

DOI: 10.17277/amt.2019.04.pp.027-034

Fabrication and Characterization of Anionic Exchange Membranes Based on Chitosan/Poly (Vinyl) Alcohol and Chitosan/Chondroitin Doped with an Amino Cumulene Derivative and Carbon Nanotubes

A.V. Gerasimova¹, A. Bustamante², L. García²,
A.V. Melezhik¹, A.G. Tkachev¹ and J. Iniesta^{2*}

¹ Tambov State Technical University, 106, Sovetskaya str., 392000, Tambov, Russian Federation;

² Department of Physical Chemistry and Institute of Electrochemistry, University of Alicante, Alicante, 03080, San Vicente del Raspeig, Spain

* Corresponding author. Tel.: + 34 965 909 850; fax: +34 965 903 537. E-mail: jesus.iniesta@ua.es

Abstract

Anionic exchange membranes mainly based on mixed matrix membranes (MMM) via the crosslinking of either chitosan (CHT) with poly (vinyl alcohol) (CHT : PVA) or CHT with chondroitin sulfate (CHT : CS) in a 50 : 50 wt% were synthesized. The doping of CHT, CHT : PVA and CHT : CS membranes with either the dispersant agent aminocumulene derivative (named AC, coming from the polycondensation of hexamethylenetetramine in an anhydrous acid medium) or with the carbonaceous inch made of multi-walled carbon nanotubes (CNT) dispersed by using AC to perform (AC/CNT) were characterized by the exploration of the topology by scanning electron microscopy, the determination of water uptake, and the analysis of X-ray diffraction spectroscopy together with the measurement of the anionic conductivity by using electrochemical impedance spectroscopy. Results revealed that the modification of the MMMs with the above inorganic carbonaceous fillers, i.e. AC or AC/CNT, improved remarkably the OH⁻ conductivity for all membranes. The modified CHT:CS blend membranes exhibited the highest ionic conductivities of the series. Water uptake increased for the modified CHT and CHT : PVA membranes, whereas a remarkable reduction of water uptake for the CHT : CS based membranes took place. The best membranes in terms of anionic conductivity were correlated with crystallinity and water uptake.

Keywords

Chitosan; poly (vinyl alcohol); chondroitin; aminocumulene; carbon nanotubes.

© A.V. Gerasimova, A. Bustamante, L. García, A. Melezhik, A.G. Tkachev and J. Iniesta, 2019

1. Introduction

A fuel cell is an electrochemical device which converts chemical energy directly into electrical energy, obtaining water as final products from, for example the electrochemical reaction regarding the hydrogen oxidation and oxygen reduction [1, 2]. Depending on the type of polymeric electrolyte membrane fuel cell (PEMFC), protons or hydroxyl ions will move through the solid polymer electrolyte (SPE) membrane, so it can be contemplated as acid or alkaline electrolyte in which ionic groups are immobilized onto the polymer backbone of the membrane [3].

Even though Nafion membranes exhibit significant advantages in terms of remarkable ionic conductivity, good thermal (close to 120 °C) and chemical stability

with long durability under severe conditions, those membranes also display persistent limitations, such as its high cost, fuel crossover, the commonly use of precious metals, and low kinetic reaction for the oxygen reduction reaction [4], among others. Alternatively, alkaline anion-exchange membranes (AAEMs) contain fixed positively charged groups. The general requirements for the AAEM to be used in PEMFC devices are: i) high permselectivity ii) high ionic conductivity (at least over 1 mS cm⁻¹), iii) good mechanical stability and low degree of swelling or shrinking, iv) thermal stability, and v) chemical stability [5]. In this regard, significant efforts are focused on the production and characterization of eco-friendly AAEMs, as alternative to proton-exchange membrane in acidic media commonly used in a PEMFC [3, 6]

On the one hand, one of the most studied materials for the preparation of eco-friendly membranes as an alternative to petroleum derived polymers regards chitosan (CHT) – this polymer, as is shown in Fig. 1a, and its derivatives have had a great growth due to their properties like low cost, hydrophobicity high mechanical and chemical resistances, and biodegradability [7]. The above features led to the introduction of CHT polymer in recent reviews of fuel and biofuel cells both as polymer electrolyte and as binder and ionic conductor for electrocatalysts preparation [8]. However, the use of unmodified CHT membranes in PEMFC devices is restricted by the low robustness and low ionic conductivity [9]. For those reasons, CHT polymer is commonly modified by either adding inorganic or organic fillers or simply blended with other polymers in order to generate ion exchange sites, thereby significantly enhancing the ionic conductivity of the mixed matrix membranes (MMMs), and increasing mechanical, hydrolytic and thermal stabilities. Hence, the incorporation of fillers into pristine CHT membranes should generally contribute to enhance the mechanical and physical stability of the material together with a decrease of the water uptake and the permeability of small alcohol molecules [10]. On the other hand, poly (vinyl alcohol) (PVA as is shown in Fig. 1b) is a synthetic polymer, odorless, non-toxic, powder that makes it an attractive polymer to be incorporated into the CHT polymeric matrix for the preparation of MMM [11]. CHT : PVA blend membranes can be performed by physical or chemical methods – one of them refers to the formation of hydrogen bonds between the hydroxyl groups of PVA and the amino and hydroxyl groups of CHT with consequences on the conductivity and mechanical properties amelioration. In this respect, the literature has reported the physicochemical properties of PVA-based membrane by incorporating CHT polymer along with a small amount of fillers such as reduced graphene oxide and graphene oxide [12], and sulfonated graphene and grapheme [13] among many others. Moreover, chondroitin (CS) is an anionic linear polysaccharide present in cartilage, bone and connective tissue. CS is a glycosaminoglycan made of repeated disaccharide units comprising an amino sugar and a glucuronic acid linked by glucosidic bonds, as shown in Fig. 1c. With respect to the synthesis of polymeric composites, there are several works related to the use of CHT and CS for the preparation of membranes through the polyelectrolyte complexation towards biomedical applications [14, 15]; however no works are devoted to the use of those membranes in electrochemical applications.

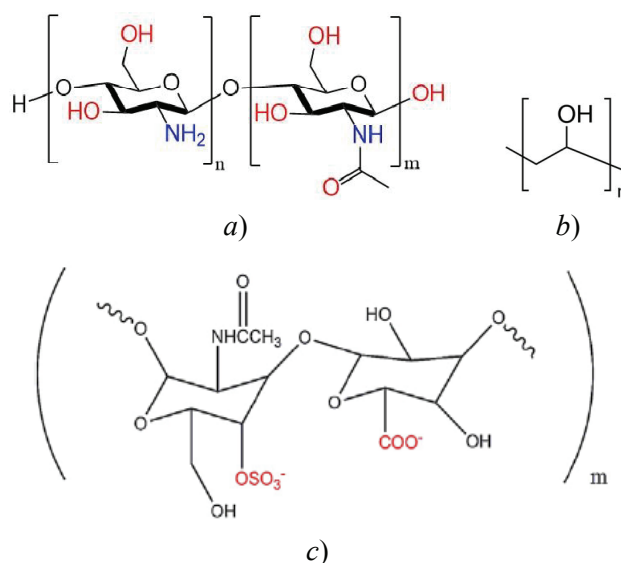


Fig. 1. Chemical structures of chitosan (a), polyvinyl alcohol (b) and chondroitine (c)

This work aims at manufacturing of membranes with enhanced mechanical properties and ionic conductivities with high electrochemical performance in PEMFCs. Hence, this article is focused on the preparation of novel membrane based on more eco-friendly chemistry which will act as alternative to petroleum derived polymers and currently being costly commercial membranes. Herein, facile and eco-friendly synthesis of the membranes based on CHT : PVA and CHT:CS blend polymer backbone were prepared by incorporating fillers of inorganic nature based for the first time on the aminocumulene AC which is formed from the polycondensation of the hexamethylenetetramine [16], as well as the use of a carbonaceous inch made of AC and multi-walled carbon nanotubes (CNT). A preliminary physicochemical characterization of such pristine and modified CHT, CHT : PVA and CHT : CS membranes were carried out by the determination of water uptake (W_u) and anionic conductivity by using electrochemical impedance spectroscopy (EIS). Membranes were selected according to the highest ionic conductivities, to perform further topological experiments by using scanning electron microscopy (SEM), and structural changes by using X-ray diffraction experiments (XRD).

2. Experimental

2.1. Materials and chemicals

Chitosan (CHT) purchased from Sigma-Aldrich (Barcelona, Spain) had a molar mass between 50,000 and 190,000 Da and with an average deacetylation of

75–85 % Poly (vinyl alcohol) (PVA), 99 % hydrolyzed, was obtained from Sigma-Aldrich with a molar mass between 85,000 and 124,000. Chondroitin sulfate (CS, Sigma-Aldrich, Spain) has a whitish appearance and in the form of lyophilized powder, with a molecular weight between 10 and 100 kDa. All CHT, PVA and CS were used without further purification. Pristine multi-walled carbon nanotubes (CNT, Taunit-M) were gently supplied by NanoTechCenter Ltd. (Tambov, Russian Federation), Sodium hydroxide (NaOH, Scharlau, 98 % purity), sodium chloride (NaCl, Applichem, 99.5 % purity) acetone (Sigma Aldrich, Spain) were of the highest available quality available and used without further purification. All solutions were prepared using doubly distilled water with a resistivity not less than 18.2 M Ω cm.

Aminocumulene derivative (AC) was synthesized via the hexamethylenetetramine polycondensation in anhydrous sulfuric acid in order to obtain an oligomeric cumulenic compounds made of carbyne like $(=C=C)_x$ fragments as a main moiety together with amino endcapping groups. The use of AC resulted to be an excellent dispersing agent in aqueous solution of multi-walled carbon nanotubes (CNT) in a wide range of concentration.

2.2. Membranes preparation

The preparation of the polymeric dispersions and their composites necessary for the synthesis of membranes are described as follows. First, the CHT based membranes were prepared according to [17, 18]. 1 wt.% CHT was added into 2 wt% acetic acid aqueous solution, and then left under moderate stirring conditions for 24 h at room temperature (r. t.), obtaining finally a transparent, viscous, homogeneous solution. Then, filtration was carried out using a standard filter paper (PRAT, DUMAS, France) under vacuum. Second, CHT : PVA based membranes were prepared following the procedure described in [17, 18]. Briefly, the CHT : PVA membrane was made of a mixture containing 1.0 wt% CHT solution in 2 wt% acetic acid aqueous solution and 4.0 wt% PVA in order to get an homogeneous gel with a 50/50 ratio (w/w).

The CHT : CS based membrane was made of 1.0 wt.% CHT in 1.0 % acetic acid and 1 wt.% CS in 2 M NaCl aqueous solution. Both solutions were adjusted to pH 5.5 using 2 M NaOH or 1.0 % acetic acid following the procedure reported in [15]. 200 mL of both CHT and CS solutions were heated up at 37 °C for 30 min, and then the CHT solution was added stepwise into the CS one at 37 °C under stirring condition. Thereafter, solution was stood about 24 h and the insoluble polymeric complex precipitated on the bottom

of the flask. Then, the supernatant was carefully removed and the remaining polymeric suspension was gently centrifuged for 15 min. The solid obtained was resuspended in 30 mL of the above supernatant solution and then dropped cast equally on four plastic Petri dishes and placed in an incubator at 35 °C until they reached dryness.

For the preparation of CHT, CHT : PVA and CHT : CS membranes modified either with AC or AC/CNT a certain amount of 1.0 % (w/v) acidic aqueous solution containing 0.2 % (w/v) of CNT dispersed in 1.0 wt.% AC. A solution of AC/CNT was added separately to the polymeric CHT based solution in a 15 mL glass flask, and then left for 24 h under stirring conditions. The homogeneous mixture exhibited a light brown color for AC and dark, brown/black one for AC/CNT containing solutions. Thereafter, solutions were degassed using an ultrasonic bath for 5 min and dropped cast on polystyrene Petri dishes (5.3 cm diameter) and placed in an incubator at 35 °C until complete evaporation of solvent. The total evaporation took place between 3 and 4 days of drying in the incubator at 35 °C. The membranes were carefully removed from the plate and weighed. Membranes stand for CHT(AC), CHT : PVA(AC) and CHT : CS(AC) when modified with AC and CHT(AC/CNT), CHT : PVA(AC/CNT) and CHT : CS(AC/CNT) when modified with the AC/CNT inch. All membranes were generally stored in water in a refrigerator at 4 °C.

2.3. Characterization techniques

2.3.1. Thickness and weight of the membrane

After a long period of dryness, all membranes were peeled off the Petri dish, and thickness at least was measured at different spots ($N=5$) of the membrane surface in order to obtain an average thickness. Thickness measurements were carried out using a micrometer (Mitutoyo Corp., Kawasaki, Japan) with an accuracy of 0.001 mm.

2.3.2. Degree of absorption of water in the membranes (W_u)

The absorption of water or swelling of the membranes is the ability to adsorb and desorb water molecules. The percentage of water absorption of the membranes was determined by the weight difference before and after hydration using equation (1),

$$W_u(\%) = \frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{dry}}} 100, \quad (1)$$

where W_{wet} is the weight of the membrane with absorbed water after a certain time, W_{dry} is the weight of the dried membrane and W_u is the percentage of absorbed water. W_u was performed at a controlled temperature of 25 °C. The surface of the wet membrane was carefully dried using filter paper in order to remove water molecules from the membrane surface.

2.3.3. Electrochemical impedance spectroscopy (EIS)

Membranes activation was carried out by immersing the membranes in 1.0 M NaOH for 1 h and then thoroughly washed with doubly distilled water to remove the excess of NaOH. Finally, the membranes were ready for the determination of the ionic conductivity.

A Bio-Logic VMP-300 potentiostat/galvanostat equipped with an impedance module with open circuit power was used for the EIS measurements. All membranes were dried using a filter paper in order to remove out the surface water from the membrane and then located at the electrochemical cell. EIS measurements were taken using a two-electrode Swagelok cell type, which consists of a Teflon coating with two cylindrical electrodes of stainless steel of 1.13 cm² each. The membrane was placed between both stainless steel disks in its activated OH- and wet form. The EIS cell was subjected to a constant pressure until reproducibility of the Nyquist plots.

Measurements were performed at open circuit potential (potentiostatic method). EIS experiments were measured over a frequency range between 100 Hz and 1.0 MHz with an amplitude potential of 0.01 V at (20 ± 2) °C. The specific ionic conductivity σ (mS cm⁻¹) was calculated using the equation (2). The specific ionic conductivities were expressed as a total contribution of carbonate/bicarbonate and hydroxyl anions to the anionic conductivity through the membrane

$$\sigma = L/RA, \quad (2)$$

where σ is the average thickness of the membrane in cm, R is the resistance of the membrane in Ohm and A is the area of the membrane in cm². The R value was obtained by the extrapolation of the Nyquist plot associated with the diffusion control – to real impedance when imaginary Z equals zero [19, 20]

2.3.4. X-ray diffraction (XRD)

Scanning electron microscopy (SEM)

XRD diffractograms were collected on a Philips X'Pert PRO MPD diffractometer operating at 45 kV and 40 mA, equipped with a Johansson germanium

monochromator which provides Cu K α 1 radiation ($\lambda = 1.5406 \text{ \AA}$), and a detector of Pixcel solid angle, with a pitch of 0.05 deg. SEM images were taken using a HITACHI S-3000N microscope, which works at 30 kV with a Bruker XFlash 3001 X-ray detector. Before the morphology and the XRD analyses, activated membranes were allowed to be dried at r.t.

3. Results and discussion

3.1. Thickness and water uptake of membranes

Fig. 2 shows a series of photographic pictures relative to pristine and modified CHT, CHT : PVA and CHT : CS based membranes by using the derivative AC and the inch AC/CNT. The pristine membranes are transparent compared to the homogeneous, brownish CHT(AC) membrane doped with AC, though the cumulenic derivative seems to be more concentrated on the periphery of the membranes -a slightly higher AC concentration in CHT(CS) membrane is also observed likely attributed to the slight uneven surface during the drying process of the membranes. However, CHT(AC/CNT) membrane displays a more homogeneous distribution of the carbonaceous compounds according to Fig. 2 (image *a*, iii). Average thickness of the membranes CHT, CHT(AC) and CHT(AC/CNT) were 249, 166 and 254 μm , respectively within a 10 % of experimental error. No significant differences were obtained between the thickness and the type of the filler.

The CHT : PVA(AC) membrane also exhibits a smooth surfaces similar to that presented by the CHT(AC), as is shown in Fig. 2 (image *b*, ii) with heterogeneous distribution of AC. In addition, CHT : PVA(AC/CNT) membranes exhibit a rougher surface with visible suspended particles seen at naked eye, which were linked to the presence of the CNT. The presence of PVA provided more rigidity to the membrane compared to those made only by CHT. The average thickness of the membranes were 289, 195 and 100 μm for CHT : PVA, CHT : PVA(AC) and CHT : PVA(AC/CNT), respectively.

Fig. 2*c* also shows the distinct pristine and modified CHT : CS membranes. The incorporation of CS into the polymeric CHT matrix made the membrane white. Moreover, the addition of AC or AC/CNT fillers provided more rigidity and roughness to both CHT : CS(AC) and CHT : CS(AC/CNT) membranes. With regards the thickness of the membranes, they exhibited an average value of 84, 125, 245 μm for CHT : CS, CHT : CS(AC) and CHT : CS(AC/CNT), respectively.

Table 1

Water uptake and ionic conductivities of CHT, CHT : PVA and CHT : CS based membranes

Membrane	W_u , %	σ_m , mS cm ⁻¹ *
CHT	164.3	0.063 ± 0.072
CHT(AC)	283.9	0.183 ± 0.159
CHT(AC/CNT)	184.6	0.170 ± 0.127
CHT: PVA	183.0	0.106 ± 0.110
CHT : PVA(AC)	261.6	0.201 ± 0.181
CHT : PVA(AC/CNT)	183.8	0.136 ± 0.117
CHT : CS	15.8	0.309 ± 0.310
CHT : CS(AC)	12.1	0.558 ± 0.295
CHT : CS(AC/CNT)	17.0	0.267 ± 0.246

* Measurements were performed in triplicate and values denote the average value ± the standard deviation of the average.

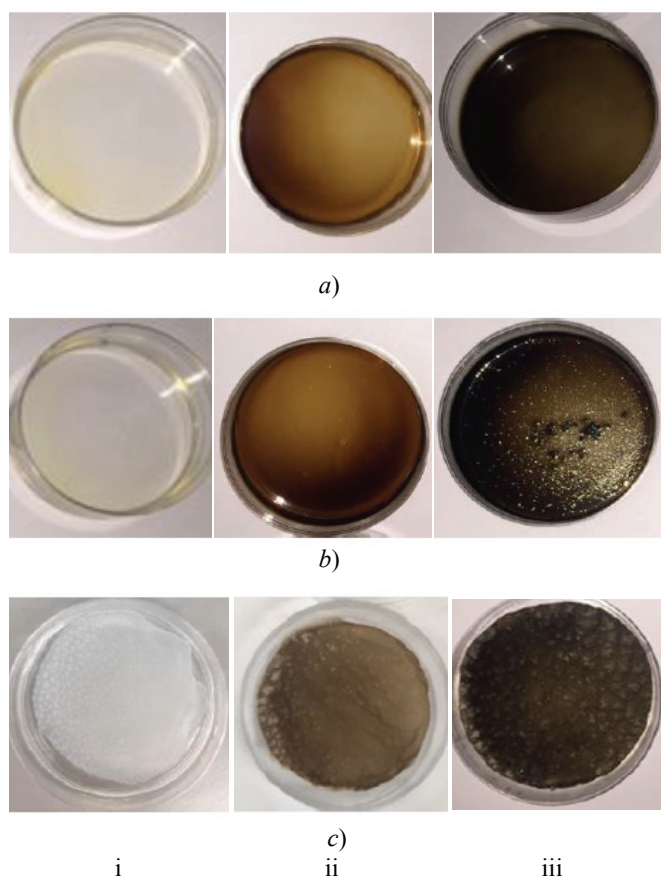


Fig. 2. Photographs of the different membranes synthesized in this work:

a – i) CHT, ii) CHT(AC), iii) CHT(AC/CNT);
b – i) CHT : PVA, ii) CHT : PVA(AC),
 iii) CHT : PVA(AC/CNT); *c* – i) CHT : CS, ii) CHT : CS (AC),
 and iii) CHT : CS(AC/CNT)

3.2. Water uptake

Water uptake (W_u) results in a significant degree of swelling, being responsible for dilution of hydroxyl anion concentration, which decreases membrane ionic conductivity, durability and membrane performance in electrochemical devices. The results on the W_u of the pristine and modified CHT, CHT : PVA and CHT : CS membranes are compiled in Table 1. The swelling capacity can depend on the interaction of water with polar groups and/or charged groups on the polymeric membrane. The value of W_u of the pristine CHT and CHT : PVA membranes are similar to those reported in [21], although the W_u value was lower with respect to the CHT membrane. As is depicted in Table 1, the membranes with the highest W_u corresponds to those comprising AC, i.e. for CHT(AC) and CHGT : PVA(AC/CNT). Due to the major presence of amino groups at the AC structure, they could have more affinity for hydrogen bonds, improving the

hydrophilic properties of the membrane and therefore the W_u of membranes based on CHT and CHT : PVA membranes.

However, when the CS polymer is mixed with CHT, W_u is dramatically reduced over ten times that values shown for the pristine membranes made of CHT and CHT : CS, as shown in Table 1. Moreover, the addition of AC into the polymeric matrix has no significant effect on the increase of W_u , depicting a slight reduction up to 12.1 which is likely attributed to the still poor charged species on the polymeric matrix or simply to the low accessibility or high blockage of water into the polymeric matrix, provoking a rigidity increase of the structure. Nonetheless, the addition of AC/CNT into the polymeric matrix of CHT : CS led to a slight increase in W_u , but without significant increase compared to the series of the membranes. In summary, the low water absorption that takes place for the CHT : CS membranes is due to the strong interaction between CS and CHT polymers yielding few hydrophilic functional groups susceptible to interaction with water molecules.

3.3. Anionic conductivities of CHT, CHT : PVA and CHT : CS based membranes

Table 1 also shows the average ionic conductivity values of the pristine and modified CHT, CHT : PVA and CHT : CS membranes. The ionic conductivity that is measured is basically due to the movement of the carbonate/bicarbonate/ and hydroxyl ions; the former ones caused by a partial carbonation) of the membrane

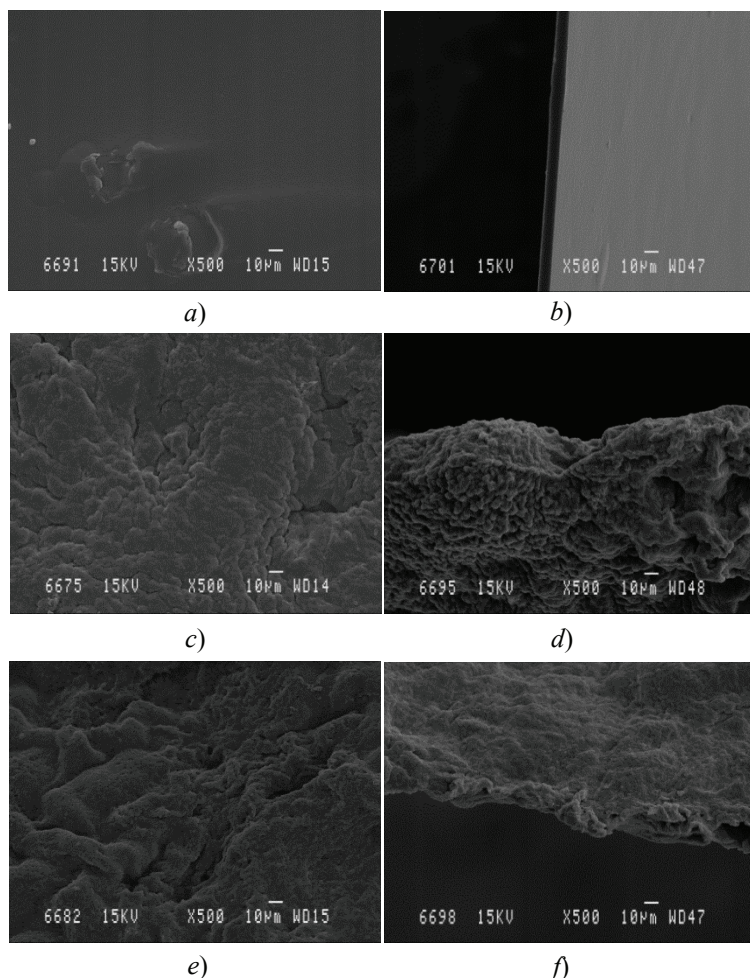


Fig. 3. SEM images of CHT : PVA(AC) (a, b), CHT : CS (c, d), and CHT : CS (AC) (e, f):

left column corresponds to plane section of the membrane surfaces, and right column corresponds to cross section of the membranes

exposed in air. As was expected, the anionic conductivity σ_m for the CHT membrane was the smallest of the series, whereas the use of PVA and CS into the polymeric matrix slightly increased for the pristine CHH : PVA and provided a much higher σ_m for the CHT : CS, the later associated likely with the lowest W_u of the series.

The CHT : PVA(AC) exhibits the highest σ_m with a value of 0.201 mS cm^{-1} whereas the CHT(AC) shows a σ_m with a value of 0.183 mS cm^{-1} . Nonetheless, the CHT : PVA (AC/CNT) membranes resulted to be detrimental for an enhancement of the σ_m probably due to the negative effect of CNT on the positive contribution of the cumulenlic derivative inside the polymeric matrix.

With regards the CHT : CS blend membranes, results show that σ_m value for the pristine membrane is almost three fold that one of the CHT membrane. This can be attributed to the low W_u and/or structural

changes or crystallinity in the polymeric matrix (*vide infra*) which might lead to a better ions movility through the membrane. Moreover, the CHT : CS(AC/CNT) membranes displayed lower σ_m compared to the highest σ_m depicted for the CHT : CS(AC) membrane (see Table 1).

3.4. Scanning electron microscopy (SEM)

The results obtained by the analysis of the ionic conductivities of all membranes explored in this series reveal that the incorporation of the dispersant AC inside the polymeric matrix of CHT : PVA and CHT : CS as well as the introduction of CS into the CHT exhibited the highest anionic conductivities. Accordingly, we next explored the morphology and crystallinity of CHT : PVA(AC), CHT : CS and CHT : CS(AC). Fig. 3 depicts the SEM images of the in plane and cross section of the above chosen membranes. The membrane CHT : PVA(AC) shows a smooth surface in plane section; it is also clear to identify a compact structure with the absence of holes or cracks at the cross section of the membrane, which might be related to the hydrogen bond-like interactions that take place mostly between the amino groups of AC and the hydroxyl and amino functional groups of the polymer mixture. As far as the contribution of CS inside the polymeric matrix, the membrane CHT : CS depicts a rough, homogeneous surface although it also reveals few morphological differences compared to the same membrane with the presence of AC. In this regard, it is worth noting from the cross section of Fig. 3f that a more compact structure compared to the pristine one is observed (see Fig. 3d). Once again, we can establish that the presence of the dispersant agent AC provides a much smoother structure in the cross section of the membrane compared to the pristine CHT : CS membrane.

3.5. X-ray diffraction

Fig. 4 depicts the X-ray diffraction (XRD) measurements of the CHT : PVA(AC), CHT : CS and CHT : CS(AC) membranes, which might shed light on the crystallinity of the blend membranes. It is well known that PVA and CHT exhibit a semi-crystalline structure [22]; however, the introduction of the AC additive likely alters the crystalline structure of the polymers. The CHT : PVA(AC) membrane displays a pronounced peak at 20° , which is assigned to the crystallites of PVA and CHT in agreement with results

reported in the literature [23]. The crystallinity of the membranes is due to hydroxyl groups in the side chain of CHT and PVA, which forms intramolecular hydrogen bonds. Moreover, the AC inside the matrix polymer, might produce a much stronger cross-linking bonding between the OH and NH_2 groups inside the CHT : PVA matrix and the NH_2 groups in AC, thereby weakening the intramolecular hydrogen bonds between CHT and PVA polymers. Therefore, this leads to a slight decrease in the crystallinity of the membranes compared to the other membranes. In addition, the CHT : CS membrane displays a slight reduction of the peak at 20° , which demonstrates a low crystallinity compared to the modified membrane CHT : CS(AC). This peak is due to the appearance of the CS polymer as well as the CHT [24]. Furthermore, the CHT : CS(AC) membrane exhibits two diffraction peaks where one of them corresponds to the CHT : CS mixture at 20° and the other with the presence of AC at 10° , which is also shown for the membrane CHT : PVA(AC). The addition of AC inside the CHT : CS matrixes reduces the crystallinity of the membrane associated with a much stronger electrostatic interaction between NH_3 of the polymer formed between CHT + AC and $-\text{NH}_2$ and OSO_3 of the CS.

A comparison between the CHT : PVA(AC) and CHT : CS(AC) provided unclear difference, although the presence of PVA makes the membrane slightly less crystalline, which may be ascribed to the lower intensity and broader peak at 20° . The decreasing trend in crystallinity of the membranes was as follows: CHT : CS > CHT : CS (AC) > CHT : PVA(AC). In this regard, the ionic conductivity of our membranes is also related to crystallinity. The slightly high crystallinity of CHT : CS membrane discourages the transport of carbonate / bicarbonate and / hydroxyl anions through the membrane, i.e. the ionic conductivity of CHT : CS is less compared to its relative modified with AC. Moreover, the decreasing trend of W_u from the CHT : CS till the CHT : CS(AC) correlates well with an increase in ionic conductivity and a reduction of the

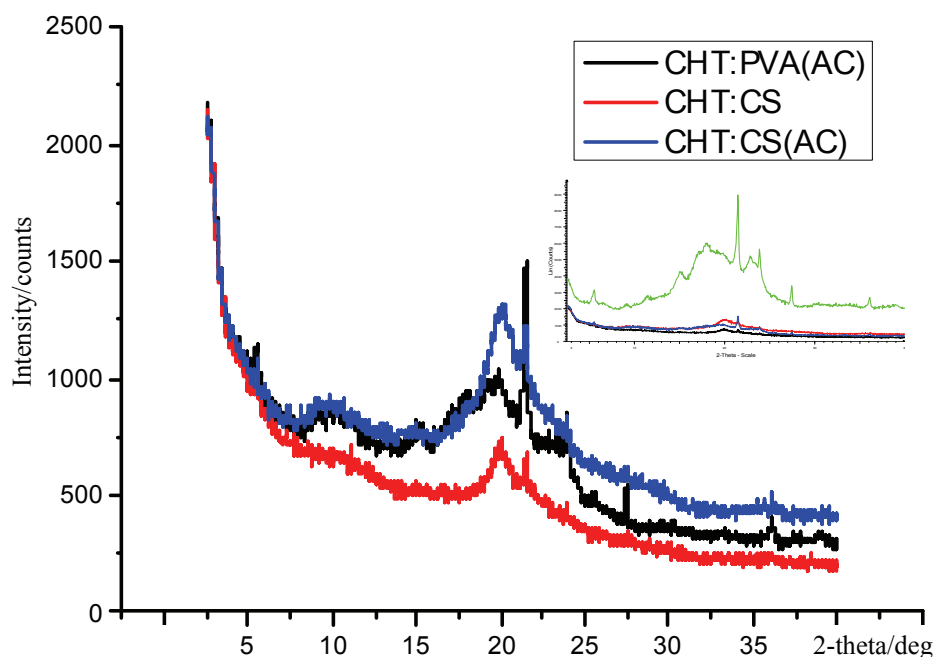


Fig. 4. XRD diffractograms of CHT : PVA(AC) (black trace), CHT : CS (red trace) and CHT : CS(AC) (blue trace)
(Fig. inset. XRD diffractogram of the same membranes but including the XRD diffractogram of modelling clay (green trace) which is used as support of the membranes for comparison purposes)

crystallinity of the AC containing membrane. Finally, when comparing both membranes CHT : PVA(AC) and CHT : CS(AC), the presence of CS instead of CHT favored positively the reduction of W_u and the enhancement of the ionic conductivity.

4. Conclusion

Chitosan polymer, and chitosan-poly (vinyl alcohol) and the chitosan-chondroitin- blend polymers modified with the dispersant agent aminocumulene AC and the aqueous inch made of multi-walled carbon nanotubes in the presence of AC were performed for applications as anionic alkaline exchange membranes. The membranes were examined through the determination of water uptake and the carbonate/ bicarbonate and hydroxyl anionic conductivity. The effect of the incorporation of the inorganic additive AC in membranes CHT and CHT : PVA enhanced the percentage of W_u and the value of the anionic conductivity, whereas the incorporation of the inch (AC/CNT) exhibited more disadvantageous in terms of anionic conductivity. Moreover, the incorporation of CS into the CHT matrix instead PVA led to a notable reduction of W_u , but providing the highest increase of anionic conductivity of the membranes series. The membranes CHT : PVA(AC), CHT : CS and CHT : CS(AC) were chosen for the examination of the

morphology and the structure by SEM and XRD experiments. In this regard, the incorporation of AC into the CHT : PVA was almost negligible in terms of topological changes, while the presence of AC inside the CHT : CS gave rise to a more compact structure together with slight reduction of crystallinity.

Acknowledgements

The research was carried out at the expense of a grant from the Russian Science Foundation (project No. 15-13-10038). AG acknowledges the Presidential fellowship programme of the Ministry of Education and Science of the Russian Federation. Also LGC and JI are grateful to the Spanish MINECO through the project CTQ2016-76231-C2-2-R.

References

1. Dhrab, S.S.; Sopian, K.; Alghoul, M.A.; Sulaiman, M.Y. Review of the membrane and bipolar plates materials for conventional and unitized regenerative fuel cells. *Renewable & Sustainable Energy Reviews* 2009, *13*, 1663-1668, doi: 10.1016/j.rser.2008.09.029
2. Pettersson, J.; Ramsey, B.; Harrison, D. A review of the latest developments in electrodes for unitized regenerative polymer electrolyte fuel cells. *J. Power Sources* 2006, *157*, 28-34, doi: 10.1016/j.jpowsour.2006.01.059
3. Xu, T.W. Ion exchange membranes: State of their development and perspective. *J. Membr. Sci.* 2005, *263*, 1-29, doi:10.1016/j.memsci.2005.05.002
4. Markovic, N.; Gasteiger, H.; Ross, P.N. Kinetics of oxygen reduction on Pt(hkl) electrodes: Implications for the crystallite size effect with supported Pt electrocatalysts. *J. Electrochem. Soc.* 1997, *144*, 1591-1597, doi: 10.1149/1.1837646
5. Strathmann, H.; Grabowski, A.; Eigenberger, G. Ion-Exchange Membranes in the Chemical Process Industry. *Industrial & Engineering Chemistry Research* 2013, *52*, 10364-10379, doi: 10.1021/ie4002102
6. Merle, G.; Wessling, M.; Nijmeijer, K. Anion exchange membranes for alkaline fuel cells: A review. *J. Membr. Sci.* 2011, *377*, 1-35, doi: 10.1016/j.memsci.2011.04.043
7. Xu, D.; Hein, S.; Wang, K. Chitosan membrane in separation applications. *Mater. Sci. Technol.* 2008, *24*, 1076-1087, doi:10.1179/174328408x341762
8. Ma, J.; Sahai, Y. Chitosan biopolymer for fuel cell applications. *Carbohydr. Polym.* 2013, *92*, 955-975, doi: 10.1016/j.carbpol.2012.10.015
9. Wan, Y.; Creber, K.A.M.; Peppley, B.; Bui, V.T. Ionic conductivity of chitosan membranes. *Polymer* 2003, *44*, 1057-1065, doi: 10.1016/s0032-3861(02)00881-9
10. Kikelbick, G. Concepts for the incorporation of inorganic building blocks into organic polymers on a nanoscale. *Prog. Polym. Sci.* 2003, *28*, 83-114, doi: 10.1016/s0079-6700(02)00019-9
11. Maiti, J.; Kakati, N.; Lee, S.H.; Jee, S.H.; Viswanathan, B.; Yoon, Y.S. Where do poly(vinyl alcohol) based membranes stand in relation to Nafion (R) for direct methanol fuel cell applications? *J. Power Sources* 2012, *216*, 48-66, doi: 10.1016/j.jpowsour.2012.05.057
12. Feng, X.; Wang, X.; Xing, W.; Yu, B.; Song, L.; Hu, Y. Simultaneous Reduction and Surface Functionalization of Graphene Oxide by Chitosan and Their Synergistic Reinforcing Effects in PVA Films. *Industrial & Engineering Chemistry Research* 2013, *52*, 12906-12914, doi: 10.1021/ie402073x
13. Yang, J.-M.; Wang, S.-A. Preparation of graphene-based poly(vinyl alcohol)/chitosan nanocomposites membrane for alkaline solid electrolytes membrane. *J. Membr. Sci.* 2015, *477*, 49-57, doi: 10.1016/j.memsci.2014.12.028
14. Sousa, M.P.; Cleymand, F.; Mano, J.F. Elastic chitosan/chondroitin sulfate multilayer membranes. *Biomedical Materials* 2016, *11*, doi: 10.1088/1748-6041/11/3/035008
15. Rodrigues, M.N.; Oliveira, M.B.; Costa, R.R.; Mano, J.F. Chitosan/Chondroitin Sulfate Membranes Produced by Polyelectrolyte Complexation for Cartilage Engineering. *Biomacromolecules* 2016, *17*, 2178-2188, doi: 10.1021/acs.biomac.6b00399
16. Tkachev, A.G.; Melezhik, A.V.; Alekhina, O.V. New cumulene substance useful for producing nitrogen-containing carbon films, and for dispersing and exfoliating graphite materials, comprises chain of cumulated double carbon-carbon bonds, and has end groups comprising amino groups. RU2016137247-A; RU2661876-C2.
17. Garcia-Cruz, L.; Casado-Coterillo, C.; Irabien, A.; Montiel, V.; Iniesta, J. Performance Assessment of a Polymer Electrolyte Membrane Electrochemical Reactor under Alkaline Conditions – a Case Study with the Electrooxidation of Alcohols. *Electrochim. Acta* 2016, *206*, 165-175, doi: 10.1016/j.electacta.2016.04.110
18. Garcia-Cruz, L.; Casado-Coterillo, C.; Iniesta, J.; Montiel, V.; Irabien, A. Preparation and characterization of novel chitosan-based mixed matrix membranes resistant in alkaline media. *J. Appl. Polym. Sci.* 2015, *132*, 42240-42240.
19. Yun, S.-H.; Shin, S.-H.; Lee, J.-Y.; Seo, S.-J.; Oh, S.-H.; Choi, Y.-W.; Moon, S.-H. Effect of pressure on through-plane proton conductivity of polymer electrolyte membranes. *J. Membr. Sci.* 2012, *417*, 210-216, doi: 10.1016/j.memsci.2012.06.041
20. Niya, S.M.R.; Hoorfar, M. Study of proton exchange membrane fuel cells using electrochemical impedance spectroscopy technique - A review. *J. Power Sources* 2013, *240*, 281-293, doi: 10.1016/j.jpowsour.2013.04.011
21. Garcia-Cruz, L.; Casado-Coterillo, C.; Iniesta, J.; Montiel, V.; Irabien, A. Chitosan:poly (vinyl) alcohol composite alkaline membrane incorporating organic ionomers and layered silicate materials into a PEM electrochemical reactor. *J. Membr. Sci.* 2016, *498*, 395-407, doi: 10.1016/j.memsci.2015.08.040
22. Cheng, X.; Li, Y.; Zuo, Y.; Zhang, L.; Li, J.; Wang, H. Properties and in vitro biological evaluation of nano-hydroxyapatite/chitosan membranes for bone guided regeneration. *Materials Science & Engineering C-Biomimetic and Supramolecular Systems* 2009, *29*, 29-35, doi: 10.1016/j.msec.2008.05.008
23. Jia, Y.-T.; Gong, J.; Gu, X.-H.; Kim, H.-Y.; Dong, J.; Shen, X.-Y. Fabrication and characterization of poly (vinyl alcohol)/chitosan blend nanofibers produced by electrospinning method. *Carbohydr. Polym.* 2007, *67*, 403-409, doi: 10.1016/j.carbpol.2006.06.010
24. He, D.; Xiao, X.; Liu, F.; Liu, R. Chondroitin sulfate template-mediated biomimetic synthesis of nano-flake hydroxyapatite. *Appl. Surf. Sci.* 2008, *255*, 361-364, doi: 10.1016/j.apsusc.2008.06.151