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Sorption and permeation of water through Plasma Enhanced Chemical Vapour Deposited phosphonic acid-based membranes

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Phosphonic acid-based membranes were prepared by Plasma Enhanced Chemical Vapor Deposition (PECVD) with an input power of 100 W in a continuous or pulsed glow discharge. Comparing both kinds of plasma discharges makes appear that the pulsed configuration gives rise to PECVD materials with longer hydrocarbon chains and thus higher flexible polymer network which consequently present better sorption properties than those prepared from a continuous plasma discharge. Being more hydrophilic and richer in acidic functions than Nafion® 212, PECVD membranes (whatever the kind of plasma discharge, pulsed or continuous, during the deposition of films) present a better water sorption ability. Nevertheless, having a more highly cross-linked structure, they have a lower water diffusion/permeation capacity. Consequently PECVD membranes show singular water management properties which could be a great advantage for the final Proton-Exchange Membrane Electrolyte Cells and Proton-Exchange Membrane Fuel Cells applications.

1. Introduction

In the field of low-temperature electrolysis and fuel cells, Proton Exchange Membranes have attracted extensive attention in the recent years, due to their advantageous dual transport properties: protons transport to ensure internal conduction in the cells and gas barrier property to prevent fluids at both electrodes from interacting [1–4]. Most of the PEMECs (Proton-Exchange Membrane Electrolyte Cells) and PEMFCs (Proton-Exchange Membrane Fuel Cells) in the literature use sulfonic acid-based membranes notably Nafion® (by DuPont de Nemours) due to its several advantages such as excellent chemical, mechanical and thermal stabilities and high proton conductivity (60–100 mS.cm⁻¹) in the temperature range 30–80 °C [5,6]. However, the dependence of Nafion® proton transport mechanism on water (due to its high acidic character) has motivated the research to develop alternative membranes being less water dependent such as imidazole [7,8] and phosphonic acid-based membranes [9–13].

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Compared to imidazole, phosphonic acid-based groups are more amphoteric and possess a relatively high dielectric constant. The combination of these two properties leads to a high degree of auto-dissociation which favors the formation of a hydrogen-bonding network making the proton conductivity independent of relative humidity and temperature. Thus the proton transport through an anhydrous conduction mechanism known as the Grotthuss mechanism [14] is favored. Although phosphonic acid-based membranes are likely to operate in an anhydrous medium, the presence of water in these membranes remains an important factor facilitating proton transport and conditioning the maintenance of good performance of PEMECs and PEMFCs for a relatively long operating time [15,16].

Although the preparation of membranes containing phosphonic acid groups has enabled to improve the performance of electrolyte membranes in anhydrous conditions, these membranes still suffer from some limitations such as low mechanical stability and a poorly effective barrier effect on liquids and gases which strongly limit their competitiveness [17]. Therefore, the development of polymer electrolyte membranes that can efficiently conduct protons but block liquids and gases permeation has been envisaged by using Plasma Enhanced Chemical Vapor Deposition (PECVD) [18]. This dry-route synthesis method is considered as a promising way to prepare dense, uniform and mechanically resistant membranes [19,20]. It has been reported in the literature that electrolyte membranes prepared by PECVD exhibit superior properties, such as higher thermal and chemical stability, lower liquid and gas permeability and higher water retention (with a quite similar protons conduction level) when compared with classical polymer membranes, which provide them with great potential as membranes for PEMECs or PEMFCs applications [15,18]. However PECVD is a very complicated process in terms of synthesis mechanisms which are noticeably influenced by the plasma parameters in the preparation of membranes. Now synthesis mechanisms directly control the properties of the obtained membranes, in particular water sorption and permeation properties [21–23].

This work is a sequel to a previous study by our group [15] which consisted in studying the influence

of the plasma deposition conditions, especially the nature (continuous or pulsed) and the input power (in the range of 60 - 100 W) of the plasma discharge on the materials structural and proton conduction properties. The main objective of this paper is to investigate the water sorption and permeation properties of phosphonic acid-based membranes prepared at 100 W plasma input power (considered as the optimal plasma input power according to our previous study) in a continuous or pulsed discharge in comparison with those of the sulfonic acid-based membrane Nafion® 212 (as a commercial reference). Another objective of this study is to demonstrate the improvement of the membrane water sorption properties by using the pulsed plasma deposition configuration. The structural and physicochemical properties of the prepared phosphonic acid-based plasmopolymerized membranes were performed using different experimental methods, i.e. Scanning Electron Microscopy (SEM) for the membranes morphology and thickness, X-ray photoelectron spectroscopy (XPS) for the materials chemical composition and contact angle method for the membranes surface hydrophilicity/hydrophobicity. In terms of transport properties, water sorption behavior of phosphonic acid-based plasmopolymerized membranes was investigated by ellipsometry coupled with water sorption and by Cahn microbalance; their water permeability was evaluated by diffusion measurements through a permeation cell.

2. Experimental section

2.1. Membranes preparation procedure

The membranes preparation procedure is the same as that described in a previous paper by our group [15]. The PECVD device used was centrally composed of a 30 L lab-scale capacitively coupled

plasma reactor operating with a radio-frequency (RF) discharge at 13.56 MHz (manufactured by MECA2000). The precursor used was the dimethyl allylphosphonate ([757–54–0], SP-61–001, supplied by SPECIFIC POLYMERS) and the gas carrier was argon (purity > 99.999%, supplied by AIR LIQUIDE).

Two different types of substrates were used to support phosphonic acid-based plasma-polymerized membranes: boron-doped p-type silicon wafer (100) (from Monsanto Electronic Materials, resistivity: 1–50 Ω .cm) for structural characterizations (SEM, XPS and ellipsometry) and Nafion® 212 (from Sigma-Aldrich) for SEM observations, contact angle investigation and water transport properties characterizations (sorption and permeation of water). Before each deposition process (continuous or pulsed), supports (silicon wafer and Nafion® 212) were 15 min long plasma pre-treated (in a 100 W continuous plasma discharge), in order to clean the supports and improve plasma film adherence on them.

In this study, the plasma discharge power was fixed at 100 W; the only variable plasma parameters during deposition was the plasma discharge configuration (continuous or pulsed). The pulsed configuration consisted in performing the deposition by alternating T_{on} (time during which the plasma was on, equal to 5 ms) and T_{off} (time during which the plasma was off, equal to 5 ms). Pulse frequency was fixed at 100 Hz. So the duty cycle (DC), defined by Eq. (1) was equal to 0.5, i.e. 50%. The DC has been fixed at 50%, based on our previous paper [15] which was based on some references in the literature. As example, Z. Jiang et al. [22] has worked on the synthesis and optimization of proton exchange membranes prepared using a pulsed plasma enhanced chemical vapor deposition technique and has proved that a DC comprised between 0.1 to 0.5 could allow a softer fragmentation and thus, a better plasma polymerization, compared to higher DC values.

$$DC = \frac{T_{on}}{T_{on} + T_{off}} = T \times \text{pulse frequency} \quad (1)$$

2.2. Morphological, structural and physico-chemical characterization techniques

2.2.1. SEM analysis

The influence of the type of support on the PECVD membranes morphology and thickness (error ~ 10%) was investigated using a scanning electron microscope S-4800 Hitachi (using an operating voltage between 2 and 8 kV). Before the SEM analysis, the membranes deposited onto Nafion® 212 were immersed and broken in liquid nitrogen in order to have a neat cut of the samples cross-section. Before each observation, all the samples (deposits on silicon wafer or on Nafion® 212) were Pt-metalized by sputtering under vacuum in order to make the membrane surface electron conductive and so more easily observable.

2.2.2. XPS analysis

The chemical composition of the PECVD membranes deposited on silicon wafer was determined by XPS on an ESCALAB 250 from Thermo Electron (monochromatic source of Aluminium 1486.6 eV; diameter of the analyzed surface: 400 μ m). The background signal was removed using the Shirley method [24]. The surface atomic concentrations were determined from photoelectron peaks areas using the atomic sensitivity factors reported by Scofield [25]. Binding energies (BE) of all core levels were referred to the C = C of C1s carbon at 284.4. eV.

2.2.3. Contact angle method

The contact angle method was performed to evaluate the surface wettability of the PECVD membranes deposited on Nafion® 212 (in comparison with the virgin Nafion® 212). The device used was a homemade equipment. The procedure consisted in depositing a drop of water of approximatively

6 μL on the surface of the analyzed sample. From the photo of the drop deposited on the material surface (taken 3 seconds after the drop deposition), the contact angle could be evaluated by averaging the contact angle (left and right) of 3 successive measures in order to determine the surface wettability of the analyzed membrane, using ImageJ utility with the drop shape analysis plugin.

2.3. Water sorption and permeation characterization techniques

2.3.1. Ellipsometry coupled with water sorption analysis

Ellipsometry analysis was used to investigate the PECVD membranes behavior to the water sorption by using a Semilab GES5E spectroscopic ellipsometer (spectral range: 1.23–4.97 eV; Xenon lamp) completed with a lab-made set up for automatic adsorption-desorption with different intrusive vapor probes. Before each water sorption analysis, the sample (film deposited on silicon wafer) was vacuumed down to the limit pressure of 5 Pa (Alcatel Drytel 1025). Then, ultra-pure water (Milli-Q® purification system, Millipore) was introduced progressively in the analysis chamber by monitoring the ratio P/P_0 with P being the water partial pressure and P_0 being the saturated vapor pressure of water at the analysis temperature. The thickness and refractive index (RI) on the full spectral range were simultaneously calculated from the ellipsometer data collected every 60 s in steady state, using the optical model Cauchy law.

2.3.2. Water sorption measurements by Cahn microbalance

2.3.2.1. Experimental procedure. Measurements of water vapor sorption through the PECVD membranes and Nafion® 212 were carried out using a Cahn D200 microbalance with electromagnetic compensation, DVS (Dynamic Vapor Sorption), supplied by Surface Measurement Systems (SMS, England) with a resolution of 0.1 μg . This apparatus enables to measure the mass variation of a sample, following the adsorption or the desorption of a penetrant in vapor form, with a prescribed activity a such that:

$$a = \frac{p}{p_{\text{sat}}} \quad (2)$$

With P variable vapor pressure and P_{sat} saturated vapor pressure (of water in our case) at a controlled temperature (25 °C in this work).

The dry sample (50 mg for PECVD membranes and 5 mg for the Nafion® 212 membrane) was placed in the measuring nacelle within the thermoregulated chamber. Before each measurement, a conditioning step was carried out by imposing a sweep of dry nitrogen (Technical Nitrogen, Air Product) at a flow rate of 200 $\text{cm}^3 \cdot \text{min}^{-1}$ to dry the sample and to remove all traces of humidity in the device. The mass of the sample after this step was recorded as the dry mass M_0 . Then a sequence of water vapor activity programmed from 0.05 to 0.95 was imposed on the sample. Each level of activity a gave rise to a variation of the mass as a function of time until a sorption equilibrium was reached. For each water activity, the establishment of a sorption kinetic of the sample allowed to determine both the intrinsic diffusion coefficient (in head period of the transient regime) and the sorption equilibrium (in the second period of the kinetic, at the plateau). The so obtained sorption isotherm was read for physical interpretations of the mechanisms involved.

2.3.2.2. Theory and modeling. Depending on the nature and strength of the interactions between penetrant and substrate, the shape of a sorption isotherm varies. In literature, different models exist [26] to explain the behavior of small molecules interacting with a substrate. These models have been classified by Rogers [27]. Taking into account the shape of the isotherms obtained in this study and

knowing the nature of the system penetrant/substrate, the representations of DualMode type and type BET II (Brunauer, Emmett, Teller) are relevant and described below.

The dual-mode sorption mechanism results from a combination of the Henry and Langmuir type sorption isotherms. The shape of the isotherm (generally concave then linear) is characteristic of a double sorption model. It generally concerns glassy polymers and obeys the additivity law:

$$C = k_H \cdot a + \frac{A_L \cdot b_L \cdot a}{1 + b_L \cdot a} \quad (3)$$

With A_L the average concentration of Langmuir sites, b_L the affinity constant of the penetrant molecules for these Langmuir sites, and k_H the solubility coefficient also called Henry constant.

Concerning the Park model [28], it takes into account the formation of water aggregates in addition to the combination of the Langmuir and Henry type sorptions, or of the BET II type. This model is usually relevant in the case of water sorption in hydrophilic polymers or having polar functions or physical sites such as microvoids (as in glassy polymers). Park model can be mathematically described in the following form:

$$C = \frac{A_L \cdot b_L \cdot a + k_H \cdot a + n \cdot K_a \cdot a \cdot k_H n \cdot a n}{(1 + b_L \cdot a)} \quad (4)$$

With K_a the equilibrium constant for the aggregation reaction (formation of water clusters), n the number of water molecules per aggregate and k_H the Henry constant.

2.3.3. Water permeation measurements

For water permeation measurements, the sample (PECVD film or Nafion® 212 membrane) was placed between two compartments of a permeation cell which was itself inserted in a thermostatically controlled enclosure at 25 °C (Fig. 1). The measurement was done in two steps. The preliminary step called "purge" consisted in drying the assembly (cell + film) with an inert and dry sweeping gas at a flow rate of 560 ml.min⁻¹ (upstream: technical nitrogen, Air product; downstream: nitrogen beep, Air Product). Then a cooled mirror hygrometer (1311XR probe from General Eastern, USA) continuously measured the dew point temperature T_R of sweeping gas in the downstream compartment as function of time. When the dew point temperature T_R reached a constant value close to -70 °C (corresponding to about 2.5 ppmV of water), the upstream nitrogen flow was then substituted by pure liquid water (18 MΩ). Due to the water concentration gradient established between both sides of the film, the water molecules could migrate through the film, from the upstream compartment to the downstream compartment where the flow of dry nitrogen could be charged in humidity; thus the mirror probe recorded the rise in dew point temperature T_R as function of time. The flux (flux density) of water molecules having passed through the film $J(L, t)$ was determined by:

$$J(L, t) = \frac{d \cdot 10^{-6} \cdot (x_{out} - x_{in})}{A} \cdot \frac{R \cdot T}{p_t} \quad (5)$$

Where d is the flow rate of sweeping gas the downstream compartment ($d = 560 \text{ mL} \cdot \text{min}^{-1}$), A is the active surface of the film ($A = 2.5 \text{ cm}^2$),

R is the constant of the perfect gases ($R = 0.082 \text{ atm} \cdot \text{cm}^3 \cdot \text{K}^{-1} \cdot \text{mmol}^{-1}$), p_t is the total pressure ($p_t = 1 \text{ atm}$). x_{out} and x_{in} (ppmV) are respectively the water contents in the flushing gas at the inlet and outlet of the downstream compartment and are calculated as follows:

$$x = e^{\left(\frac{-b}{TR} + c \right)} \quad (6)$$

Where b and c ($b = 6185.66$ K and $c = 31.38$) are empirical constants and valid for a dew point temperature range of -70 to $+20$ °C [29].

The permeability coefficient Pe is directly proportional to the flux of molecules passing through the film at the stationary state J_{st} , according to:

$$Pe = \frac{J_{st} \cdot L}{\Delta a} \quad (7)$$

With L the wet thickness and Δa the activity change defined as follows:

$$\Delta a = a_{am} - a_{av} \approx 1 \quad (8)$$

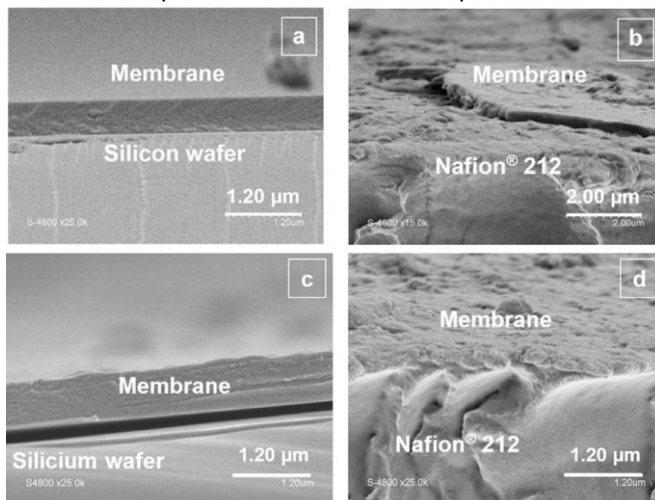
With a_{am} and a_{av} representing the water activities in the upstream and downstream compartments, respectively.

3. Results and discussions

3.1. Morphology and thickness observations of PECVD membranes

Fig. 2 shows a SEM cross-section view of a typical PECVD membrane deposited at 100 W plasma input power on silicon wafer (Fig. 2-a and c) and on Nafion® 212 (Fig. 2-b and d) for 1 hour deposition time. As already observed in a previous paper by our group [15], the PECVD coating on silicon wafer is dense, uniform, defect-free and very adherent on support (Fig. 2-a) and a slide detachment from the support is observed in the case of Fig. 2-c due to preparation of the sample only. Concerning the coating deposited on Nafion® 212 (Fig. 2-b), it can be noticed the presence of fractures and detachment of the film from the support probably due to the difference of mechanical properties between the film and the polymer support which certainly induces a decohesion of the bi-layered material during its preparation for SEM analysis (even if carried out by cryofracture in the liquid nitrogen). Only an inhomogeneity of the surface is displayed for the PECVD membrane prepared in continuous discharge (Fig. 2-d).

Despite the deposition time was the same (1 h), the thicknesses of the films varied noticeably depending on the type of support. The thicknesses were respectively ~ 1 μm for the membranes deposited on silicon wafer and ~ 300 nm for the membranes deposited on Nafion® 212. This thickness disparity can be justified by the surface state of the supports which is different from one support to another. This point will be examined in part 3.3.



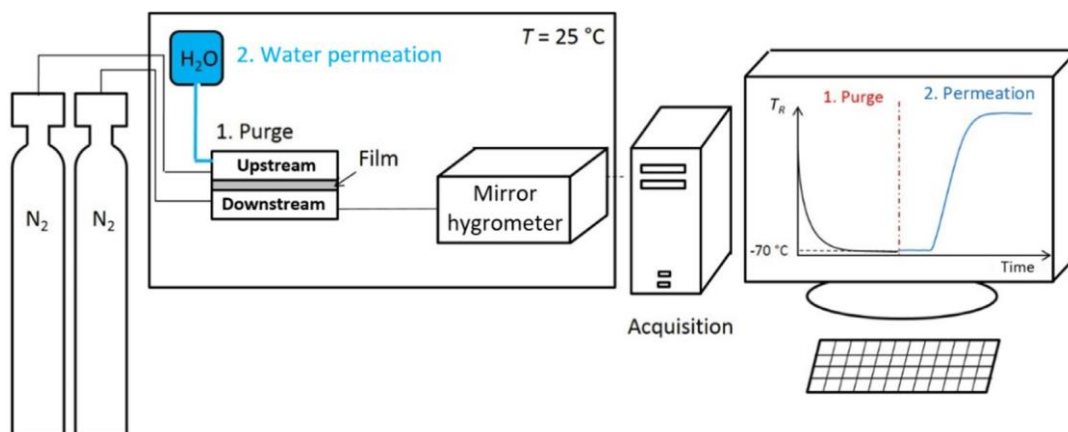


Fig. 1. Water permeation device.

Fig. 2. PECVD membrane deposited at 100 W with respectively a pulsed plasma discharge on (a) silicon wafer and (b) Nafion® 212 and a continuous discharge on (c) silicon wafer and (d) Nafion® 212.

3.2. Chemical composition of PECVD membranes

In order to investigate the chemical structure of PECVD membranes, XPS analyzes were performed. These analyzes were focused on the three chemical elements phosphorus, oxygen and carbon whose atomic percentages are presented in Table 1 for analyzed PECVD membranes and also for Nafion® 212 (from results extracted from the literature [30]). According to these results, PECVD membranes are supposed to be potentially more richer in acidic functions than Nafion® 212 assuming that a significant part of phosphorus elements corresponds to the phosphonic acid-based groups. Furthermore, the chemical composition gap between the two families of PECVD membranes (i.e. prepared with a continuous or pulsed plasma discharge) is related to the fragmentation-recombination mechanism of species during the deposition. Indeed, in the pulsed plasma discharge, the precursor containing hydrocarbon

Table 1

XPS atomic percentages of carbon, oxygen and phosphorus in PECVD membranes in comparison with chemical composition of Nafion® 212 in literature.

Membrane / at. %	C	F	O	S	P	-SO ₃ H
Nafion® 212 (from [30])	33.2	59.9	5.8	1.1	-	~ 1%
Membrane 100 W - continuous plasma	38.2	-	43.5	-	18.3	-
Membrane 100 W - pulsed plasma [DC = 50%]	49.1	-	36.3	-	14.6	-

chains is less fragmented in the gaseous phase and thus the obtained material resulting from the combination of bigger fragments contains longer hydrocarbon chains and more carbon than the film prepared with the continuous plasma discharge. The consequence of PECVD materials containing more hydrocarbon chains is that they contain less phosphonated groups or phosphonic acid groups and thus less oxygen and phosphorus elements [15]. The chemical composition of the PECVD membranes can directly affect their physico-chemical properties such as their hydrophobic/hydrophilic nature characterized from contact angle measurements. It can be justified by the fact that,

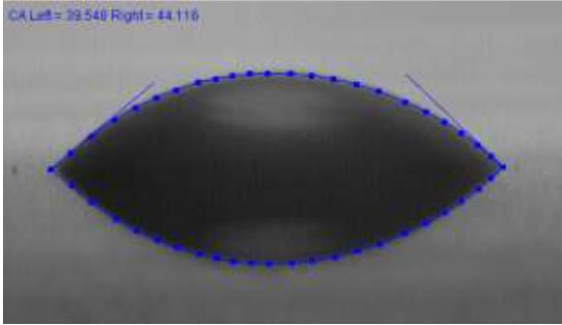
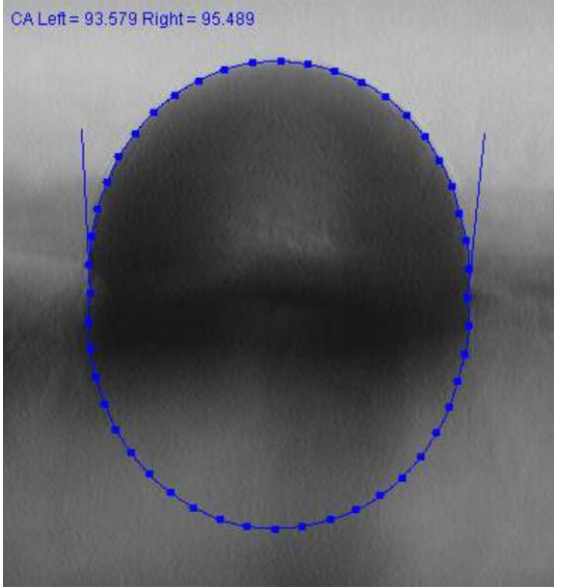
hydrophily/hydrophoby properties depend on the membrane surface state and thus on the presence of active functions on the surface of the membrane [31], which will be investigated in part 3.3.

3.3. Evaluation of the hydrophilic / hydrophobic character of PECVD membranes

Before everything else, the contact angles of virgin supports (i.e. silicon wafer and Nafion® 212) were measured in order to determine their surface wettability (hydrophilic or hydrophobic nature). Table 2 presents the shape of the drop on the sample surface and the corresponding contact angle obtained for each support. For each sample, three contact angle measurements were realized, then all measured angles (six in total due to left and right sides for each drop) were averaged in order to obtain the corresponding mean contact angle θ (°). As expected, Nafion® 212 (with a contact angle $\theta > 90^\circ$) presents a much more hydrophobic surface than silicon wafer ($\theta = 42 \pm 2^\circ$), which explains why the growth rate of deposit on its surface is noticeably less than that on silicon wafer (as presented in part 3.1).

Fig. 3 shows the mean contact angles θ for the virgin supports (silicon wafer and Nafion® 212) already presented in Table 2 compared with the contact angles obtained for the PECVD membranes (prepared in both continuous and pulsed plasma discharges) deposited on silicon wafer. Thereby, the contact angle of the membrane prepared in pulsed conditions is lower than the contact angle of the material deposited in continuous conditions, which is also lower than that of the supports. Thus the pulsed

Table 2
Shape of the drop and corresponding mean contact angle θ of both supports.

Support	Contact angle θ (°)	Shape of the drop on the surface
Virgin silicon wafer	42 ± 2	
Virgin Nafion® 212	95 ± 2	

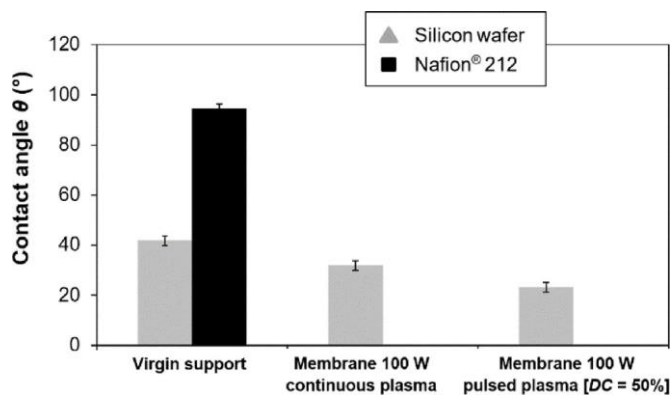
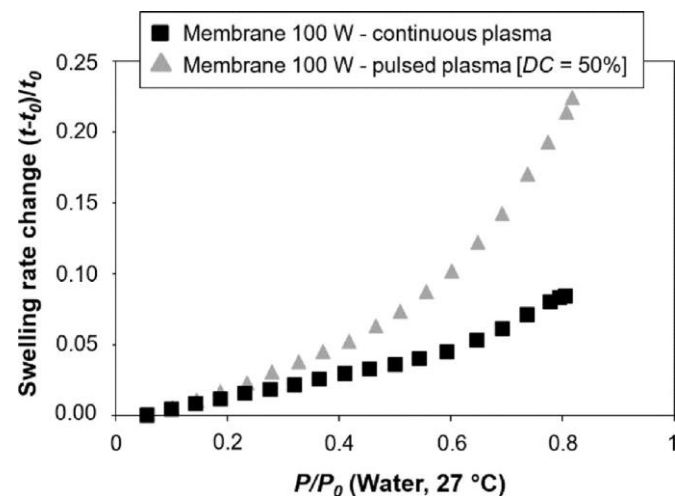


Fig. 3. Mean contact angles of both virgin supports and PECVD membranes deposited on silicon wafer.



discharge gives rise to more hydrophilic materials than the continuous one. This can be explained by the fact that the contact angle depends on the surface wettability, therefore on the roughness and the surface chemistry of the material [31]. Kale et al. [32] demonstrated that the use of a pulsed plasma discharge made it possible to obtain more hydrophilic tetraethylorthosilicate and hexamethyldisiloxane polymers than those obtained in continuous plasma discharge from the same precursors because of the lower density and more organic nature of the materials obtained in pulsed synthesis conditions. While Inagaki et al. [33] have shown that the surface properties are rather related to the surface chemistry of the materials (presence of active function on the surface of the membrane) when the plasma films are totally amorphous. In our case, there is clearly a competition between roughness and surface chemistry because although the film prepared in pulsed plasma deposition mode is less rich in active functions (i.e. phosphonated groups or phosphonic acid groups as mentioned in part 3.2) than that prepared in continuous plasma, it nevertheless has the most hydrophilic surface. Unfortunately the surface roughness was not evaluated in this study to confirm this hypothesis.

Fig. 4. Swelling rate change following water sorption in PECVD membranes.

3.4. Swelling rate change following water sorption of PECVD membranes

The water sorption properties of PECVD membranes were foremost studied by ellipsometry coupled with water sorption. Fig. 4 shows the swelling rate change $(t-t_0)/t_0$ of films as a function of water activity P/P_0 . By increasing the water activity from 0 to 0.85, whatever the membrane is, the swelling rate change increases, i.e. to the amount of adsorbed water increases. This amount is less in the material prepared with the continuous plasma discharge. Despite the material prepared in the pulsed configuration presents the worst chemical composition in terms of concentration of active functions (in particular phosphonic acid groups), it shows the best ability to adsorb water. Indeed, the adsorption capacity of water is directly related to the length of the polymer chains. As already explained in the part 3.2, in pulsed plasma conditions, the resulted deposit contains longer hydrocarbon chains. Longer chains certainly induce higher flexibility of the polymer network and that allows a higher increase of the free volume as the water molecules penetrate the material.

3.5. Water sorption isotherms of PECVD membranes and modeling

In addition to the previous results displayed by ellipsometry coupled with water sorption, water vapor sorption measurements at 25 °C were carried out using a sorption microbalance on PECVD membranes (deposited on silicon wafer) and compared to those performed on the plasma pre-treated Nafion® 212 membrane and untreated Nafion® 212 (as reference materials).

Fig. 5 shows two successive sorption isotherms and an intermediate desorption isotherm with water vapor for both plasma pre-treated Nafion® 212 and untreated Nafion® 212. These isotherms represent the water mass gains, at the sorption equilibrium, as a function of the applied water activity. In both types of Nafion®, it can be seen that the desorption isotherms are slightly greater than the sorption isotherms, revealing a hysteresis conventionally encountered, and secondly that the second sorption isotherms are superimposed on the first sorption isotherms, indicating that there is no retention of sorbed water during the first sorption number one, and that the sorption-desorption mechanism is completely reversible. In the case of the sorption isotherms of the plasma pre-treated Nafion® 212, it is noted that there is no rise in water sorption isotherms at water activities above 0.7, probably due to the plasma pre-treatment carried out on the support Nafion® 212. The effect of the plasma pre-treatment most certainly leads to extreme surface cross-linking which results in the reduction of water uptake at high water activities. In fact, it is generally observed a strong rise in the water mass gain at the highest water activities, knowing that Nafion® is known to form water clusters with the famous Schroeder paradox between the vapor

state and the liquid state of the water as it is the case for the untreated Nafion® 212. Then, the application of mathematical models to decouple the different contributions to water sorption of both plasma pre-treated Nafion® 212 and untreated Nafion® 212 as a

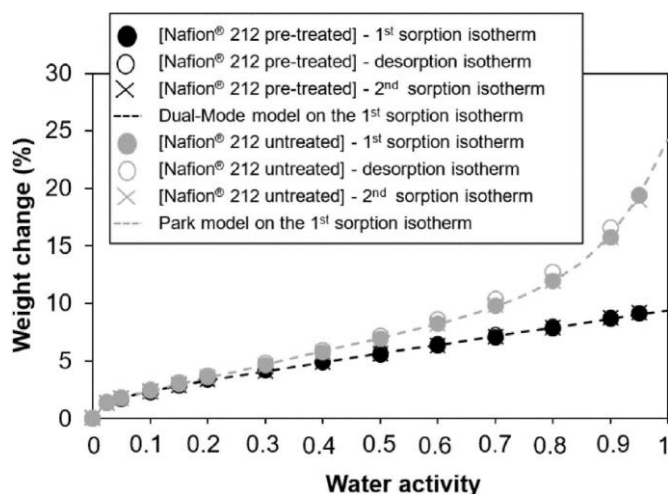


Fig. 5. Sorption isotherms for the plasma pre-treated Nafion® 212 and untreated Nafion® 212 according to the protocol: 1st rise in water activity / desorption / 2nd rise in water activity and modeling of 1st sorption isotherms.

Table 3

Parameters obtained after modeling (1) by the Dual-Mode model of the first sorption curve (1st sorption isotherm) of the plasma pre-treated Nafion® 212 and (2) by the Park model of the first sorption curve (1st sorption isotherm) of the untreated Nafion® 212.

	Nafion® 212 plasma pre-treated	Nafion® 212 untreated
A_L	2.0	1.3
b_L	51.3	233.8
k_H	7.5	11.4
$k_{Hn.Ka.n}$	—	11.5
K_a	—	3.0×10^{-10}
n	—	9.1

function of water activity was implemented.

In the case of plasma pre-treated Nafion® 212, Dual-Mode model comprising a Langmuir contribution $A \frac{bL}{1+bL}$, for low water activities (less than 0.2), and a Henry contribution $K_H a$, for higher activities, has been applied. The shape of the isotherm, concave then linear, is typically characteristic of this model with dual sorption mode [27]. Concretely, the Dual-Mode type isotherms correspond to a rapid saturation of the Langmuir sites before the dissolution of the penetrant in the matrix becomes preponderant [34]. After applying the Dual-Mode model equation on the first sorption curve (1st sorption isotherm), the modeling curve is perfectly superimposed on the experimental points, as shown in Fig. 5. The different parameters obtained from the modeling are summarized in Table 3.

In the case of untreated Nafion® 212, it can be seen that the sorption curve obtained is comparable to those usually reported in the literature [35,36]. Indeed the shape of the sorption isotherm is sigmoidal; it is typical of sorption resulting from a complex combination of several modes of sorption, which can be mathematically described using the Park model [27]. In addition to take into account Langmuir's

contribution to low water activities and Henry's contribution to intermediate activities, Park's model considers also a phenomenon of aggregation of the penetrant in the film with high water activities (here greater than 0.7). After applying the Park model equation on the sorption curve number one (1st sorption isotherm), the modeling curve is also perfectly superimposed on the experimental points, as showed in Fig. 5. Finally the different parameters obtained from the modeling are summarized in Table 3.

Regarding the experimental data and the modeling curves, it can be stated that the Dual-Mode model and the Park model are in perfect agreement with the experimental data and best describe respectively the experimental sorption isotherms of the plasma pre-treated Nafion® 212 and untreated Nafion® 212 in the entire range of water activity (from 0 to 0.95).

Fig. 6 shows the sorption isotherms of PECVD membranes deposited on silicon wafer. Water sorption was performed on one side of the membrane because the deposit was in contact with water on only one side, the second face being in contact with the silicon wafer on which it was deposited. Because the deposits were characterized with their silicon support (mass significantly larger than the deposits themselves), the experimental values of mass gains are particularly low, less than 0.0010 (g/g). Smoothed curves, for which water mass gains were recalculated by mathematical smoothing of experimental sorption kinetics, were added in Fig. 6. Since the mass gains are small, the difference between the measured values and the smoothed values is negligible. Moreover, the sorption isotherms, whether derived from experimental measurements or obtained by smoothing these measurements, have a similar and classic look of the sigmoidal type. The comparison of the isotherms according to the type of plasma discharge (continuous or pulsed) leads to believe that the membrane prepared in pulsed plasma discharge have a greater capacity to adsorb water than the one prepared in continuous plasma discharge, as previously observed by ellipsometry coupled with water sorption.

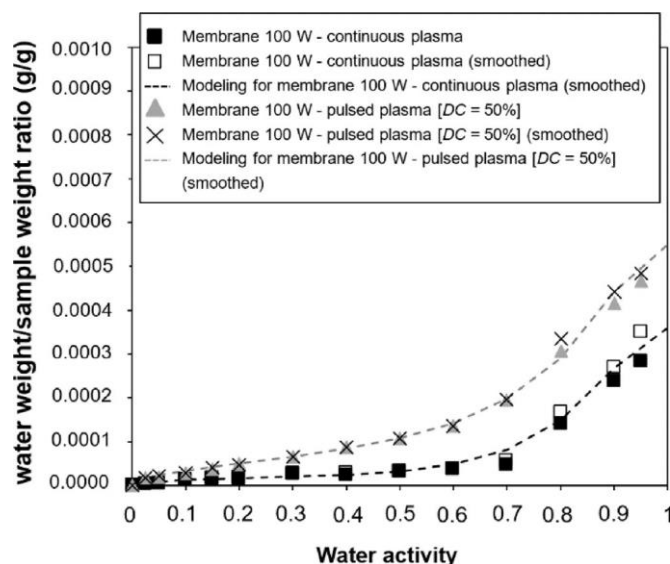


Fig. 6. Sorption isotherms of PECVD membranes obtained from the measurement data (in g/g), after mathematical smoothing (in g/g) and modeling by application of the equation of the Park model.

From a fundamental point of view, the application of mathematical models on the sorption isotherms of the PECVD deposits was carried out by applying the Park model because of the sigmoidal shape of the sorption isotherms. The convex form would indicate the water clustering in the film at water activities greater than 0.7. Indeed, Park model takes into account this hypothesis of aggregate formation resulting from penetrant-penetrant interactions stronger than the penetrant-substrate interactions. Because of their size, these water aggregates result in a restriction of the transport of the penetrant through the

substrate (membrane), which generally induces a decrease in the diffusion coefficient. This model is found in the case of sorption of water in hydrophilic polymers or polymers with polar functions or with ionic groups such as polyelectrolyte [28].

After applying the Park model on the experimental sorption data, the different parameters from the modeling were obtained; they are summarized in Table 4. The lowest value of the constants pair A_L , b_L (Langmuir contribution), obtained for the membrane prepared in the continuous plasma discharge, is characteristic of the reduction of surface solubility by water molecules. Indeed, the Langmuir sites correspond to the presence of specifically charged domains or micro-voids in which the water molecules can be sorbed. The decrease of the Langmuir A_L and b_L constants in the case of the membrane prepared in continuous plasma conditions is directly related to its less hydrophilic surface state and its less flexible polymer network compared with the membrane deposited in the pulsed plasma discharge. Thus the surface affinity with the water molecules is reduced when the deposit is made in continuous mode in comparison with that made in pulsed mode. Considering that the second mode of sorption is Henry contribution, which implies a random adsorption of water molecules, the k_H constant (Henry's constant) is also affected by the continuous deposition mode. Indeed, the lower k_H value in the case of deposition carried out in continuous mode is also justified by the accessibility of the water molecules inside the micro-cavities of the polymer matrix. As regards to the aggregation phenomenon that takes place in the core of the material and characterized by the constant K_a , we can observe that it is high in the case of the membrane prepared in continuous mode for the same reasons mentioned above, namely that the polymer membrane has less hydrophilic surface state and less polymer network flexibility and thus the accessibility of water in the bulk of the material is not facilitated. In fact these higher restrictions in the membrane prepared in continuous mode would lead to confinement effect which favors the water molecules to bond together and to form clusters. If the number of water molecules per aggregate (n) seems to go in the same direction as the aggregation constant K_a , namely higher in the case of the membrane prepared in continuous mode, it is not surprising that the size of water clusters (~ 6 molecules per aggregate) are rather similar for both plasma deposits modes which leads to comparable water sorption behaviors.

By observing the values of the constants A_L , b_L (Langmuir contribution) and k_H (Henry contribution) obtained for all types of material, namely plasma pre-treated Nafion® 212 and untreated Nafion® 212 (Table 3) and PECVD membranes (Table 4), it is observed that they are all much lower in the case of PECVD materials. This may lead to the conclusion that PECVD membranes have a lower water sorption capacity than Nafion® 212. However, for a better reliability of the comparisons between PECVD membranes and Nafion® 212, it is better to reason with the water uptakes of PECVD films without their support. Thus Fig. 7 shows the sorption isotherms as a function of water activity for the plasma pre-treated Nafion® 212 and untreated Nafion® 212 and PECVD membranes without support contribution. The support contribution was extracted by applying a factor of 1000 to the experimental sorption data, because after calculation, taking into account the mass density of the plasma films (from electronic densities measured in a previous work by our group [15]) and their estimated volume, the ratio deposit mass/(deposit+silicon wafer mass) was in the order of 1/1000. It should nevertheless be noted that water sorption was performed on only one side of the PECVD membranes (because their other side is in direct contact with the silicon wafer as a support) while it was performed on both sides of materials for the plasma pre-treated Nafion® 212 and untreated Nafion® 212. This should not change the sorption results as long as one or two faces are exposed to water, the water infiltrates quantitatively in the same way inside the microporosity until it is completely filled, but with more or less time depending on the thickness of the film. From a quantitative point of view, we found that

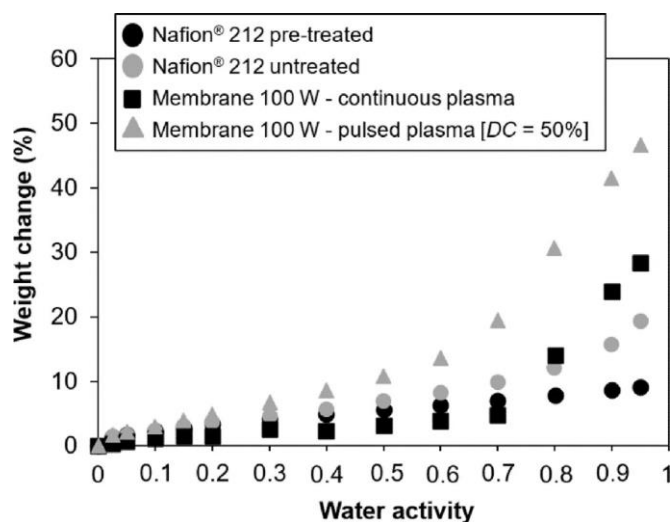


Table 4
Parameters obtained after modeling by Park model of smoothed sorption curves of PECVD membranes.

	Membrane 100 W - continuous plasma	Membrane 100 W - pulsed plasma [DC = 50%]
A_L	0.000015	0.000022
b_L	21.4	50.0
k_H	0.000022	0.00015
$k_{Hn.Ka.n}$	0.00044	0.00051
K_a	6.46×10^{23}	2.36×10^{17}
n	6.0	5.6

Fig. 7. Sorption isotherms of the plasma pre-treated Nafion® 212, untreated Nafion® 212 and PECVD membranes without support contribution.

PECVD membranes have higher water mass uptake (2 to 5 times higher at $a_w > 0.7$) compared to Nafion® 212 (plasma pre-treated or untreated one). This is certainly related to the fact that the water sorption mechanism of polymer membranes is mainly governed by surface chemistry (presence of acid functions) [21]; the PECVD membranes are more hydrophilic and potentially richer in acidic functions than Nafion® 212 [30] as evidenced by the XPS analyzes. In addition, the water intake gap between the two families of PECVD membranes (i.e. continuous and pulsed discharge prepared deposits) is 1.6 to 4 times greater in the medium and high water activity ranges ($a_w > 0.3$). As confirmation of the observations made previously, the PECVD membrane prepared in pulsed plasma discharge clearly have a greater capacity to adsorb water than the one prepared in continuous plasma discharge, despite its lower concentration of phosphonic acid functions. This is certainly due to its more flexible polymer network induced by its longer hydrocarbon chains and its more hydrophilic surface state as already mentioned.

3.6. Water permeability of PECVD membranes

Following the water sorption measurements, water permeation measurements were carried out at 25 °C by using a plane permeation cell, on PECVD membranes deposited on a plasma pre-treated Nafion® 212 and compared with virgin plasma pre-treated Nafion® 212 and untreated Nafion® 212. Water permeation is a process that occurs in 3

steps: water sorption on the upstream side of the material, water diffusion through the material and water desorption on the downstream side of the material [37]. Fig. 8 shows the water permeability coefficients of all investigated materials calculated from the stationary permeation flux (J_{st}) obtained from the permeation kinetic measurements. The calculation of permeabilities takes into account the thicknesses of plasma layers measured in dry conditions by SEM and corrected by the swelling rate (at 100% relative humidity) evaluated by ellipsometry. Thus, PECVD membranes have the following wet thicknesses: 234 nm for the film prepared in continuous plasma discharge, 348 nm for the film prepared in pulsed plasma discharge; and virgin plasma pre-treated Nafion® 212 and untreated Nafion® 212 have a wet thickness of 57 μm (thickness measured with a sliding calipers). It can be seen in Fig. 8 that PECVD membranes have water permeabilities 10 to 30 times lower than that of virgin plasma pre-treated Nafion® 212 and untreated Nafion® 212. This is the consequence for a very low intrinsic diffusion capacity for the plasma deposits (directly related to their intrinsic highly crosslinked nature), which the good sorption capacity cannot counterbalance. These results are in good agreement with previous studies by Roualdès et al. [38] and Jiang et al. [39] on intrinsically sulfonic plasma membranes at least 10 times less permeable to methanol than Nafion® 117. Despite their intrinsic low diffusion ability, PECVD membranes are nonetheless competitive because of their small thickness. Concerning the permeabilities of Nafion® 212, we can say that the plasma pre-treatment has a small influence on the water transport probably due to the fact that plasma pre-treatment certainly leads to extreme surface cross-linking but doesn't affect the bulk of the Nafion® membrane which results in the rather close water permeabilities. The comparison of both families of PECVD membranes (i.e. continuous and pulsed discharge prepared deposits) shows a slight permeability increasing for the pulsed mode because of the structural differences previously mentioned such as: surface chemistry and polymer network flexibility.

4. Conclusion

Phosphonic acid-based membranes with competitive sorption and permeation properties have been prepared in a RF-PECVD reactor by using a mixture of argon and precursor dimethyl allylphosphonate in the gaseous phase. Two different kind of supports have been used for the membranes preparation and characterization: silicon wafer (for SEM, XPS and ellipsometry analyses) and Nafion® 212 (for water contact angle, sorption and permeation investigations). The major interest of PECVD as the membranes preparation method comes from the fact it allows to obtain stable materials being dense, homogeneous, and strongly adherent on all types of support. Contact angle measurements revealed that phosphonic acid-based PECVD membranes are more hydrophilic than Nafion® 212 due to their higher concentration in acidic functions as proved by XPS analyzes. As a consequence of these differences of chemical nature, PECVD membranes present better water sorption properties (measured by ellipsometry or Cahn microbalance) than Nafion® 212. Comparing both kinds of PECVD membranes (prepared in both types of discharges), the PECVD membrane prepared in a pulsed plasma discharge presents the best sorption properties whereas it is less rich in acidic functions compared to the membrane deposited in a continuous plasma discharge. This may be due to the fact that the adsorption capacity of water in PECVD materials is partially controlled by the chain segment mobility which depends on the length of the polymer chains; now the pulsed plasma conditions enable deposits containing longer hydrocarbon chains and thus polymer chains with greater flexibility. Finally, as expected, permeability measurements have revealed that membranes prepared by PECVD (continuous or pulsed discharge prepared deposits) are 10 to 30 times less permeable to water than Nafion® 212 because of the very high diffusion resistance of the plasma deposits directly related to their intrinsic highly crosslinked nature compared to Nafion® 212. Presenting both higher water sorption ability and poorer water diffusion than Nafion®, PECVD membranes should show singular water management properties which could be a great advantage and a real interest for the final PEMEC and PEMFC applications.

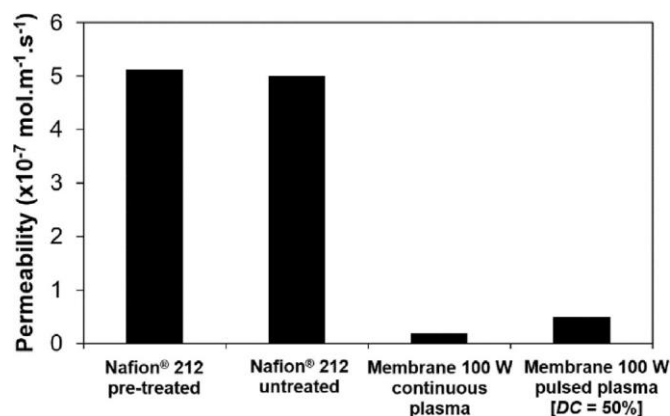


Fig. 8. Water permeability of PECVD membranes, plasma pre-treated Nafion® 212 and untreated Nafion® 212.

Acknowledgments

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