FABRICATION OF HYBRID PROTON EXCHANGE MEMBRANES USING A BRANDNEW HIGH TEMPERATURE IONIC LIQUID AS CHARGE TRANSPORTING AND CLAY MODIFIER

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Abstract

The search for more compatibility between ionic liquids and polymer matrices in Proton Exchange membrane fuel cells (PEMFC) is one of the ways in which ionic liquid (IL) leaking from Proton Exchange Membranes (PEM) could be minimized. In this work, it is presented the synthesis of an aromatic HTIL (High Temperature Ionic Liquid), which, incorporated into an aromatic matrix such as sulfonated poly ether ether ketone (sPEEK), is expected to diminish the IL leaking that normally affects PEMFC. Phenyl ethyl ammonium trifluoromethane sulfonate (PhetaTfO) was successfully synthesized and characterized. Its melting point of 88 °C makes it to classify as a HTIL and it was employed as modifier of natural Montmorillonite, forming the Phenyl ethyl ammonium intercalated montmorillonite (MmtPheta) and thus, ternary membranes containing PhetaTfO, MmtPheta and sPEEK were prepared and characterized. Immersion tests demonstrated a higher compatibility of PhetaTfO with matrix when compared to the reference DemaTfO, which was reflected in up to 30 % lower ionic liquid loss by the synthesized ionic liquid than the DemaTfO; X-rays diffraction (XRD) patterns demonstrated that the modified clay was properly dispersed inside the membranes, while Dynamic mechanical analyses (DMA) results indicated a strong plasticizer effect along the increase of PhetaTfO content inside the membrane, while at the same time, the conductivity increased in an exponential manner, which permitted to identify an empiric exponential equation to evaluate the effect of concentration on ionic conductivity. The maximum conductivity obtained at ionic liquid concentrations of around 38 wt% was 0.2 mS/cm. It could be expected high ionic conductivities of 10 mS/cm when the concentration of this ionic liquid is 60%, nevertheless, in order to achieve that, it should be done crosslinking treatments to give the membranes enough mechanical resistance.

Introduction

Fuel shortage and environmental consequences of the increasing consumption of fossil energy sources are encouraging research in cleaner technologies for energy conversion; solar, geothermic and wind energy have had their contribution to energy market exponentially grown since the last 30 years, nevertheless, those forms of energy conversion are not easily applied for direct use as fuel for automobiles movement ¹. The development of fuel cells (FC) has become an important alternative for mobile energy generation with zero CO₂ emissions. Among those fuel cells can be accounted the PEMFC, which are devices that convert the chemical energy contained in a fuel (namely methanol, hydrogen, among others) in electricity by using a hybrid polymer membrane that selectively allows the pass of protons from one electrode to the other, completing thus the catalytic conversion of hydrogen into water and electricity that can be used for vehicles movement ^{2,3}.

An important feature of a PEMFC is the selective transportation of protons through its structure while keeping isolated the anodic and cathodic compartments ⁴; the transportation of protons is possible when there are polar species that can carry the transported charges while it has the mechanical strength to resist the pressure of the fuel. A polymer structure can accomplish those tasks by having a rigid backbone and polar pending groups such as sulphate or phosphate groups, thus, the glass transition is high enough for maintaining dimensional stability while transporting charges through its own structure ⁵. Sulfonated poly ether ether ketone (sPEEK) is a remarkable candidate for this purpose, since it possesses the desired properties and additionally, they are relatively inexpensive compared to the reference Nafion polymer ^{6,7}. The efficiency of a fuel cell is determined by the presence of ionic transport agents, which are small molecules responsible for carrying the charges through the polymer structure ⁸; normally this function can be properly performed by water, nevertheless, water evaporates easily at the normal operation temperatures of a fuel cell, reason by which, ionic liquids (IL) are incorporated into PEM, which has become a hot research topic in the field of PEMFC, due to their high ionic conductivity and their capacity to act as charge transporting agent, having the advantage of operating at elevated temperatures, where water cannot exist inside membrane and catalytic efficiency of fuel decomposition is higher ⁹. The possibility of operating at elevated temperatures is desired, since it inhibits the catalytic poisoning that occurs at low temperatures, which is responsible for diminution of PEMFC performance ¹⁰. According to the literature, charge transport from anode to cathode occurs as a synergic process that combines hopping and diffusion mechanisms ¹¹, diffusion of charge transporting agent through the solid involves the possibility of leaking, which has previously observed to be a threat for ionic liquid incorporation into PEM's, aiming device durability ^{12,13}. Several approaches have been proposed for the ionic liquid immobilization into PEM matrix, such as phosphoric acid doping of polybenzimidazole membranes ¹⁴, grafting of ionic liquids to titanate nanotubes ¹⁵, grafting of imidazolium poly-ionic liquids onto silica nanoparticles ¹⁶, crosslinking of sPEEK with organometallic frameworks ¹⁷ or even the insertion of cross-links in the very structure of the polymer matrix as it was proposed by ^{18,19}. One less explored way

way to overcome these issues is the incorporation of modified montmorillonite as an “anchor” as described by previous study ²⁰. Another possibility for avoiding the lixiviation of ionic liquid during operation could be found in the increase of the compatibility between the ionic liquid and polymer matrix, which has been tried by using copolymers containing segments with ionic liquid compatible structures ^{21,22}. No reports of synthesizing ionic liquids for increasing compatibility with a common polymer matrix as sPEEK have been found; following that course of reasoning, this work proposes the synthesis and the evaluation of the potential for its application in PEM, of a brandnew High temperature ionic liquid (HTIL) named as PhetaTfO. This HTIL comes from the acid-base reaction between phenylethylamine and triflic acid, this way the phenylethylammonium triflate, whose structure is showed in Scheme 1, can be used as ionic transporting agent and also as modifier of natural montmorillonite surface through ionic exchange reaction. The hybrid PEM's were prepared using sulfonated polyether-ether-ketone, which is known by its potential for cationic transport properties and relatively low price compared to the commercial Nafion ^{6,7}. The novelty of this work lays in the synthesis of a high temperature ionic liquid which, to the best of our knowledge, has not been found in the literature as ionic transport agent in PEMFC. This ionic liquid, due to the presence of the phenyl ring, is expected to have a higher compatibility with sPEEK matrix, and thus, it is expected to minimize the leaching or lixiviation effect when in operation.

Along the present work, it is described the synthesis of a HTIL, as well as its incorporation into montmorillonite surface, aiming to increase the previously observed “anchor effect” for lixiviation protection ^{20,23}, which is anticipated to be reinforced by an expected higher compatibility between cation and matrix, explained on the aromatic nature of phenylethylammonium cation and sulfonated sPEEK matrix.

Scheme 1. Structure of phenylethylammonium trifluoromethanesulfonate (PhetaTfO) and its action as montmorillonite surface modification agent. Source: created by the author

EXPERIMENTAL

Materials

80 % Sulfonated polyether-ether-ketone (sPEEK80) and diethylmethyammonium trifluoromethanesulfonate (Dema-TfO) were synthesized according to previous work ²⁰ from commercial PEEK, supplied by Victrex®. Phenylethylamine was acquired from sigma Aldrich and used as received. Triflic acid was purchased from TCI chemicals America while sodium montmorillonite was supplied by Bentogel do Nordeste, Brazil.

Synthesis of 2-Phenylethylammonium trifluoromethanesulfonate

The synthesis of the HTIL was performed through the acid-base reaction between diethylmethyammonium and triflic acid in ethanol under nitrogen atmosphere. First of all, an ethanol solution of the triflic acid was prepared (20 wt%) and poured in a three-neck round-bottom flask under constant nitrogen flow and magnetic stirring, then, an equimolar amount of diethylmethyammonium dissolved in ethanol (20 wt%) was added dropwise through an addition funnel coupled to the central neck of the flask and the reaction was maintained for 1 h, reaction scheme is illustrated in Scheme 2. The solvent was removed by rotary evaporation and a drying step was carried out in a vacuum oven at 180 °C.

Scheme 2. Schematic representation of experimental reaction and structure of synthesized HTIL.

Montmorillonite modification

Chemical modification of mineral clay was performed through the treatment of natural montmorillonite with an aqueous solution (20 wt%) of the synthesized PhetaTfO and DemaTfO protic ionic liquids under ultrasonic bath (40 kHz) at 60 °C for 3 h. The solid was filtered and dried under vacuum at 80 °C for 24 h.

Membranes fabrication

The membranes fabrication process was carried out as previously reported using DMF as solvent²⁰. Table 1 shows the different clay, ionic liquid and polymer compositions of the membranes evaluated during the present work.

Table 1. Membranes prepared during the present study and the mass fractions of each component

Sample	sPEEK80 fraction	PhetaTfO fraction	MmtPheta fraction
C1	0.859	0.097	0.044
C2	0.762	0.192	0.046
C3	0.669	0.289	0.042
C4	0.574	0.383	0.043

Dynamic mechanical analyses

Membranes of around 180 µm thickness were cut in rectangles of 4 x 0.5 cm and fixed in film strain clamp. The analyses were performed in a DMA Q800 from TA instruments. Deformation of 0.1% was applied at a frequency of 1 Hz along the temperature range between 30 and 230 °C at a rate of 3 °C/min.

X-rays diffraction

X-rays analyses were performed in a Rigaku Miniflex diffractometer, with CuK α radiation of 1.541 Å, 40 kV and 20 mA. The range of analysis was from 2 to 80 ° with a resolution of 0.05°/s and exposition time of 1s.

Fourier Transform Infrared spectroscopy (FTIR)

The analyses of ionic liquid and clay was performed through FTIR using a Perkin-Elmer Frontier FTIR with scan resolution of 4 cm⁻¹ and 32 scans between 600 and 4000 cm⁻¹, equipped with an ATR (Attenuated Total Reflectance) accessory.

Electrochemical impedance spectroscopy (EIS)

Membranes were cut in circular sections of 1 cm² and average thickness of 180 μm (the calculation of ionic conductivity considers the difference of thickness among samples) and then placed between two circular sections of carbon foil (150 μm thickness); this “sandwich” containing the sample in the middle was set in in a steel electrochemical cell, equipped with two circular platinum electrodes with polished face in contact with the carbon foils; the orientation of these circular electrodes is given by a Teflon internal structure, which allows to make electronic measurements in dry conditions while avoiding short circuit with the steel chassis of the electrochemical cell. The electrochemical cell was closed and its terminals were connected to a PGSTAT30 potentiostat/galvanostat from Metrohm Autolab. Impedance measurements at frequencies between 1 MHz and 10 Hz were done, in order to find a value of ionic conductivity.

PEM membranes were previously dried in a vacuum oven at 80 °C for 1 h for moisture removal, then, after placing the sample into the electrochemical cell and oven temperature set (80 °C), 1 h was used as stabilization time before the EIS measuring process. The FRA32 software provided by the fabricant was used, which provided scanning of different values of imaginary resistance as a function of real resistance throughout a frequency range between 1 MHz and 10 Hz, which produced a characteristic semicircle; the intercept on real impedance axis, corresponded to the desired impedance result. 24 h of consecutive analysis were performed in every sample and the reported value corresponds to the ionic conductivity when the impedance values reached stability.

RESULTS AND DISCUSSION

After the reaction between amine and triflic acid described in Scheme 2, a pale brown waxy solid (89% yield) was obtained, and its melting point was determined as 88 ± 2 °C. This feature would permit the low leaking of the mobile phase in the membrane, reason by which the synthesized ionic liquid fits in the category of high temperature ionic liquid (HTIL). FTIR analysis is showed in Figure 1; the stretching vibration modes detected in the bands at 3088, 1280 and 1167 cm^{-1} correspond respectively to the N-H, C-N and S=O bonds of the quaternary salt.²⁴ The C-F stretching vibration and angular deformation modes are detected at 1244 and 1033 cm^{-1} , which agrees with reports made by Wang and co-workers, who performed the synthesis of an ionic liquid using triflate anion. A low intensity band at 882 cm^{-1} corresponding to the stretching vibration of S-O bond was detected²⁵. The bands located at 1619 and 1602 can be attributed to the stretching of C=C bond in the aromatic portion of Pheta cation. The bands at 1457 and 1518 may belong to the bending of the C-H bond in the methyl group and the methylene respectively. The S=O stretching mode is present as a strong band at 1167 as well as a weak band at 882 of C-F correspond to the triflate anion²⁶. The band at 2995 cm^{-1} is normally attributed to the stretching vibration of SP2 C-H bond, which comes from the phenyl ring of the cation, confirming that the waxy solid contains all the expected vibrations for its proposed structure²⁷.

Figure 1. FTIR spectrum of PhetaTfO HTIL

The thermal degradation of the HTIL is presented in Figure 2, where mass and dm/dt are plotted as a function of temperature. Two clear degradation steps are observed with maximum degradation temperatures of 258.7 and 358.4 °C; onset degradation temperature was detected at 229 °C, which implies that this solid can be safely used in temperatures under 200 °C, enough for operation of a high temperature PEM. A reference ionic liquid as DemaTfO has degradation onset at around 305 °C^{28,29}, which is significantly higher than the here reported ionic liquid; Nonetheless, for the desired application, the synthesized ionic liquid has the necessary thermal stability, since the operation temperatures are commonly found between 80-90 °C²⁷⁻²⁹, thus, its application in PEMFC is studied along the present work, not only as charge transporting agent (CTA), but as modifier of natural montmorillonite.

Figure 2. Thermal and differential thermal degradation of the synthesized Pheta+TfO-

PhetaTfO ionic liquid contains aromatic ring, which is expected to have greater compatibility with the polymeric matrix and thus be more easily maintained within the membrane structure.

Organic modification of sodium montmorillonite

In order to evaluate crystalline structure and cation incorporation within the interlayer space of sodium montmorillonite structure, X-ray diffraction analysis was performed to visualize the difference in interplane spacing between natural and modified clay; Bragg's law (Equation 1) describes the value of the basal space corresponding to the diffraction peaks.

Equation 1.

$$n\lambda = 2d \cdot \sin\theta$$

Where n: integer value

d: interplanar space

θ : diffraction angle

λ : Incident beam wavelength (1,541 Å)

Modifications on sodium montmorillonite were made according to the experimental procedure. Figure 3 shows the X-ray diffractogram corresponding to natural and Pheta+ modified montmorillonite at low angles; this range of angles has been chosen due to the fact that the interplanar spacing between montmorillonite lamellae is usually found at low angles according to literature³⁰. The MmtPheta diffraction pattern shows a slight 0.12° shift to smaller angles relative to sodium montmorillonite. There is also a narrowing of the peak represented by the diminution of Full Width at Half Maximum (FWHM); commonly, this diminution implies a higher size of the organized domains in a solid, which could be the result of the incorporation of the cation into the interlamellar space, reflected also by the slight diminution of interlamellar space to 15.6 Å.

Figure 3. X-ray diffractogram corresponding to Montmorillonites sodium and modified with Pheta+ cation.

Figure 4 shows the FTIR spectrum of Pheta⁺ cation modified clay and sodium clay spectrum (natural without modification) for comparison. Clay spectra overlap in the high-wavelength regions, but at 3087 cm⁻¹ and 2851 cm⁻¹ the characteristic peaks of the asymmetric and symmetrical elongations of the CH sp² bond that belong to the aromatic hydrogens of the phenylethylammonium cation structure appear, revealing the presence of the organic Pheta⁺ cation. The behavior of the modified clay spectrum over the analyzed wavelength range suggests an additivity between the cation and sodium clay peaks. This, in addition to the evidence provided by the XRD analysis suggest that ionic liquid cation was incorporated.

Figure 4. Comparison between FTIR spectra of sodium clay (pointed) and MmtPheta (continuous line). Analyses performed in ATR mode between 600 and 3700 cm⁻¹.

Thermal degradation curves of the modified clay were recorded according to the procedure described in the experimental method, contrasting each curve with the thermal degradation of the sodium clay used as the basis for the organic modification process. Figure 5 shows the degradation curve of the MmtPheta clay compared with the thermal degradation curve of the natural clay. The steps of the degradation of the PhetaTfO ionic liquid slightly reflected in the curve of the modified Pheta⁺ cation clay can be verified; it has a total loss of 12.47% compared to the 15.46% loss of sodium clay leaving a total of 2.99% by weight of Pheta⁺ cation incorporated in the clay.

Figure 5. Comparison between thermal degradations of modified MmtPheta clay and natural sodium clay. TGA analyses performed under nitrogen between 30 and 70 °C.

Characterization of hybrid membranes

Thermogravimetric analysis

The thermogravimetric analyzes were performed according to the procedure mentioned in the experimental method session and the results are presented in Figure 6. There is a clear tendency for the membrane curves to resemble the ionic liquid curve, the higher the proportion of it in its structure. Likewise, the onset of degradation temperature increases as the ionic liquid content decreases, yet in neither case the onset of degradation temperature of hybrid membranes is significantly higher than the onset of degradation temperature of the pure polymer. This means that although the ionic liquid does not have a window of thermal stability as wide as that of DemaTfO, when analyzing this system, the thermal stability of the polymer remains the limiting factor of a membrane. Higher thermal resistance polymer matrices are then required when it comes to medium and high temperature fuel cell membranes.

Figure 6. Thermal degradation curves of pure polymer membrane, pure HTIL, MmtPheta and hybrid membranes, compared with the degradation curves of system components. Analyses performed between 30 and 700 °C under nitrogen at 10 °C/min

X-ray diffraction

The X-ray diffraction of the pure polymer, the pure MmtPheta and the hybrid membranes was carried out according to experimental procedure shown in the Experimental section and results are displayed in Figure 7. The diffractograms of the hybrid membranes present similar profile to the one belonging to the pure polymer, just an amorphous halo; nevertheless, it should be highlighted the absence of the diffraction peaks of the montmorillonite in the hybrids membranes, which is considered to be a sign of proper membrane preparation, implying the absence of high agglomerations of non-dispersed clay particles. A slight shift of amorphous halo to lower angles was detected in the hybrid membranes, which is explained by the addition of two plasticizers: clay and ionic liquid, which are able to increase interchain distance, therefore, shifting diffractograms to lower angles. This evident plasticizer effect is expected to significantly decrease mechanical properties of membranes, which is a consequence of the gain in ionic conductivity obtained through the increase of montmorillonite concentration.

Figure 7. XRD diffractograms of pure polymer, modified montmorillonite and hybrid membranes containing modified montmorillonite and HTIL. Analyses performed between 4 and 40 ° at 0.05°/min at room temperature.

DMA analysis

Dynamic mechanical analysis of the pure polymer and the hybrid membranes was conducted as mentioned in the Experimental section. The results are showed in Figure 8 (storage modulus (top) and Tan (δ) as a function of temperature (bottom)). The storage modulus (which describes the elastic response of the polymer) of the three samples analyzed (C1, C2, and C3) is lower at room temperature compared to the pristine sPEEK80 membrane. The storage modulus at all temperatures decreases as the ionic liquid content increases, which was already predicted by the XRD of the composites as previously mentioned. One of the explanations for the observed results when the ionic liquid concentration increases, is found in the fact that over 200 °C, the thermal stability of the ionic liquid can harm the structure of the samples. The presence of ionic liquid in increasing concentrations can increase the distance between polymer chains, augmenting free volume and molecular mobility, which is reflected in the drastic diminution of storage modulus along with the increase of ionic liquid content inside membrane. The damping factor Tan (δ) is defined as ratio of the loss modulus (related to the viscous response of the polymer) to the storage modulus and is used to characterize the viscoelastic behavior of the material. The α -relaxation temperature obtained from the Tan (δ) peak maximum can be related to the glass transition temperature T_g , and it decreases from 209.1 °C in the pure sPEEK to 132.3 °C in membrane C3. This glass transition in the membranes decreases along with temperature, which is a

response of the augmented mobility of the ionic liquid and the possibility of degradation as previously mentioned.

Figure 8. DMA results for the hybrid sPEEK membranes. Storage modulus (left) and tan delta (right) as a function of temperature. Membrane C4 did not behave well and its result is not presented.

Immersion tests

An important test to be applied in this series of samples is the immersion test, which evaluates the ability of these membranes to retain ionic liquid and thus, to project the preparation of systems with higher phase compatibility. The test results in Table 2 showed a tendency to increase Ionic Liquid Loss (ILL) as the proportion of ionic liquid inside the membrane increases, which is expected, since increasing this proportion leaves less polymeric chains available to surround the ionic liquid. An ionic liquid retention of 83.25% was obtained for the membrane containing the smallest proportion of it. These results are promising regarding the importance of the compatibility of all system components in order to diminish ionic liquid lixiviation²¹. As a comparison, analogous hybrid membranes containing the same modified clay and DemaTfO ionic liquid were submitted to the same immersion tests. It was verified that DemaTfO leaks more easily, leading to higher ILL in all the studied times and concentrations of ionic liquid, which demonstrates the effectiveness of using a HTIL as CTA.

Table 2. Ionic liquid loss after immersion of hybrid membranes containing PhetaTfO/MmtPheta and analog membranes containing demaTfO/MmtPheta in deionized water for 1 and 18 h.

I.T (h)	Sample	ILL	ILL
		DemaTfO	PhetaTfO(%)
1	c1	25.56	16.76
	c2	29.09	21.31
	c3	33.45	26.99
	c4	37.43	34.65
18	c1	62.68	56.56
	c2	74.87	59.52
	c3	92.04	63.11
	c4	100.7	70.16

Electrochemical Impedance Spectroscopy (EIS)

EIS analyses were performed as related in experimental section at 90 °C and conductivity results are summarized in Table 3, which presents the conductivities of hybrid membranes in comparison to analogue membranes prepared using the commercial demaTfO IL instead of the proposed PhetaTfO. The conductivities presented by these membranes are low compared to the ionic liquid based membranes reported in literature^{31–33}, which is probably due to the relatively low mobility of the Pheta⁺ cation when compared to the structure of more mobile Dema⁺ cation, used for most of the PEM reported in literature. A conductivity value of 0.2 mS/cm was obtained for the membrane containing 38.31 wt% of PhetaTfO. The PhetaTfO:clay ratio was kept constant in all the membranes, in order to evaluate the sole influence of ionic liquid concentration. For purposes of comparison, the same clay was used to produce analogue membranes containing DemaTfO as CTA. Table 3 displays the comparison between conductivities achieved for the membranes containing PhetaTfO and the reference DemaTfO. It was verified that DemaTfO induces a significant conductivity response when compared to PhetaTfO. Nevertheless, as previously observed in immersion test, the PhetaTfO is able to resist more strongly the lixiviation effect exerted by water during immersion tests, which means that it is meaningful to use an ionic liquid with higher compatibility with matrix.

Table 3. EIS results of DemaTfO reference membranes compared to PhetaTfO based membranes at 90 °C in membranes of 180 microns and electrodes platinum in carbon foil 1 cm² sandwich

Samples	PhetaTfO (%)	Conductivity of Dema based membranes (mS/cm)	Conductivity of Pheta based membranes (mS/cm)
C0	0	0.002	0.002
C1	9.67	0.49	0.007
C2	19.15	0.58	0.03
C3	28.93	4.15	0.1
C4	38.31	5.10	0.2

Table 4 and Figure 9 summarize the conductivity, glass transition temperature and storage modulus at RT as a function of PhetaTfO proportion in membranes. It is worthwhile to notice that membranes containing 38.31% PhetaTfO did not present valid results for DMA analysis. There is a sensitive loss of mechanical properties along with a diminution in glass transition temperature when ionic liquid proportion was augmented, which is due to the plasticization effect exerted by the incorporation of the small molecule. In spite of a certain compatibility that was expected between stationary and mobile phase, it was not enough to keep the ionic liquid confined. As mobility of ionic liquid inside membrane increased, the conductivity became higher, presenting an exponential profile.

Table 4. Storage modulus at RT, glass transition temperature and ionic conductivity of PhetaTfO based membranes as a function of MmtPheta load.

PhetaTfO (%)	Storage Modulus at RT (MPa)	Tg (°C)	Conductivity (mS/cm)	Resistance (x10⁻³ Ohm)
0	1150.1	209.1	0.002	9.04
9.67	772.5	178.2	0.007	2.53
19.15	188.6	156.5	0.03	0.59
28.93	178.9	132.3	0.1	0.18
38.31	--	--	0.2	0.09

Figure 9. Storage modulus at RT, glass transition temperature and ionic conductivity of PhetaTfO based membranes as a function of MmtPheta load

Figure 10 displays the natural logarithm of ionic conductivity ($\ln \lambda$) as a function of PhetaTfO load. The linear correlation coefficient was 0.98, high enough to arrive to equation 2, which permits to predict the ionic conductivity of the PhetaTfO system at any PhetaTfO load at 90 °C. This equation applies for PhetaTfO loads under 30 %, where the mechanical performance is still feasible for the application. The variable C corresponds to the concentration in mass percentage, λ_0 is the ionic conductivity at 0% MmtPheta.

$$\lambda = \lambda_0 e^{0.141C} \quad \text{Equation 2}$$

Figure 10. Linear fit for the logarithm of ionic conductivity of PhetaTfO-MmtPheta hybrid membranes as a function of PhetaTfO concentration

Outlook and Conclusions

The present work related the synthesis and characterization of a new containing aromatic ring. Its melting point around 88 °C classifies it as HTIL, having potential for applications in which other IL can be found, such as PEMFC. It was used for successful modification of natural montmorillonite, producing the new MmtPheta. Both PhetaTfO and MmtPheta were applied to sPEEK80 hybrid membranes, producing homogeneous membranes with good macroscopic properties. The hybrid membranes showed to have a higher resistance to ionic liquid leaking by water, which indicates that the initial goal of increasing compatibility between IL and matrix is partially achieved through the use of PhetaTfO as CTA. The mechanical performance of sPEEK dropped along the incorporation of higher amounts of ionic liquid, explained in the backbone separation exerted by the RTIL. Nevertheless, an exponential increase of ionic conductivity was observed for this system along the augmentation of ionic liquid concentration inside membrane; the maximum ionic conductivity of 0,2 mS/cm was found when about 40 % ionic liquid was incorporated. Studies on the influence of mineral clay concentration should be done in order to study the influence of clay distribution (being a compatibilized clay) on the ionic liquid retention capacity and other properties. The results show that hypothetical membranes based on this system would exhibit good stability (respect of the “bleeding” phenomenon) over the operating time.

Acknowledgements

This study was financially supported in part by the Coordenação de Aperfeiçoamento de Pessoal de Nível Superior - Brazil (CAPES) - Finance Code 001. We would like to thank CNPQ and FAPERJ for their support.

List of abbreviations

80 % Sulfonated polyether-ether-ketone (sPEEK80)
 ATR (Attenuated Total Reflectance)
 Charge transfer agent (CTA)
 diethylmethylammonium trifluoromethanesulfonate (Dema-TfO)
 Electrochemical impedance spectroscopy (EIS)
 Fourier transform infra-red spectroscopy (FTIR)
 Full Width at Half Maximum (FWHM)
 High Temperature Ionic Liquid (HTIL)
 ionic liquid (IL)
 Phenyl ethyl ammonium intercalated montmorillonite (MmtPheta)
 Phenyl ethyl ammonium trifluoromethane sulfonate (PhetaTfO)
 Poly ether ether ketone PEEK
 Proton Exchange membrane fuel cells (PEMFC)
 Proton Exchange Membranes (PEM)
 sulfonated poly ether ether ketone (sPEEK)
 X-rays diffraction (XRD)

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