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Impact of acid containing montmorillonite on the properties of Nafion® membranes

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Abstract

The counter-ions of montmorillonite have been exchanged for ammonium cations containing either a sulfonic acid or a carboxylic acid in order to improve the performances of sulfonated membranes in direct methanol fuel cell. These layered silicates have been dispersed within Nafion® by solution mixing. Comparison with conventional organo-modified montmorillonite (Cloisite 30B) shows that the incorporation of carboxylic acid in the clay galleries improves the filler dispersion and, consequently, the methanol barrier properties. Moreover, the negative impact of Cloisite 30B on the ionic conductivity is restricted.

Keywords: Fuel cell; Nafion; Montmorillonite

1. Introduction

Direct methanol fuel cell (DMFC) is a possible option for electricity generation because of a high energy density and simplicity of operation compared to systems in which a reformer is used to produce hydrogen from liquid fuel. The DMFC technology relies on fuel cells equipped with a proton exchange membrane (PEMFC), that plays the role of the electrolyte. Nowadays, few membranes have been tested with some success, including perfluorosulfonate ionomer (PFSI), such as Nafion® [1-3], polyaromatics, such as sulfonated polysulfone (PSU) [4-6], sulfonated polyetheretherketone (SPEEK) [7-9], sulfonated polyphenylene oxide (SPPO) [10-11] and polybenzimidazole (PBI) [12-14]. Except for PBI that needs doping by a strong acid for being conductive, all the other polymers combine high chemical stability and high ionic conductivity. Nevertheless, these polymers suffer from drawbacks that must be overcome. Indeed, the ionic conductivity at high temperature (T>100 °C) must be improved which implies a better water retention at these temperatures and the methanol permeability of the membrane must be decreased without sacrificing too much the ionic conductivity (maximization of the balance between protonic conductivity (C) and methanol permeability (P), i.e. the C/P ratio (Δ)), which is a challenging task because hydrated proton and methanol have similar properties.

Two main strategies have been proposed to tackle these problems. The first one consists of the synthesis of new polymer membranes. For example, Kim et al. have synthesized new sulfonated poly(arylene ether sulfone) copolymers with a C/P ratio three times higher than Nafion® [15]. The second strategy relies on the modification of ion-conducting polymers by inorganic fillers. For instance, several authors proposed to incorporate silica particles in Nafion® by in situ polycondensation of tetraethoxysilane [3 ; 17-18]. An improved water retention at high temperature and a C/P ratio approximately 1.5 better than neat Nafion® were reported. Similarly, Ruffmann et al. added sulfonated polyetherketone (SPEK) with both zirconium phosphate (ZrP) and zirconium oxide (ZrO_2) [19]. Both the methanol permeability and the ionic conductivity were increased upon addition of ZrP, whereas the opposite effect was observed with ZrO_2. Actually, the best compromise was reported for SPEK membranes loaded with 20 wt% of ZrP and 10 wt% of ZrO_2. The C/P ratio was then increased 2.3 times compared to unmodified SPEK membranes. Kim et al. dispersed Pd nanoparticles within Nafion® [20]. These nanoparticles trigger water formation as result of oxygen reduction and also methanol consumption by oxidation. This type of self-humidified membrane with a lower methanol cross-over exhibits a C/P ratio of 1.5 higher than neat Nafion®.

Recently, multi-layered alumino-silicates, mainly montmorillonite (MMT), have been used to improve the performances of Nafion® [21-25] and SPEEK fuel cell membranes [26] with a special effort for decreasing the methanol permeability. Indeed, several studies showed that addition of this type of nanofiller is able to improve the barrier properties of several polymers towards various gases, as result of a high length-to-width ratio of the additive. Upon dispersion and complete exfoliation of 1–5 wt% of layered alumino-silicates, the permeability of the polymer matrix can be decreased by 60% [27-31].

However, the addition of multi-layered alumino-silicates results in decreased ionic conductivity in parallel to lower methanol permeability [21-24]. Rhee et al. have proposed to overcome this drawback by grafting an organic sulfonic acid containing compound onto the surface of the alumino-silicates layers by silane condensation [25]. However, this strategy suffers from the poor thermal stability of the modified MMT between 100 and 200 °C.

In this study, we propose an alternative strategy to prepare more thermally stable modified montmorillonite that consists in the exchange of the counter-ions of montmorillonite by alkyl ammonium cations containing either a sulfonic acid or a carboxylic acid group. The accordingly modified nanofillers have been dispersed within Nafion® by solvent casting. Methanol permeability and ionic conductivity are the main properties of the prepared membranes that have been measured.

2. Experimental part

2.1. Materials

Nafion® solution (5 wt%) in low aliphatic alcohols, 6-aminocaproic acid (ACA), dimethyloctadecyl(3-sulfopropyl) ammonium hydroxide (DMOSPA) were purchased from Aldrich. Behenyl betaine (BHB) was supplied by Greyhound chromatography. Native sodium montmorillonite (Cloisite Na) with a cationic exchange capacity (CEC) in the 80–95 mequiv/100 g range and montmorillonite organomodified by hydroxyl containing alkyl ammonium (Cloisite 30B) (Fig. 1) were supplied by Southern clay products (USA). H-Substituted montmorillonite (Cloisite H^+) was prepared by ion-exchange of Na-montmorillonite with a hydrochloric acid solution. Typically, a 1-g sample of air-dried Na-montmorillonite was treated with 50 ml of 10^{-1} M HCl solution for 3 h [32]. The Cloisite suspension was filtered, and the final product was thoroughly washed with distilled water. MMT (1 g) was modified by ACA and by BHB, respectively, by mixing with 3 equiv of ACA (or BHB) with respect to Na^+ and 3 equiv of HCl in a 50/50 THF/water mixture, at 40 °C for 3 h. MMT (1 g) was also modified by DMOSPA by mixing with 1 equiv of DMOSPA and 1 equiv of HCl in a 25/75 THF/water mixture at 40 °C for 3 h.

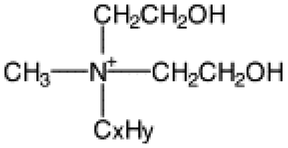

Fig. 1. Structure of the counter-ion in Cloisite 30B (x=14 (5%), 16 (30%) and 18 (65%)).

2.2. Membrane preparation

The Nafion® membranes were prepared by addition of a required amount of montmorillonite to a Nafion® solution in a mixture of water and low aliphatic alcohol added with ethylene glycol (1.5 equiv compared to Nafion®). This solution was ultrasonicated before casting and evaporation at high temperature (130 °C). The membranes were stored in deionized water. Before characterization, they were pre-treated in a standard manner, i.e. 1 h in a boiling 5%H_2O_2 aqueous solution, 1 h in boiling 1 M H_2SO_4 solution, and repeated washing with Milli Q water (18 MΩ).

2.3. Transmission electron microscopy (TEM)

Clay dispersions were observed with a transmission electron microscope PHILIPS M100 at an accelerating voltage of 100 kV. Thin sections (90 nm) were prepared by ultramicrotomy (ULTRACUT E from REICHERT-JUNG) at −130 °C. Micrographs were analyzed by using the KS 100 (Kontron Imaging System) software.

2.4. X-ray diffraction (XRD) and thermogravimetric analysis (TGA)

Inter-layer distances of native and modified montmorillonites were measured by X-ray diffraction (XRD). XRD patterns were recorded with a Siemens D5000 diffractometer with the Cu Kα radiation. XRD data were collected between 1.5 and 15° by step of 0.01° with a X-ray generator at λ=0.154 nm.

Thermogravimetric analysis (TGA) was performed under a nitrogen flow (60 cm^3/min) at a heating rate of 20 °C/min, from room temperature to 800 °C, with a Hi-Res TGA Q500 from TA Instruments.

2.5. Methanol permeability [33]

Methanol permeability was measured with a two-compartment cell. One compartment (V_A=100 ml) was filled with a mixture of methanol (8 vol%) and 1-butanol (0.2 vol%) in deizoned water. The other compartment (V_B=100 ml) was filled with a 1-butanol (0.2 vol%) solution in deizoned water. The membrane (surface area=28 cm^2) was clamped between the two compartments and the methanol concentration in the receiving compartment was measured as a function of time by gas chromatography with 1-butanol as an internal reference. The time dependence of the methanol concentration agreed with Eq. (1).

$$c_B(t) = \frac{A}{V_B}\frac{DK}{L}c_A(t-t_0) \tag{1}$$

where c is the methanol concentration, A and L are the membrane area and thickness, respectively, D and K stand for the methanol diffusivity and the partition coefficient between the membrane and the adjacent solution, respectively. D was assumed constant throughout the membrane, and K is independent of concentration. The product DK is the membrane permeability, calculated from the slope of the (c_BL) vs time straight line. For each membrane, the measurements were repeated at least three times and more if poor consistency was observed. The relative error was found smaller than 10%.

2.6. Ionic conductivity

The cell is schematized in Fig. 2. Current was fed to the membrane (4×1 cm^2) by two platinum (wires) electrodes 4 cm apart. Two platinum wires 2 cm apart allowed the potential drop along the membrane to be measured. A rod is used to press the membranes on the Pt wires.

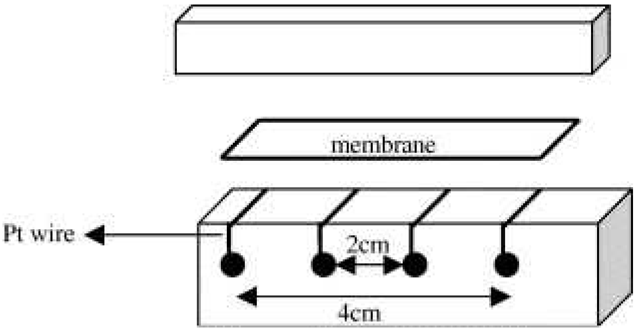

Fig. 2. Schematic view of the cell used for measurement of the ionic conductivity.

These electrodes were screwed in a polycarbonate support riddled with holes that allowed the membrane to be equilibrated with the atmosphere.

Measurements were reported for 100% humidity, at room temperature. The membrane conductivity was thus measured in the longitudinal direction and calculated by Eq. (2).

$$\sigma = \frac{l}{RS} \tag{2}$$

where σ is the ionic conductivity, l the distance between the reference electrodes, R is the resistance of the membrane, and S is the cross-sectional area.

Impedance was measured in the frequency range from 1 Hz to 500 kHz, with a potentiostat and a frequency-response analyser (Autolab model PGSTAT 30). For each membrane, the measurements were repeated at least three times and more if poor consistency was observed. The relative error was found smaller than 5%.

3. Results and discussion

3.1. Characterisation of modified MMT

Native MMT and H^+-MMT have been modified by exchange of the internal counter-ions by ammonium cations containing, respectively, a carboxylic acid group and a sulfonic group, as schematized in Fig. 3. The efficiency of this counter-ion exchange has been determined by thermogravimetric analysis. Fig. 4 shows that native MMT (Cloisite Na) is stable up to 550 °C, except for a weight loss at low temperature due to residual water. A weight loss is observed for all the modified MMT at higher temperature (>190 °C), which is characteristic of the ammonium cations involved. The temperature range in which neat ammonium cations start to degrade and are completely lost is listed in Table 1 and compared to MMT containing each of these cations. ACA is a small molecule that evaporates before degradation, which explains why the weight loss is complete over only 20 °C, in contrast to BHB and DMOSPA, which require at least 120 °C for 100 wt% loss to be observed. After incorporation in MMT, the weight loss profile of the carboxylic acid containing ammonium cations is shifted towards higher temperature, which is the signature of strong interaction between these ammonium cations and MMT. In contrast, the sulfonic acid containing ammonium cation starts to degrade at the same temperature before and after dispersion within MMT, and a two-step profile is observed for the modified MMT, consistent with interaction of only a part of the ammonium cations with the nanoclay. The theoretical weight loss reported in Table 1 has been calculated on the assumption that each Na^+ or H^+ cations have been actually exchanged for an ammonium cation. The exchange yield is high for the two carboxylic acid containing ammonium cations, in contrast to the sulfonic acid counterpart. The difference in acidity between MMT-H^+, carboxylic acid and sulfonic acid can account for this observation. Indeed, the acidity of MMT-H^+ is in between that of the two acids [34], which means that the equilibrium, shown in Fig. 5, is not displaced in the same direction and that organomodification of MMT is favourable in case of carboxylic acid containing ammonium and not when a sulfonic acid is involved. It must be noted from Table 1 that all the modified montmorillonites are thermally stable up to 190 °C.

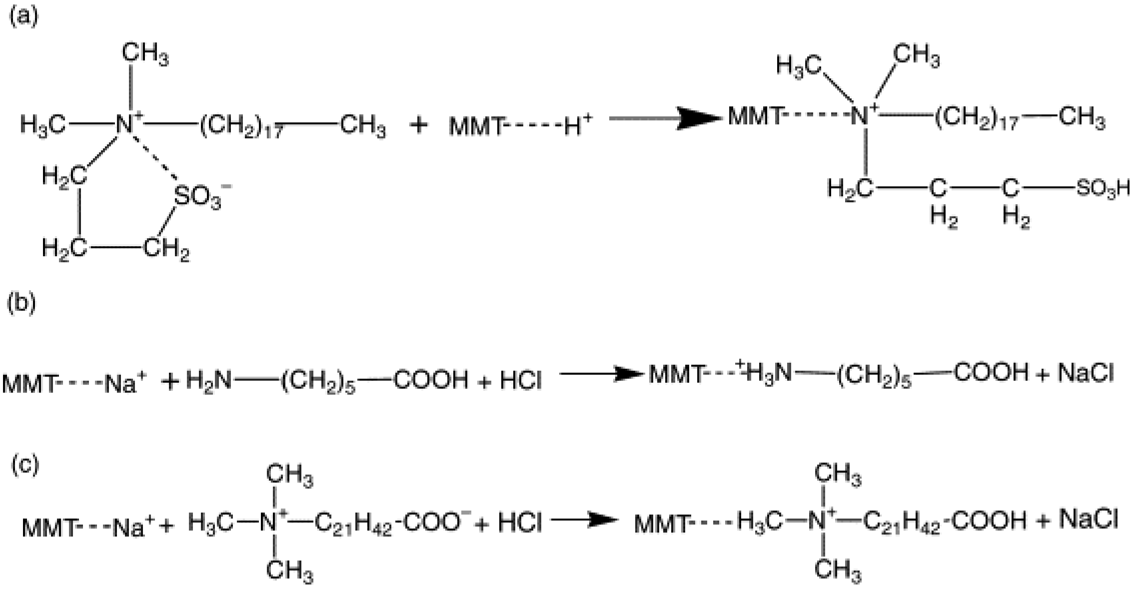

Fig. 3. Schematic structure of the ammonium cations involved in the cation exchange with MMT: (a) dimethyloctadecyl(3-sulfopropyl) ammonium (hydroxide) (DMOSPA), (b) 6-aminocaproic acid (ACA) and (c) behenyl betaine (BHB).

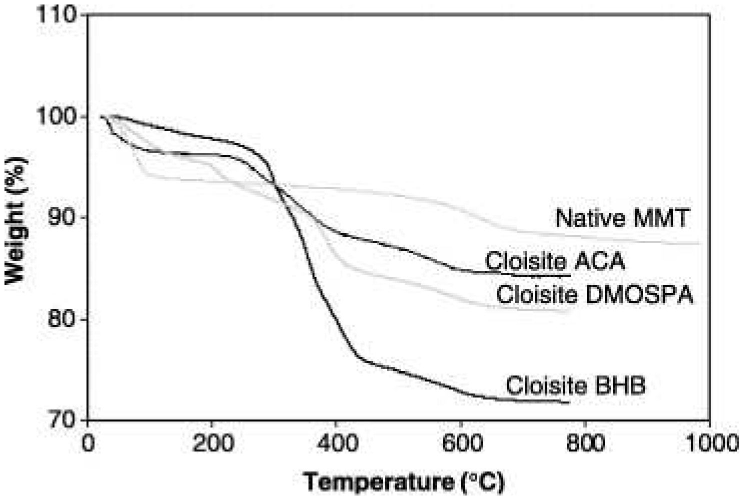

Fig. 4. TGA curves for native MMT, Cloisite DMOSPA, Cloisite ACA and Cloisite BHB

Table 1. TGA data for Cloisite DMOSPA, Cloisite ACA and Cloisite BHB and the parent ammonium cations

	Temperature range (°C)	**Theor. wt. loss (%)**	**Exp. wt. loss (%)**	**Exchange yield (%)**
Cloisite ACA	237–412	11.5	8.1	71
Cloisite BHB	264–456	28.4	22.7	80
Cloisite DMOSPA	190–441	29.5	6.7	22.5
ACA	185–205		100	
BHB	190–350		100	
DMOSPA	190–316		100	

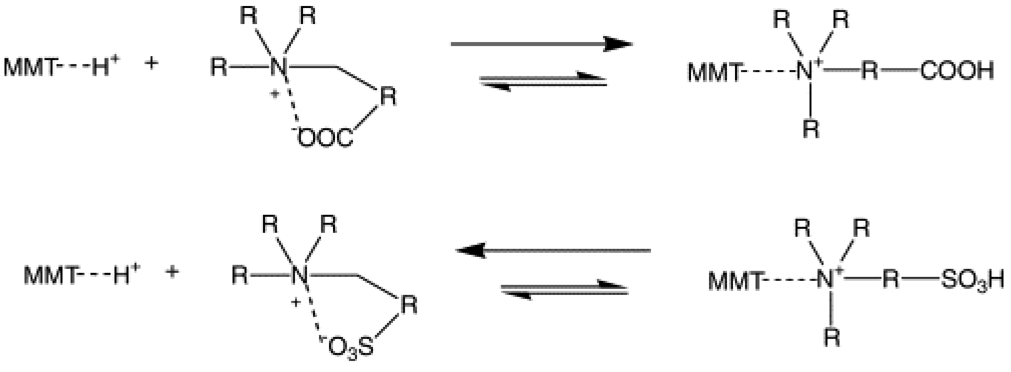

Fig. 5. Equilibrium of cation exchange between H^+-MMT and acid containing ammonium cations.

The counter-ion exchange has also been analyzed by X-ray diffraction, i.e. by the measurement of the interlayer distance of MMT. Indeed, this distance is expected to increase as result of the exchange of the original sodium cations for more voluminous ones. Fig. 6 compares the X-ray diffractograms for native montmorillonite and the three modified samples. The interlayer spacing of MMT is actually increased from 1.18 to 1.28 nm for Cloisite ACA, to 1.4 nm for Cloisite DMOSPA, and to 2.02 nm for Cloisite BHB. The small increase observed for Cloisite DMOSPA is the consequence of the poor efficiency observed for the counter-ion exchange. This increase is even smaller in case of Cloisite ACA because of the small size of the cation. The interlayer spacing of Cloisite BHB is largely increased as result of the high efficiency of the exchange of this voluminous counter-ion.

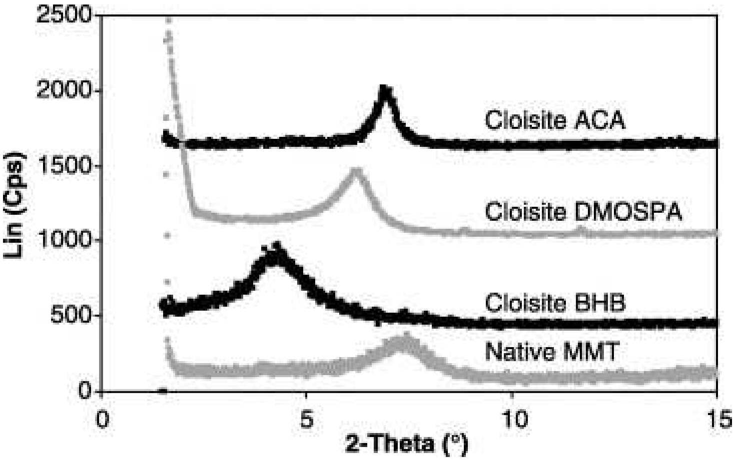

Fig. 6. X-ray diffraction patterns for native MMT, Cloisite DMOSPA, Cloisite ACA and Cloisite BHB.

Because the exchange of H^+ of H^+-MMT for the sulfonic acid containing ammonium cation is too low for improving the dispersion of MMT in the sulfonated polymer, only the Cloisite ACA and Cloisite BHB samples have been studied further.

3.2. TEM analysis

TEM micrographs for Nafion® membranes prepared by solvent casting are shown in Fig. 7. The gross dispersion observed for native MMT is only slightly improved when MMT is modified by hydroxyl containing ammonium cations (Cloisite 30B). In contrast, Cloisite BHB is remarkably dispersed within Nafion®. Although the nanoclay is not completely exfoliated, individual platelets can be observed within stacks of few of them, which result in a highly anisotropic filling of the polymer. This substantial improvement indicates that there should be favourable interactions between the acid groups of BHB and the sulfonic acid functions of Nafion® during mixing so contributing to the delamination of the silicate layers. Dispersion of Cloisite ACA is not as good as that one of Cloisite BHB, which might reflect the negative impact of the shorter spacer between the ammonium and the acid in ACA (5 carbon atoms in ACA vs 21 in BHB) on the interaction with the sulfonic acid function of Nafion®.

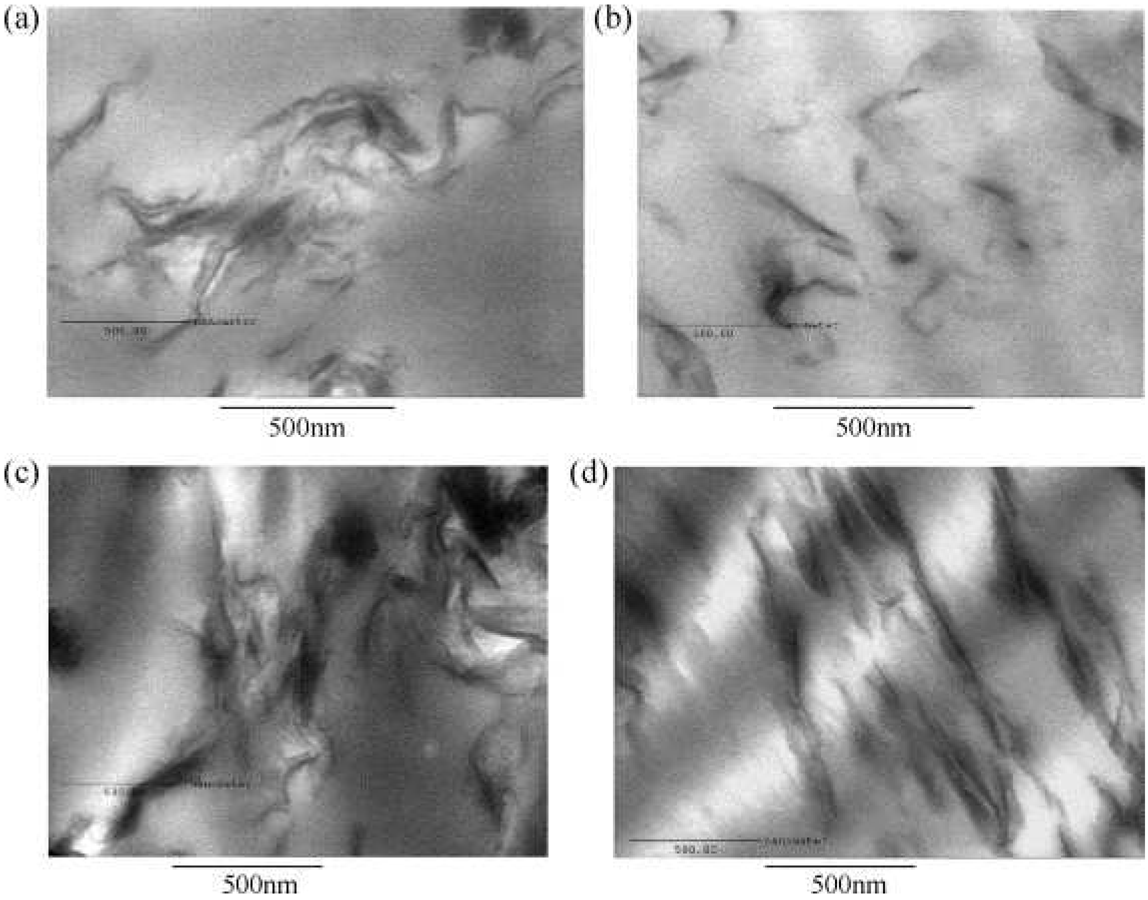

Fig. 7. TEM micrographs for Nafion® membranes filled with 2 wt% of (a) native MMT; (b) Cloisite 30B; (c) Cloisite ACA and (d) Cloisite BHB.

MMT dispersions have also been analysed by X-ray diffraction (Fig. 8), which gives information on the interlamellar distance of the silicate additive. Indeed the diffraction peak characteristic of the clay remains unchanged in case of dispersion without intercalation and exfoliation. A shift of the diffraction peak towards larger interlamellar distance is the signature of chain intercalation, whereas this peak is no longer observed in case of exfoliation. The poor dispersion of native MMT and Cloisite ACA is confirmed by the diffraction peak characteristic of the nanoclay which remains unshifted after dispersion within Nafion® (*d*=1.2 nm for native MMT and *d*=1.36 nm for Cloisite ACA). The shift of the diffraction peak of Cloisite 30B from 1.85 to 3.41 nm confirms the slightly better dispersion observed by TEM. Fig. 8 also shows that Cloisite BHB is delaminated within Nafion® to the point where no diffraction peak is observed by X-ray analysis.

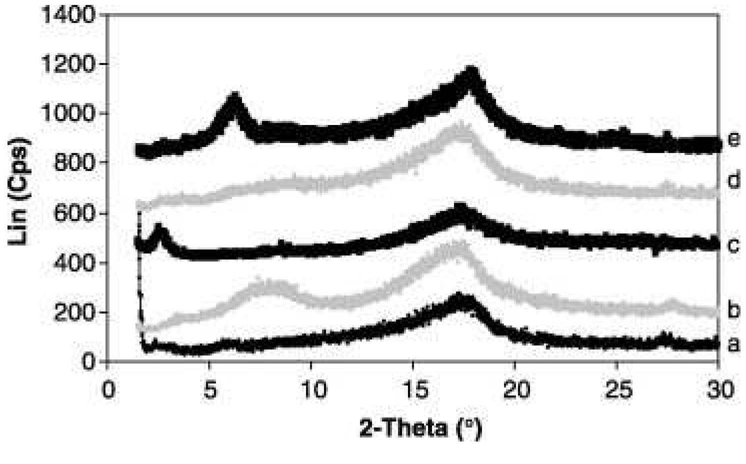

Fig. 8. X-ray diffraction patterns for (a) Nafion® membranes and Nafion® membranes filled with 3 wt% of (b) Native MMT, (c) Cloisite 30B, (d) Cloisite BHB and (e) Cloisite ACA.

3.3. Methanol permeability

Methanol permeability, i.e. the DK product, has been measured for the Nafion® membranes in relation to the amount of MMT and the counter-ion it contains (Fig. 9). No beneficial effect is observed upon addition of the poorly dispersed native MMT and Cloisite ACA. In contrast, Cloisite 30B and Cloisite BHB have a favorable impact on the methanol permeability with a more important effect in case of the better dispersed Cloisite BHB. At a 4 wt% loading of Cloisite BHB, the permeability is decreased by 51% which is almost as high as the decrease observed for completely exfoliated MMT (60%) [27-30].

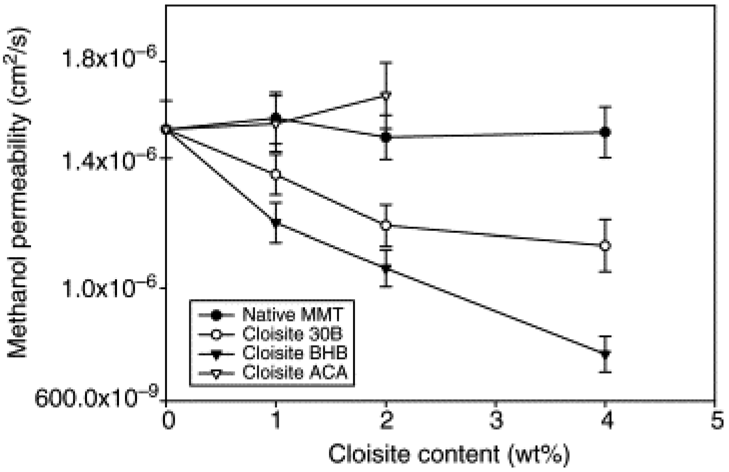

Fig. 9. Dependence of the methanol permeability on the content of native and modified MMT in Nafion® membranes prepared by 'solvent casting'.

3.4. Ionic conductivity

Fig. 10 reports ionic conductivity data for all the membranes under consideration in this study. The ionic conductivity of the unfilled membranes tends to decrease upon addition of MMT modified or not. This effect is, however, very small (less than 10% for nanoclay content up to 3 wt%) except in case of Cloisite 30B, thus MMT modified by a voluminous counter-ion without carboxylic acid attached to it. Nevertheless when a carboxylic acid is part of the voluminous counter-ion (Cloisite BHB), this deleterious impact on the proton transport is restricted.

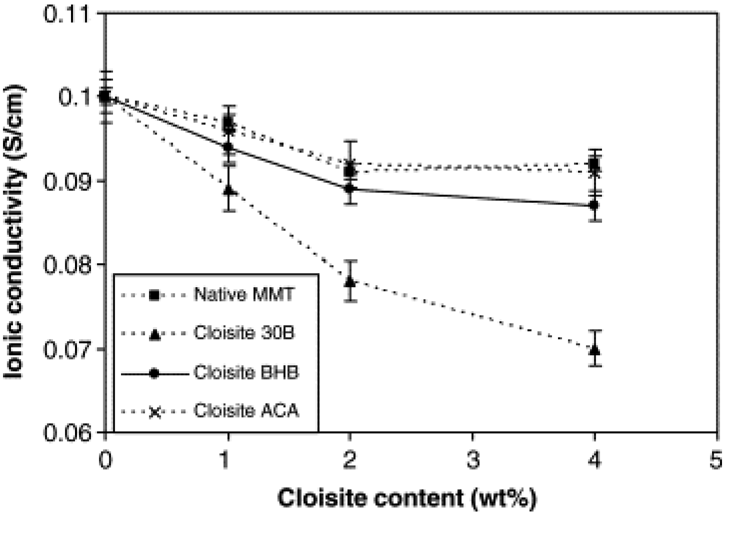

Fig. 10. Ionic conductivity vs content of native and modified MMT in Nafion® membranes.

From the experimental data of methanol permeability and ionic conductivity, it appears that modification of MMT by BHB is the best compromise as assessed by plotting the conductivity (*C*) to methanol permeability (*P*) ratio against the filler loading (Fig. 11). The higher is the *C*/*P* ratio, and the better the membrane performances are improved. Clearly, Cloisite BHB is the more effective additive with an approximatively two-fold increase in *C*/*P* ratio compared to neat Nafion®.

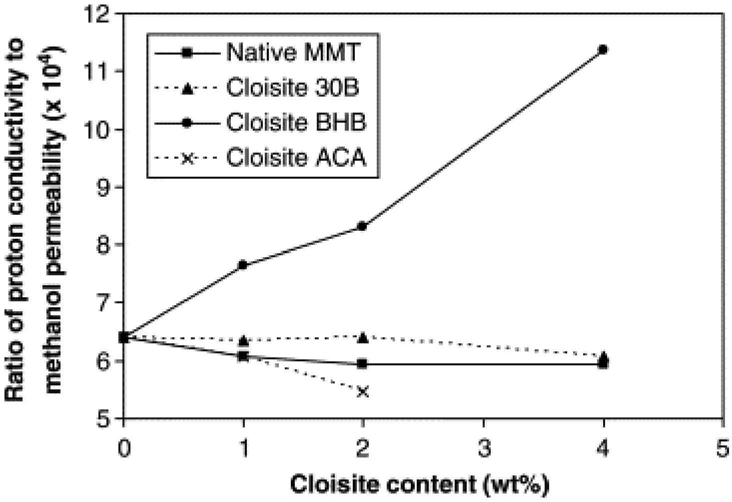

Fig. 11. Dependence of the C/P ratio on the content of native and modified MMT in Nafion® membranes.

4. Conclusions

Montmorillonite has been organo-modified by exchange of the Na^+ or H^+ cations by ammonium cations and dispersed within Nafion® in order to restrict the methanol permeability without prejudice to ionic conductivity. The best compromise has been observed by filling the sulfonated polymers by MMT modified by carboxylic acid containing ammonium cations. Favourable interaction between the carboxylic acid attached to the ammonium cations of the nanoclay and the sulfonic acid attached to the polymer might account for a reasonably good dispersion within Nafion®. These carboxylic acids also restrict the deleterious impact that conventional organo-modified MMT usually have on the ionic conductivity. Moreover, in addition to his favorable impact on the *C*/*P* ratio (a two-fold increase compared to neat Nafion®), Cloisite BHB is suspected to improve the water retention and the mechanical stability of Nafion® at high temperature. This expectation will be assessed as soon as reliable measurements at high temperature will be possible in the laboratory.

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