-plane dimensions (Figure 3), while the z-axis is increased by as much as 100% accommodating the excess of the acid that is filling the membrane as shown from the results in Table 1.

### 2.2. X-ray Photoelectron Spectroscopy (XPS) and Depth Profile Analysis.

High-resolution XPS spectra of C1s, N1s, F1s, and P2p core levels are shown in Figure 4 for LP, DLP, RCP, and RDCP1 samples. The S2p core level was also

![Figure 2](https://dx.doi.org/10.1021/acsomega.0c01039)

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### Table 2. Percentage of Alive Double Bonds of the Membranes before (RCP) and after Cross-Linking (RDCP1 and RDCP2)

| Membrane | area at 965 cm⁻¹/area at 1009 cm⁻¹ | alive DBs (%) | cross-linked DBs (%) | DBs alive in the total mass of the copolymer (%) | copolymer cross-linking degree (%) |
|----------|----------------------------------|--------------|---------------------|-----------------------------------------------|-----------------------------------|
| RCP      | 0.5280                           | 100          | 0                   | 30                                            | 0                                 |
| RDCP1    | 0.0741                           | 14.0         | 86.0                | 4.2                                           | 25.8                              |
| RDCP2    | 0.0575                           | 10.9         | 89.1                | 3.3                                           | 26.7                              |

summarizes the cross-linking percentage of the membranes after their doping in H3PO4 85% at 100 °C and at 120 °C as deduced from the analysis of the ATR peaks at 965 cm⁻¹ and at 1009 cm⁻¹, corresponding to the “alive” side double bonds and to the C−N bond of the pyridine groups along the polymer backbone, respectively (Figure 2).
investigated, but it showed no changes between the samples. The N1s spectra change considerably for both samples that were doped. Initially, the membrane in its pure state, LP, has three peaks alone, whereas DLP, the doped membrane, shows four peaks (Table 3). According to the literature, these four peaks are related to different protonation states of pyridine\textsuperscript{16,17} the more protonated the pyridine molecule becomes, the higher its binding energy, with the fourth peak assigned to the fully protonated pyridine. Its appearance and the higher percentage of the third and fourth peaks (Table 4) are expected results of the doping process, where the phosphoric acid reacts with the basic sites of nitrogen changing the shape of the spectrum.

The copolymer used for studying the reinforced cross-linkable membranes is based on the 2,6-disubstituted pyridine (CP, Figure 1b). For these copolymer-based reinforced membranes (RCP), the pyridines’ protonation tendency is enhanced since a shift to higher binding energies compared to LP is seen and a fourth peak already appears. After doping, for the RDCP1 sample, the first peak related to the pure pyridine is completely absent, while the fourth peak has the highest percentage of all samples. RCP membranes have higher pyridine contents in comparison to LP, which means that there was more pyridine available for protonation in the doping process, so changes were expected. It is also observed that the chemical shift was too significant when comparing the changes in both doped and nondoped membranes. This is an indication that the reinforcement has a positive effect on the acid doping of the membrane. It can be argued that the fluorine presence changes the system in a way that makes the nitrogen sites more accepting for protonation. This can be seen

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure4.png}
\caption{C1s, N1s, F1s, and P2p core level XPS spectra based on fluorine reinforcement and phosphoric acid doping. LP: the membrane without modification or doping. DLP: the doped linear membrane. RCP: the membrane with fluorine reinforcement. RDCP1: the reinforced and doped membrane.}
\end{figure}
Table 3. Binding Energies and Assignment of the XPS Peaks for the Analyzed Membranes

| element | peak | assignment | binding energy (eV) |
|---------|------|------------|--------------------|
| nitrogen | N₁ | pyridine | 398.4 |
|         | N₂ | weakly H-accepting pyridine | 400.0 |
|         | N₃ | strongly H-accepting pyridine | 401.0 |
|         | N₄ | pyridinium | 402.5 |
| carbon  | C₁ | phenyl and meta-carbons in pyridine/C=C | 284.4 |
|         | C₂ | ortho- and para-carbons in pyridine/C-S/sp³ carbon | 285.3 |
|         | C₃ | C−O−C/C=OH/C=NH | 286.1 |
|         | C₄ | carbonyl | 288.1 |
|         | C₅ | CH₂−CF₂/C=CF | 288.9 |
|         | C₆ | tetrafluoroethylene | 292.1 |
|         | C₇ | trifluoromethane | 293.2 |
|         | F₁ | CH₂−CF₂/C=CF | 688.3 |
|         | F₂ | tetrafluoroethylene | 689.0 |
|         | F₃ | trifluoromethane | 690.0 |
| phosphorus | P₁ | dihydrogen phosphate | 133.2 |

Table 4. Atomic Percentage (%) of the Peaks in the XPS Spectra of the Analyzed Membranes

| sample | LP | DLP | RCP | RDCP1 |
|--------|----|-----|-----|-------|
| C₁     | 74.9 | 78.2 | 68.4 | 60.3  |
| C₂     | 12.0 | 10.0 | 8.3  | 16.0  |
| C₃     | 7.4  | 10.5 | 4.2  | 6.4   |
| C₄     | 4.7  |      |      |       |
| C₅     |      |      | 2.8  |       |
| C₆     |      |       | 15.7 | 11.4  |
| N₁     | 33.4 | 17.6 | 39.8 |       |
| N₂     | 58.8 | 16.7 | 36.9 | 30.2  |
| N₃     | 7.8  | 59.2 | 14.1 | 48.8  |
| N₄     | 6.4  | 9.2  | 21.0 |       |
| F₁     |      |       | 24.5 |       |
| F₂     | 82.5 | 66.6 |      |       |
| F₃     | 17.5 | 8.9  |      |       |

in the differences between both nitrogen spectra before and after reinforcement.

Regarding the C1s spectra, the two different binding energies for the C−C species in the peaks C₅ and C₆, compared to the usual value of 284.8 eV are a result of the presence of nitrogen in the ring and the effective charge shifts that occur on carbon atoms related to it because of its higher electronegativity. Because of this, there are two different C−C peaks, one with lower energy, related to carbons in the meta- and phenyl positions in relation to the nitrogen atom, and one with higher energy due to a δ⁻ effective charge, related to carbons in the ortho- and para-positions.

The C₁ peak is also related to carbon double bonds, which have a lower binding energy than the usual single bond between two carbon atoms. The LP and DLP samples show a different behavior in comparison to the RCP and RDCP1 in this case. While LP has a lower percentage of C₁ than DLP, the opposite occurs in the RCP and RDCP1 samples. This change can be correlated with the cross-linking reactions between the double bonds of the polymer chain occurring via cationic polymerization, giving place to single bonds between the polymeric chains. The C₁ peak also has a much higher percentage in the doped membrane, indicating a higher number of single bonds between carbon atoms, which corroborates this assumption.

The third peak C₄ assigned not only to the C−O−C species but also to C=OH and N−H⁺, has the same pattern observed in the N₁s spectra, with the doped membranes having a peak with a higher intensity than the undoped ones. The very weak C₄ peak is an indicative of a carbonyl type bond. Since this peak appears only in the LP sample, its occurrence might be due to oxidation of adventitious carbon.

For the reinforced samples, more peaks in the C1s spectrum appear, which was expected because of the new species containing C−F type bonds. In the membrane without doping, there are two different peaks: C₅ assigned to the tetrafluoroethylene species, and C₆ assigned to the trifluoromethane species. The C₅ is related to chain terminations of the fluoropolymer.

The doped reinforced membrane C1s spectrum has one more peak, C₆. The origin of this peak is not clear. It can be attributed to C=CF that can be formed from dehydrofluorination of possible partially fluorinated units in PTFE due to the irradiation process of the measurements in the presence of the H₃PO₄. C=CF is an indicative of structural change breaks or rearrangements forming unsaturated species due to higher temperature and the presence of the pyridine units, giving place to more thermal stable molecules within the membrane, and also may be related to cross-linking in the film.

The assignment of C₅ to a fluorine-related peak can also be corroborated with the lowering intensity of both C₅ and C₆ peaks in the same spectrum. These data are in agreement with the F1s spectra as well, where there are three peaks in the doped spectrum, with one, the F₁ peak, being related to the new peak formed during doping.

The P2p spectra are present only at the doped membranes DLP and RDCP1 and show little changes, only the expected doublet. This doublet is assigned to the dihydrogen phosphate species, the phosphoric acid with one less hydrogen. This result shows that the acid only participates in the protonation of the basic sites in the membrane, which is very important for the proton conducting properties of the membrane and is corroborated by results in the literature.

The depth profile analysis of both membranes (Figure 5) shows that the phosphorus in both membranes diffuses in a similar way. Since the phosphorus contained in the samples occurs only because of the doping and the P2p spectra demonstrate that it does not react apart from the protonation, the phosphorus presence can be attributed to the dihydrogen phosphate species along the depth of the samples. The depth profile indicates that the phosphorus atomic percentage is on a similar level along both membranes until the end of the analysis since it is well regarded in the literature that the cross-linking makes the polymeric structure more compact, which decreases the doping ability. This outcome might be an indication that the reinforcement might have a positive influence regarding the doping process.

2.3. Reflection Electron Energy Loss Spectroscopy (REELS) Analysis. REELS spectra of the undoped samples are presented in Figure 6. For REELS studies, the RCP sample was analyzed in both sides, at the reinforced and without reinforcement sides. The hydrogen peak intensity changes in the three spectra, where the LP sample presents the highest and the RCP in the fluorine side presents the lowest contribution. This outcome is probably due to the hydrogen
being more tied to the basic sites in the RCP membrane, related to the difference in how the fluorine reinforced samples have a higher percentage of protonated groups than the samples without reinforcement in the spectra shown in Figure 6.

The band gap was also evaluated after REELS spectra for the three cases (Table 5), and it consistently gets lower values along with the higher presence of the reinforcement. This is an expected result according to the literature due to the fluorine presence.

2.4. Near-Edge X-Ray Absorption Fine Structure (NEXAFS) Analysis. Angle-resolved TEY and FY NEXAFS spectra of the polymeric membranes at the sulfur K-edge are shown in Figure 7: two peaks appeared in all spectra, the most intense peak (peak 2), with an energy of 2480.1 eV, and the first peak (peak 1) at 2477.3 eV, followed by broad features in the continuum. These spectra are similar to previously reported S1s NEXAFS spectra of sulfone derivatives: poly-(ether sulfone) resin, di[4-(4-diphenylaminophenyl)phenyl]sulfone film, and 1,10-sulfonyldibenzene powder. Following the assignment of Behyan et al. peak 2 is mostly attributed to the sulfur $1s \rightarrow \sigma^*(S-O)/\sigma^*(S-C)$ transition and peak 1 is attributed to the sulfur $1s \rightarrow \pi^*(S-O)/\pi^*(S-C)$ transition that mixes with the $\pi^*(C=C)$ density of the phenyl ring. The shoulder on the lower energy edge of peak 2, mentioned by Behyan et al., was neither observed here in the TEY NEXAFS spectra nor at Calderon and Zhang et al. works. Since NEXAFS is a local chemical probe, groups that are electronically isolated from the sulfone groups may not interfere, and based on this, we believe that this is the proper assignment, dominated by contribution of the sulfone bond.

At the FY NEXAFS spectra, the intensity of peak 1 seems to increase more relative to peak 2 and the spectra are broader, which might suggest that the third component of the NEXAFS spectra, as measured and simulated by Behyan et al., is more easily observable in the bulk of the membranes.

By varying the angle of incidence of the synchrotron light, it is possible to observe that the intensity of the peaks changes similarly and not in an opposite way, indicating no specific orientation of the sulfone units. This corroborates the analysis and assignment suggested by Behyan et al. and reinforces the contribution of the sulfone bond to the spectra.

One interesting point to mention here is the different behavior presented by the LP and CP membranes: while the linear copolymer membranes (LP and DLP) show an increase in the intensity of peaks 1 and 2 going from normal to grazing incidence angles, the opposite is verified by the reinforced membrane of the cross-linkable polymer (RCP); to these peaks, intensities grow by varying the angle of incidence from 20 to 85°. This may indicate differences in the rearrangement of the S–O bonds in these films.

Regarding the linear copolymer membranes (LP and DLP), it seems that the doping process leads to more uniform films. According to the literature, the appearance of lower-valence sulfur species in the NEXAFS spectra might be related to degradation occurring in the membrane due to the X-ray beam interacting with the solid and damaging it to some extent. This may explain the weak feature appearing in the TEY and FY NEXAFS spectra of the RDCP1 membrane. According to Chuang and Hsu, PBI membranes with fluorine addition are more exposed to degradation and rearrangement processes due to the doping procedure. So, it is possible that the fluorine

![Figure 5. Depth profile analysis: percentage comparison of phosphorus in both doped membranes until 450 nm.](https://dx.doi.org/10.1021/acsomega.0c01039)

![Figure 6. REELS spectra of selected samples before and after the reinforcement process (from left to right: LP, RCP, and RCP with fluorine).](https://dx.doi.org/10.1021/acsomega.0c01039)

| sample              | band gap (eV) |
|---------------------|---------------|
| LP                  | 3.50          |
| RCP                 | 3.35          |
| RCP with fluorine   | 3.00          |

Table 5. Electronic Band Gap as Determined by REELS
reinforcement made the membrane more susceptible to degradation due to X-ray irradiation.

3. CONCLUSIONS

In this work, polymer electrolyte membranes of aromatic polyethers bearing pyridine main chain units having two substitution patterns, either 2,5- or 2,6-, as well as with or without the presence of cross-linkable side double bonds have been studied before and after doping in phosphoric acid. In addition, in order to enhance the membrane robustness, reinforcement using a PTFE fabric was performed that led to the stabilization of the membranes’ dimensions after the doping process. The most pronounced effect was observed for the cross-linkable reinforced membranes for which the membranes maintained their x- and y-dimensions while they only swelled along their z-axis. This latter fact is of major importance for their efficient application in HT PEMFCs since it minimizes the expansion-shrinkage of the membranes at the on−off cycles of the cell. The membranes were characterized by XPS, XPS with depth profile, REELS, and NEXAFS spectroscopic techniques. The reinforced samples showed a high protonation capacity in their pyridine sites after the doping procedure in comparison to the un-reinforced membrane. There is also an indication that there are cross-link rearrangements not only in the membrane itself but also in its reinforcement, which might influence how the membrane works in the fuel cell ensemble. The depth profile indicates that the presence of the reinforcement has a positive effect on the protonation process and the acid diffusion capacity in the membrane. Surface-sensitive TEY and bulk-sensitive FY S K-edge NEXAFS spectra may indicate a different organizational configuration with regard to the sulfone sites of linear and cross-linked copolymers, although no specific orientation could be concluded. REELS analysis shows the lowering of the electronic band gap in the reinforced membrane.

4. EXPERIMENTAL SECTION

4.1. Materials. The nomenclature of the herein examined polymer electrolytes is given in Table 6.

Both polymers LP (5-(4-oxyphenyl)-2-(4-(4-((4-(3,3′,5,5′-tetramethyl-4′-(4-tosylphenoxy)-1,1′-biphenyl]-4-yl)oxy)-phenyl)sulfonyl)phenoxy)phenyl)pyridine) and CP (2-(4-oxy-
dissolved membranes were collected, dried under vacuum for 3 days at 160 °C, and weighed. The solubility of the membranes was obtained from the weight losses observed.

4.3. Sample Selection for Spectroscopic Characterization. For the extended spectroscopic characterization, two membranes were selected, a membrane based on the linear copolymer LP and a reinforced membrane of the cross-linkable polymer CP. The linear membrane was doped at 120 °C for 48 h, named DLP after the doping, while the reinforced membrane was doped at 100 °C for 110 h, named RDCP. The reinforced cross-linkable membrane (RCP) was selected since the reinforced membrane of the linear copolymer RLP cannot reach acid uptakes higher than 150 wt %, which is way below the required value of 250 wt %, as shown in Table 1, that is necessary to obtain the required conductivity for fuel cell application.

4.4. Spectroscopic Characterization and Data Acquisition. Attenuated total reflectance (ATR) spectra were recorded on a Bruker Optics Alpha-P Diamond ATR spectrometer of Bruker Optics GmbH. X-ray photoelectron spectroscopy (XPS) spectra were obtained through measurements using a Thermo Scientific ESCALAB 250Xi spectrometer with a base pressure of ~10⁻⁹ mbar. The analysis was conducted using a monochromatic Al Kα source (1486.6 eV), and the binding energy scale was calibrated using the Au 4f/2 line at 83.96 eV, with an estimated error of ~0.2 eV. The pass energy for the survey spectra was 100 eV, and that for the high-resolution core level spectra was 25 eV. For the depth profile analysis, the sputtering was performed using an argon ion gun with an energy of 3 kV and current equal 15 mA. The procedure used was of eight successive etching cycles with a rate of 10.45 nm/s, 5 s per cycle. In every cycle, XPS survey spectra were acquired in order to obtain the atomic percentage of phosphorus in the etched layers. C1s, N1s, and F1s core levels were fitted by Gaussian and Lorentzian functions using the Avantage v.5,982 program.

Reflection electron energy loss spectroscopy (REELS) spectra were also conducted using an ESCALAB 250Xi spectrometer, using a primary electron beam with energy of 1000 eV, a constant pass energy of 12 eV, an electron current equal 15 mA. The procedure used was of eight successive etching cycles with a rate of 10.45 nm/s, 5 s per cycle. In every cycle, XPS survey spectra were acquired in order to obtain the atomic percentage of phosphorus in the etched layers. C1s, N1s, and F1s core levels were fitted by Gaussian and Lorentzian functions using the Avantage v.5,982 program.

Table 6. Nomenclature of the Examined Polymer Electrolytes

| Electrolytes | Description |
|--------------|-------------|
| LP           | linear polymer |
| DLP          | doped linear polymer |
| RDLP         | reinforced doped linear polymer |
| CP           | cross-linkable copolymer |
| DCP          | doped cross-linkable copolymer |
| RCP          | reinforced cross-linkable polymer |
| RDCP         | reinforced doped cross-linkable polymer |
| R(LP/CP)     | reinforced blend of LP and CP |

In the case of the cross-linkable copolymer (CP) and of the reinforced cross-linkable copolymer (RCP), cross-linking was performed during doping in H₃PO₄ 85 wt % at temperatures at or higher than 100 °C for several hours as has been previously reported. Solubility of the membranes in N,N-dimethylacetamide (DMAc) was tested in order to evaluate the cross-linking success. Thus, samples of the cross-linked membranes after doping in H₃PO₄ 85 wt % and undoping in boiling water were immersed in DMAc at 80 °C for 24 h. The remaining, not

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The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes
The authors declare no competing financial interest.

ACKNOWLEDGMENTS
Research is partially supported by LNLS — National Synchrotron Light Laboratory, Brazil. M.L.M.R. thanks CNPq and CT-INFRA FINEP for financial support. Financial support from the Fuel Cell and Hydrogen Joint Undertaking (FCH JU) through the program “Development of a Portable Internal Reforming Methanol High Temperature PEM Fuel Cell System” IRMFC-FCH-JU-325358 is greatly acknowledged.

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