

Short communication

Conductivity in zeolite–polymer composite membranes for PEMFCs[☆]

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Abstract

Structured materials, such as zeolites can be candidates to be used as electrolytes in proton exchange membrane fuel cells (PEMFC) to substitute polymeric membranes, taking advantage of their higher chemical and thermal stability and their specific adsorption properties. The possibility to work at temperatures of nearly 150 °C would make easy the selection of the fuel, decreasing the influence of CO in the catalyst poisoning, and it would also improve the kinetics of the electrochemical reactions involved. In this work, four zeolites and related materials have been studied: mordenite, NaA zeolite, umbite and ETS-10. In special, the influence of relative humidity and temperature have been carefully explored. A conductivity cell was designed and built to measure in cross direction, by using the electrochemical impedance spectroscopy. The experimental system was validated using Nafion[®] as a reference material by comparing the results with bibliography data. Samples were prepared by pressing the zeolite powders, with size of 1 μm on average, using polymer PVDF (10 wt.%) as a binder. The results here obtained, in spite of not reaching the absolute values of the Nafion[®] ones, show a lower effect of the dehydration phenomenon on the conduction performance in the temperature range studied (from room temperature to 150 °C). This increase of the operation temperature range would give important advantages to the PEMFC. ETS-10 sample shows the best behaviour with respect to conductivity exhibiting an activation energy value comparable with reported for Nafion[®] membrane.

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1. Introduction

The proton exchange membranes (PEM) more widely used are those based on polymer of the perfluorosulphonic acid (PFSA) [1]. This kind of polymer requires hydration to exhibit proton conductivity and, for that reason, the maximum conductivity values take place at 100% relative humidity for every temperature [2]. Transport of protons and associated water molecules within PEMs is strongly dependent on the membrane's microstructure: Eisenberg [3] postulated the existence of ion clusters in Nafion[®] membranes in 1970. A “cluster-network” model for Nafion[®] was proposed by Gierke et al. [4], in which the solvent and ion-exchange sites separate from the perfluorinated polymer backbone forming inverted micelles (~5 nm in diameter) which are connected via short, narrow channels

(~1 nm in diameter). When Nafion[®] membranes dehydrate, the size of the water clusters within the polymer microstructure decreases, leading to a narrowing of the interconnecting channels. The mobility of the proton through the membrane becomes restricted and consequently conductivity falls [5]. Therefore, the operation temperature to use the PFSA polymer as electrolyte for proton exchange membrane fuel cells (PEMFCs) is limited to the water boiling point. Although operating at high pressures can overcome this drawback, the mechanical resistance of the polymer prevents an essential improvement in performance.

The possibility of operating at higher temperature than PFSA (range 120–200 °C) would allow several advantages. One of them is that hydrogen obtained from reforming gas could be used as a fuel due to the poisoning effect of CO traces in Pt electrocatalyst reduces noticeably with temperature. It has been proved that CO poisoning takes place from 10 ppm at room temperature, but at 150 °C the CO tolerance reaches values around 1% [6]. So, power densities similar to pure hydrogen (more expensive and difficult to produce) could be obtained operating

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at higher temperatures. Furthermore, the electrochemical reaction rate is faster, especially the oxygen reduction in the cathode that is the rate-determining step, when operation temperature increases and it improves the overall performance [7]. Finally, another additional advantage of working around 150 °C is that high-quality waste heat increases system efficiency through cogeneration and simplifies water management. Reduction of system weight, volume and complexity increases power density and make the system more durable. Therefore, a significant economic incentive exists to develop and commercialize PEMFCs that operate at high temperatures [8].

One of the most difficult hurdles facing the development of novel proton conducting membranes is understanding the proton transport mechanism. At a molecular level the proton transport mechanism for hydrated proton conductors is usually described as either a hopping mechanism (i.e. Grotthus transport) [9,10] or as a diffusion mechanism (i.e. through water solvent) [11].

Zeolites are a class of crystalline aluminosilicates, which form a framework of SiO₂ and AlO₄ tetrahedra and contain exchangeable cations on the extra-framework to maintain the electrical neutrality. The ion-exchange of cations often changes the chemical and physical properties of zeolites, such as a thermostability, adsorption capacity, amount and strength of acid site [12]. Therefore, zeolites can potentially be a candidate for novel ion-conducting materials, since the cation is mobile in the framework structure, which has been materialized as ion exchangers in an aqueous phase [13]. However, membranes made of pure zeolites are plagued by defects, such as cracks or gaps and exhibit poor mechanical properties, such as brittleness and fragility [14]. Moreover, these membranes are expensive to manufacture [15]. A zeolite–polymer composite membrane represents a compromise between the nonselective polymeric films and the brittle zeolite film. The composite combines the highly selective solid-state proton conductor with the flexibility of a polymer matrix [16]. For zeolites at 100% relative humidity, the higher temperature the higher ion conductivity up to 100 °C [17]. Above this value, conductivity in zeolites is strongly influenced by the amount of adsorbed water [18,19].

In the present work, we have prepared zeolite–polymer composite membranes using mordenite, NaA zeolite, ETS-10 and zeolite Y as zeolites and PVDF as polymer. Conductivity has been investigated at different temperatures and relative humidities and compared with conventional Nafion® 117 membrane. The morphology of powders and tablets prepared were probed by scanning electron microscopy (SEM). X-ray diffractometry (XRD) was used to study the crystallinity of the zeolites prepared.

2. Experimental

In order to prepare composites, two kind of related zeolite materials: ETS-10 (SiO₄ tetrahedra and TiO₆ octahedra) and zeolite Y (SiO₄ and SnO₄ tetrahedra and TiO₆ octahedra) were prepared by hydrothermal synthesis following the procedures described by Tiscornia et al. [20] and Sebastian et al. [21]. The other two zeolites were commercial: mordenite (Tosoh Corp.) and NaA zeolite (Industrias Químicas del Ebro). The samples

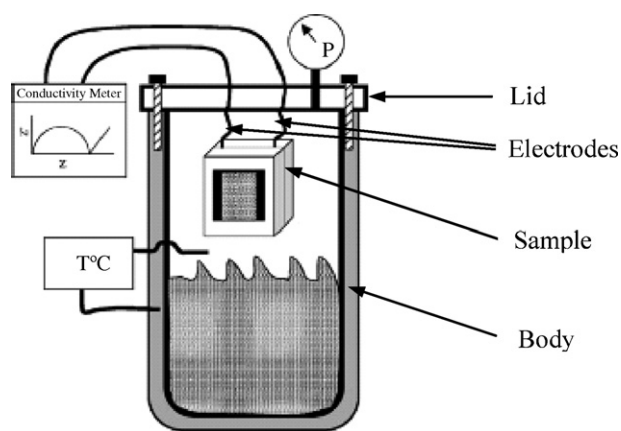


Fig. 1. Conductivity cell scheme.

obtained were ground to reach a particle size around 1 μm in a mortar. Then, the samples were added to PVDF (Fluka) dissolved into acetone to get a homogeneous mixture, around 100 mg, by stirring. Every mixture was pressed at 7 tonnes for 5 min with a stainless steel press to obtain 13 mm diameter tablets. The minimum weight percentage of PVDF to get an enough mechanical resistance tablet was determined in 10 wt.% and was used to prepare all the samples.

SEM micrographs were taken for all samples by means of an Hitachi S-2300 equipment with 4.5 nm of resolution and a range of magnification between 20× and 200,000×. XRD patterns were obtained using a Rigaku/Max System diffractometer.

The ionic conductivities were measured in a home-made conductivity cell (Fig. 1) of which electrodes were made in 18-carat gold and then 24-carat gold-plated. In order to get an easy and fast water exchange to keep a controlled humidity in the sample and homogeneous temperature in the sample environment, electrodes were designed ring in shape (11 mm outlet diameter and 6.5 mm inlet diameter). Both electrodes were joined to two thermal resistant and hermetic BNC connectors (POMONA model 4159) located in the lid of the cell with golden wires by tin–silver welding. Electrodes were supported in PTFE blocks with con-

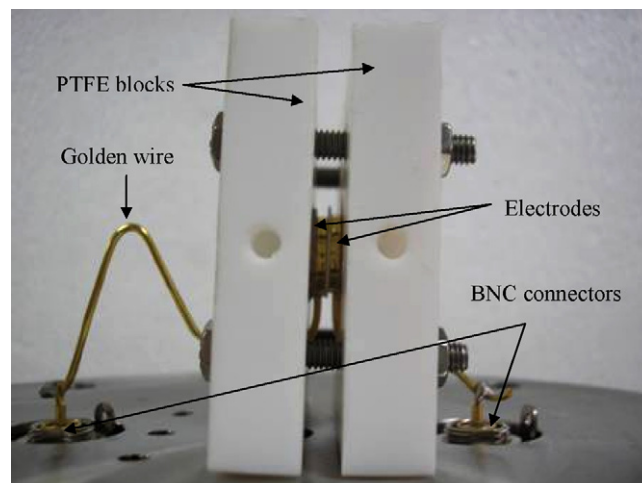


Fig. 2. Location of the sample to measure of conductivity.

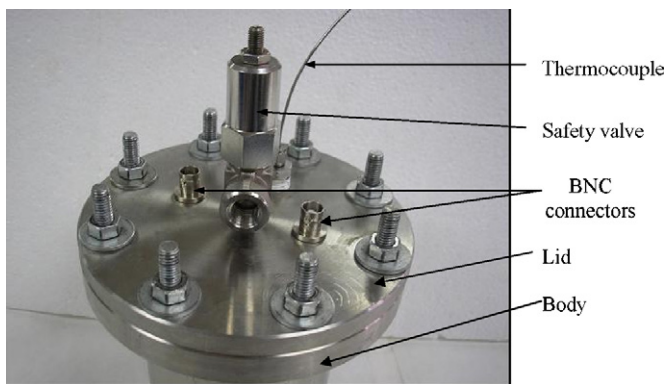


Fig. 3. Top photograph of the cell.

the cell was also circular in shape (10 cm diameter and 15 cm height) and PTFE lined inside. Lid and body were joined by 8 screws and a Viton O-ring was placed between them in order to get a good sealing (Fig. 3). Sample temperature (up to 150 °C) was reached putting the cell inside a polyethyleneglycol 400 PS (Panreac) and measured in a display connected to the thermocouple. Inside the cell, the samples were allowed to equilibrate at the at the desired relative humidity (RH) containing: silica gel for dry atmosphere and water vapour for the 100%. Saturated solutions of salts were used to reach intermediate RH values: NaOH·H₂O for 6% RH, Ca(NO₃)₂·4H₂O for the 33–53% RH range, NaNO₃ for 64–75% RH and KNO₃ for 80–92% RH. For every case, the RH was calculated as a function of temperature according to Eq. (1) [22].

$$HR = A \exp\left(\frac{B}{T}\right) \quad (1)$$

where A and B are the constants for every salt and T is the temperature in Kelvin degrees.

The conductivity cell was validated using Nafion 117 (DuPont), obtaining results comparable with other authors in

centric holes with them and put just opposite. The sample was placed between them. In order to get a good contact, both PTFE blocks were pressed by means of stainless steel screws (Fig. 2) and hung from the lid of the cell. Moreover, a 75 PSI calibrated safety valve and a thermocouple were added to the stainless steel lid, which was circular in shape (15 cm diameter). The body of

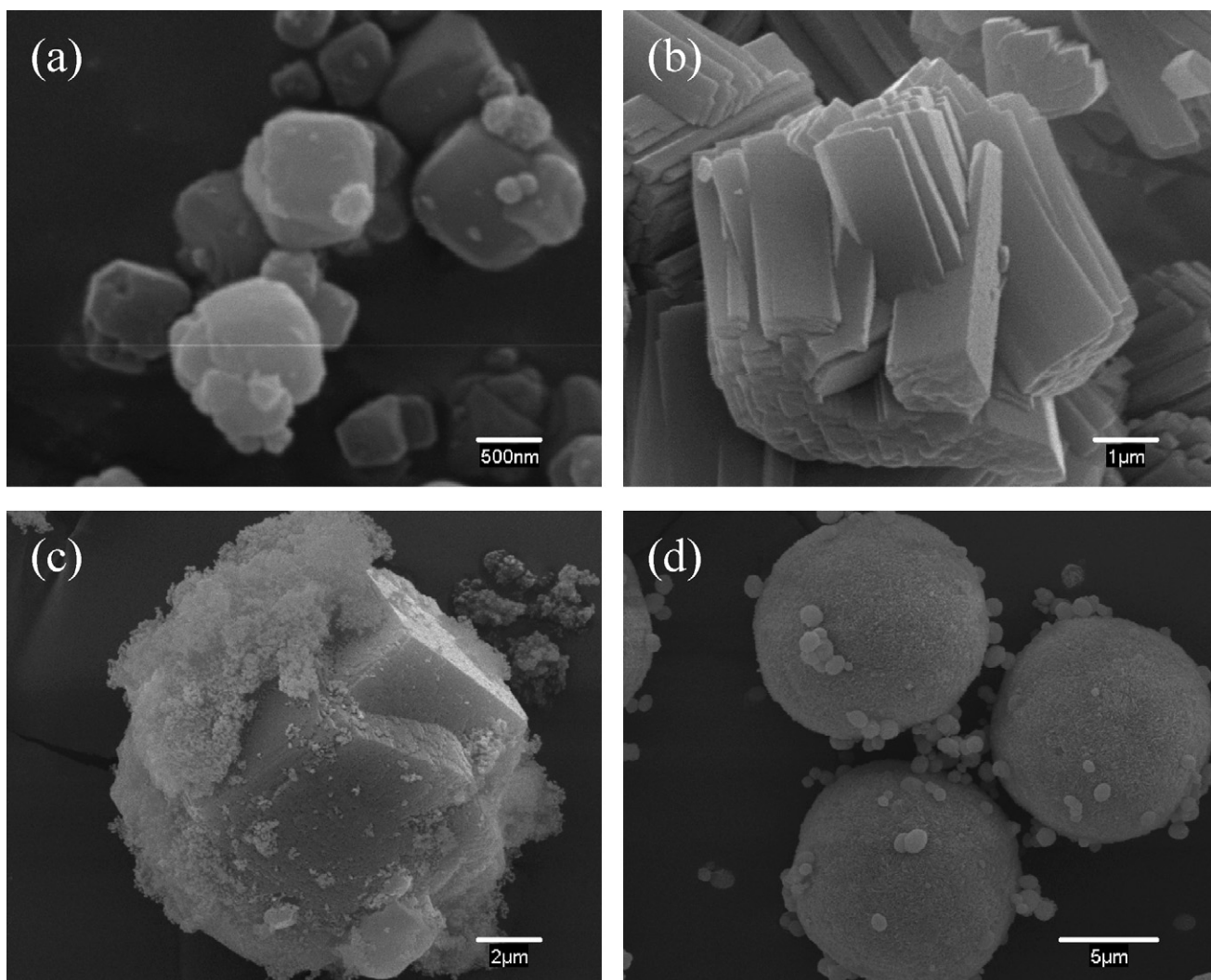


Fig. 4. SEM micrographs of the surface zeolite powders: (a) NaA zeolite, (b) mordenite, (c) ETS-10 and (d) umbite.

literature. Conductivity measurements were measured by electrochemical impedance spectroscopy (EIS) using an Agilent 4294A Precision Impedance Analyzer. The frequency was varied from 40 Hz to 110 MHz. After obtaining the Nyquist diagram for every test, the resistance value was calculated taking the point in which the semicircle plotted for high frequencies and inclined line for low frequencies join. The semicircle represents a typical equivalent circuit of a resistor and a capacitor connected in parallel corresponding to the bulk electrical properties, and the line a Warburg impedance caused by the diffusion process of protons [23]. Once obtained the resistance, the conductivity is calculated with Eq. (2).

$$\sigma = \left(\frac{1}{R}\right) \left(\frac{l}{S}\right) \quad (2)$$

where σ is the conductivity (S cm^{-1}), R the resistance (ohm), l the simple thickness (cm) and S is the contact surface with electrodes (cm^2).

3. Results and discussion

SEM micrographs of the powder obtained are presented in Fig. 4. It can be seen that umbite shows a different morphology compared with the other ones. The spherical geometry can be a drawback because the higher inter-grain void volume and the

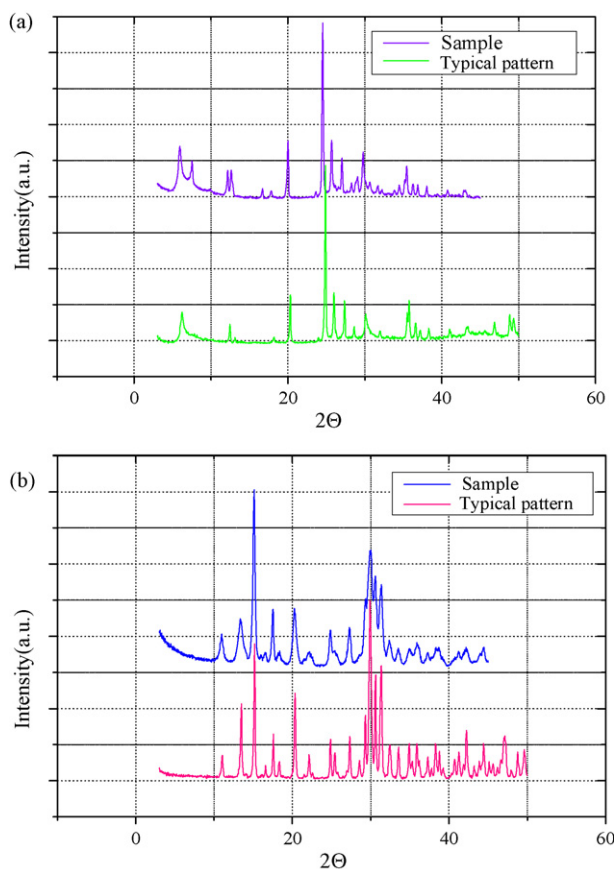


Fig. 5. XRD for samples prepared by hydrothermal synthesis: (a) ETS-10 and (b) umbite.

Table 1
Conductivity (S cm^{-1}) of the composites at different relative humidity (RH)

RH (%)	Nafion	ETS-10	Mordenite	Umbite	NaA zeolite
43	2×10^{-2}	8×10^{-4}	1×10^{-5}	2×10^{-5}	2×10^{-4}
70	3×10^{-2}	1×10^{-2}	1×10^{-5}	3×10^{-5}	3×10^{-4}
88	4×10^{-2}	1×10^{-2}	2×10^{-5}	7×10^{-5}	1×10^{-3}
100	7×10^{-2}	1×10^{-2}	6×10^{-5}	2×10^{-4}	2×10^{-3}

lower contact surface than the other three zeolites that are prism in shape.

XRD patterns for powders obtained by hydrothermal synthesis fit satisfactory with the typical diffraction pattern, which probes a suitable zeolitic structure for ETS-10 and umbite (Fig. 5).

Influence of relative humidity in the ionic conductivity for different zeolite–polymer composites are presented in Table 1 and compared with Nafion 117 in the same conditions. Tests were carried out at 40°C with saturated solutions of salts. For silica gel (0% RH) and $\text{NaOH}\cdot\text{H}_2\text{O}$ (6% RH) the resistance was so high that semicircle did not close and it could not calculate the conductivity. It can be noticed that Nafion conductivity at this temperature is higher than zeolite–polymer composites. However, it must be emphasized that ETS-10 sample shows values in the same order of magnitude than Nafion from 70% RH.

In Fig. 6, conductivity versus temperature for all the samples are plotted for RH 100% up to 100°C . Although lower values than Nafion were measured, zeolite–polymer composites shows a more stable performance at high temperatures. Ionic conductivity in solids, zeolites included, increases with temperature mainly due to higher ion mobility and the bigger quantity of adsorbed water. From 100°C , Nafion drops sharply due to the dehydration process. However, NaA zeolite continue increasing conductivity up to 120°C and ETS-10 up to 150°C . Moreover, ETS-10 was subjected at several warning-cooling cycles and did not presented hysteresis. It is indicative of negligible influence of adsorption–desorption process in the composite structure and, as a consequence, it is a reversible process. Umbite and mordenite presented the worst results. Umbite behaviour can be due to the morphology as it was seen in SEM micrographics. Morden-

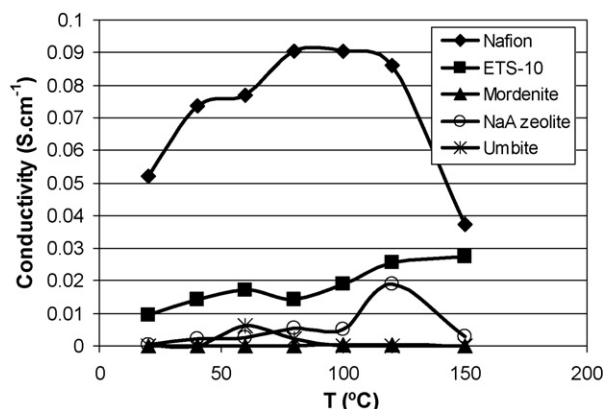


Fig. 6. Influence of temperature in conductivity.

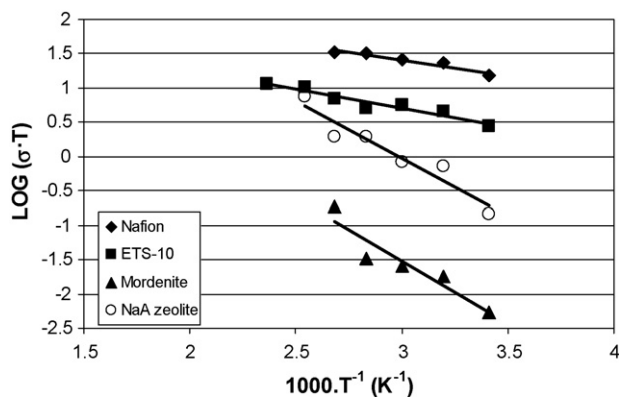


Fig. 7. Arrhenius diagram.

Table 2
Activation energy (E_a) for zeolite–polymer composites

Sample	Temperature range (°C)	E_a (kJ mol ⁻¹)
Nafion	20–100	4
ETS-10	20–150	5
NaA zeolita	20–120	14
Mordenite	20–100	15

ite conductivity was $1.86 \times 10^{-5} \text{ S cm}^{-1}$ at room temperature and 100% RH after 24 h in the cell. This value is similar to that obtained by Hibino et al. [12], $1.07 \times 10^{-5} \text{ S cm}^{-1}$, for the same conditions.

Fig. 7 is an Arrhenius plot of conductivity versus temperature to obtain activation energy E_a for the ionic conduction mechanism using the range where dehydration does not take place. For umbite it could not be calculated because it did not showed a linear fit. The presence of water acts as a vehicle in the conduction process, decreasing the activation energy for ionic mobility. Samples capable to adsorb more quantity of water will present lower activation energy and, as a consequence, a higher ionic conductivity.

After fitting data from Fig. 7, activation energy was calculated for every sample. The results are showed in Table 2. According to values obtained, Nafion presents a lower activation energy due to the easiness for hydration. However, it happens in the lower range of temperatures. ETS-10, which present an activation energy similar to Nafion, is able to be used as ionic conductor up to 150 °C. NaA zeolite and mordenite show higher E_a values although these ones are still among the lower values of energy characteristic for Grotthus mechanism of which range is from 10 to 40 kJ mol⁻¹ [24].

4. Conclusion

Ionic conductivity for zeolite–polymer composites using four zeolite materials (NaA zeolite, mordenite, ETS-10 and umbite) and PVDF as polymer has been studied. The good structure of zeolites prepared by hydrothermal synthesis was corroborated by XRD technique. SEM micrographs showed a different geometry for umbite, which could be the cause of the bad performance.

A conductivity cell has been developed to measure this property at different conditions of relative humidity (RH) and temperature. In the first case, Nafion membrane showed better results at 40 °C, but ETS-10 values are in the same order of magnitude from 70% RH. In the study of the temperature, it was corroborated that a sharp drop takes place for Nafion from 100 °C. However, zeolite–polymer composites are more stable with temperature. So, NaA zeolite continues increasing in conductivity up to 120 °C and ETS-10 up to 150 °C. The calculation of activation energy by Arrhenius diagram showed that NaA zeolite and mordenite values are among the lower values for the Grotthus mechanism. A similar value of activation energy was obtained for ETS-10 and Nafion, but ETS-10 presents the advantage of keeping the same conducting mechanism up to 150 °C, on the contrary to Nafion that suffers severe dehydration from 100 °C. So, ETS-10/polymer composite can be an alternative as ionic conductor up to 150 °C

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