

Final Draft
of the original manuscript:

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In: Fuel Cells (2008) Wiley

DOI: 10.1002/fuce.200800012

**Proton conducting membranes based on sulfonated poly(oxadiazole-triazole) copolymer for
low humidity operation**

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Abstract

This work reports for the first time the preparation of sulfonated poly(oxadiazole-triazole) copolymer membranes doped with amphoteric molecules and their characterization for application in intermediate temperature (100 - 200 °C) and low humidity polymer electrolyte fuel cells (PEFC). The membranes had not only high proton conductivities, up to $4 \times 10^{-3} \text{ S cm}^{-1}$ at 120 °C and low relative humidity (5%), but also had good mechanical properties with storage modulus of about 3 Gpa at 300°C and high thermal stability with T_g up to around 420°C. Because of their superior ion conducting and mechanical properties they have potential for fuel cell applications, in particular at high temperature and extremely low-humidity conditions.

Keywords: polytriazole, polyoxadiazole, proton conductor, fuel cells

1. Introduction

High operating temperature ($>100^{\circ}\text{C}$) is mainly advantageous for polymer electrolyte fuel cell to enhance the performance and catalyst tolerance to CO, as well as to profit from a more efficient cooling system. However practical restrictions are imposed by the currently used PEM which are perfluorinated polymers containing sulfonic groups (Nafion®, Flemion®, Aciplex-S®, and Dow® membrane), in which high proton conductivity is usually achieved at high hydration levels. The proton transport in polymer membranes is a result of vehicular diffusion and Grotthuss shuttling mechanism, as reviewed by different authors [1-5]. At temperature above the boiling point of water, the membranes dehydrate (lost of liquid vehicle molecules) and there is a significant decrease in proton conductivity. Interesting approaches to develop proton exchange membrane for high operation temperature ($> 100^{\circ}\text{C}$) and very low humidity conditions are mainly based on 1) basic polymers doped with strong acids, 2) polymers containing high boiling point protonic molecules such as liquid imidazole ($T_b \sim 257^{\circ}\text{C}$) in place of water, 3) composites of acid polymers with basic heterocycles such as imidazole, pyrazole, 1-methylimidazole, or benzimidazole [1, 3, 6, 7]. In the first case, the most used basic polymer is polybenzimidazole (PBI) doped mainly with phosphoric acid. The imidazole group acts as proton acceptor in an acid-base “reaction” with the doping acid [8, 9], but large amounts of free acid are necessary to assure high conductivity. In ideal case after protonation the imidazole group should also be able to donate the proton back to an acid molecule and further promote its effective migration (non-vehicular mechanism). However the large amount of free acid molecules (liquid moieties) acts as vehicle for the proton transport and are the real promoters of proton transport. A problem is the leaching out of this acid of the membrane during the operation conditions. Another disadvantage of these PBI-doped membranes is the low proton conductivity at room temperature. Complexity, connectivity and cooperativity are said to have important contributions to the proton conductivity [4, 5] in membranes. Attempts to better describe the proton transport and the water influence have been conducted with help of different molecular models, which include for instance approaches of nonequilibrium statistics considering the friction experienced by the proton due to interaction with water, sulfonated groups and other sites in the polymer. The connectivity is related to hydrogen bonding to water and sites in the polymer. It is believed that uniformity in the distribution of sulfonated ions (or other hydrogen bonding sites in the polymer) is very important, particularly under minimal hydration conditions. The chemical groups near the polymer site, which directly interact with the protons are relevant as well as the dielectric constant of the

proton environment. Our group has reported the protonation of sulfonated polyoxadiazole membranes with different concentrations of sulfuric acid and different immersion times in the acid bath. After the protonation of sulfonated polyoxadiazole membranes in a 1.6 M H₂SO₄ solution, the measured proton conductivity was around $1 \times 10^{-2} \text{ S cm}^{-1}$ at 50 °C and 100% relative humidity [10]. The relatively high proton conductivity values for sulfonated polyoxadiazoles and polytriazoles are believed to be due to the availability of well distributed acidic and amphoteric sites for hydrogen bonding. Especially at low humidity levels important is also how dynamic the “bonding-debonding” of protons. A very strong proton attachment to the polymer amphoteric sites might lead to an excessively high friction and therefore to a lower conductivity. Therefore the basicity of this site should not be too strong. Groups like oxadiazole and triazole besides imidazole offer a well balanced amphoteric character.

A strategy to develop proton conductive membranes for operation at nearly anhydrous conditions has been the use of basic heterocycle molecules (imidazole, pyrazole, triazole) as solvent for acidic protons in polymers [1, 2, 11]. In this kind of materials, the proton conducting mechanism might be based on a non-vehicular mechanism (Grotthuss mechanism), in which only protons are mobile from site to site without additional assistance of diffusible vehicle molecules, such as water molecules [12]. The protonated and non-protonated nitrogen atoms in the heterocycles may act as donors and acceptors in proton-transfer reactions [6, 7, 13]. There is an intermolecular proton transfer controlled by hydrogen bond breaking and forming. A short and descriptive review about this kind of materials is done by Yamada and Honma [13]. Pyrazole seems to lead to lower conductivity than imidazole due to lower tendency to form hydrogen bonded structures. Triazole similar to imidazole has been investigated to promote proton conduction and additional to the molecular motion itself and intermolecular proton exchange, intramolecular proton transfer related (tautomerization) is possible [11]. An important aspect for the proton transfer in imidazole like molecules is the dielectric constant of the medium. High dielectric constant is needed to favor the formation of the protonic charge carriers [3] and assure an effective proton conduction. Imidazole has been considered in the presence of acid to promote proton transport. The acid in this case was sulfonated polyetherketone, sulfuric and sulfanilic acid [2], imidazole helping to increase the concentration of defect protons in the acid solutions. Schechter and Savinell [1] used imidazole combined to phosphoric acid to dope polybenzimidazole and in this case they observe a decrease of conductivity. In a recent paper Honma and Yamada [13] took in account the effect of hydrogen-bonding networks in

biomaterials to propose acid-base pairs for anhydrous proton conduction. They considered for instance sulfonated pyridine rings with the proton hopping from sulfonic acid group to the pyridine ring of an adjacent molecule.

In this work, sulfonated poly (oxadiazole-triazole) copolymer membranes were investigated, which have both acidic (-SO₃H group) and basic sites (basic nitrogen) in the repeating unit. According to some previous reports [14-16], sulfonated polyoxadiazoles and polytriazole copolymers offer a very convenient possibility for formation of a hydrogen bonding network to promote proton conduction. In this paper particularly emphasis is given to the improvement of the polymer proton conductivity by doping molecules. Besides sulfuric acid, molecules containing both acidic sulfonic and imidazole groups, benzimidazole sulfonic acid (Figure 1) have been chosen for doping.

(Figure 1- structures)

2. Experimental

2.1. Materials

All chemicals were used as received: 4-aminobenzenesulfonic acid (S-ANI, 99%, Aldrich), 4,4'-diphenylether dicarboxylic diacid (DPE, 99%, Aldrich), hydrazine sulphate (HS, >99%, Aldrich), poly(phosphoric acid) (PPA, Aldrich), sodium hydroxide (NaOH, 99%, Vetec), dimethyl sulfoxide (DMSO, Merck), 1H-benzimidazole-2-sulfonic acid (BiSA, 98%, Aldrich).

2.2. Synthesis of sulfonated poly(oxadiazole- triazole) copolymer

The synthesis conditions have been selected considering previously reported synthesis method for sulfonated poly(oxadiazole-triazole) copolymers (SPOD-SPT) with high molecular weight and high sulfonation level (IEC around 1.26 mequiv g⁻¹) [15, 17]. The molar dilution rate (PPA/HS), the molar monomer rate (HS/DPE) and the molar aromatic amine-pre polymer rate (S-ANI/PH) were kept constants and equal to 10, 1.2, and 1.0 respectively. After finishing the batch and to precipitate the polymer, the reaction medium was poured into a 5% w/v of cold (0°C) sodium hydroxide solution. The pH of this precipitation bath was controlled by addition of additional amounts of 5 % (w/v) NaOH aqueous solutions. The final polymer yield was always close to 100% regarding the limiting reactant (DPE). Calc.: N/C 0.1728 S/C 0.099; Found: N/C 0.1726 S/C 0.077.

2.3. Membrane preparation

A solution containing 5 wt. % of SPOD-SPT copolymer dissolved in DMSO was stirred for 4 hours at 65°C. Meanwhile a certain amount of BiSA was added into the polymer solution and keeping the stirring. Finally, the homogeneous solution was poured on a glass plate (previously hydrophobized with octadecyl trichlorosilane) at the same temperature during 24 hours for solvent evaporation. The final film thickness was controlled by pouring the polymer solution into a stainless steel ring of 10 cm diameter. After casting, the membrane was dried in a vacuum oven for 24 hours at 80°C. The final thickness of the blue-dark membrane was around 100 μm .

2.4. Characterization

Ionic conductivity was measured by the AC impedance spectroscopy in the frequency range 10-10⁶ Hz at signal amplitude ≤ 10 mV and derived from the high frequency intercept of the complex impedance with the real axis, using a two electrode arrangement with 20 to 100% of relative humidity (RH). Measurements were performed with a flow cell purged with wet nitrogen; relative humidity was controlled by bubbling nitrogen gas in water heated at a suitable temperature between 30 and 80°C. The impedance measurements were carried out on stacks containing up to five membranes (similar cumulative thickness, around 500 μm). The spectrometer used was a Zahner IM6 electrochemical workstation.

Dynamic mechanical thermal analysis (DMTA) was used for determination of glass transition temperature (T_g), storage modulus (E'), loss modulus (E'') and loss tangent ($\tan \delta$). DMTA was performed using a TA instrument RSA 2 with a film tension mode at a frequency of 1Hz and initial static force of 0.1 N. The temperature was varied from 25 to 500 °C at a heating rate of 2°C/min and at a constant strain of 0.05%.

Infrared spectra were recorded on a Bruker Equinox IFS 55 spectrophotometer in the range 4000-400 cm^{-1} , using polymer films and BiSA powder.

3. Results and Discussion

The main scope of this work is the exploitation of sulfonated oxadiazole-triazole copolymers (SPOD-SPT) as proton conductive membranes for fuel cell operation at intermediate temperature and low humidity conditions. An important advantage of this polymer

class, besides good thermal stability, is the amphoteric character and the possibility of doping with molecules, which through the formation of hydrogen bonds or by proton acceptor-donor interaction would significantly contribute for the proton conductivity [15]. The copolymer backbone alone has a combination of acidic (-SO₃H group) and basic sites (basic nitrogen) for effective interaction with protons, water and additional doping molecules. Doping of sulfonated polyoxadiazole with sulfuric acid, analogously to what is usually performed with polybenzimidazole, has been recently reported to increase the proton conductivity [10]. In this paper the idea is to dope the sulfonated oxadiazole-triazole copolymers with small amphoteric molecules containing acid and basic groups similar to those forming the polymer background, increasing the possibility of hydrogen bond formation: benzimidazole sulfonic acid (BiSA).

The molecular structures of SPOD-SPT/BiSA composite materials were characterized by using IR analysis. Figures 2 and 3 show two different frequency ranges of the IR spectra of pure BiSA (e) and SPOD-SPT/BiSA membranes, for different doping levels (x, expressed as the molar ratio (mol %) of additive per nitrogen sites in the polymer): 0, 3, 9 and 22 mol%.

(Figure 2)

(Figure 3)

The Region 4000-2000 cm⁻¹: In the IR spectrum of BiSA (Fig. 2), there are characteristic peaks due to hydrogen bonded NH vibrations as an envelope between 2100 and 3300 cm⁻¹; for the doped materials these NH vibrations are shifted to lower wavenumber and with lower intensity, since the intensity is more pronounced for higher contents of doping agent, substantiate hydrogen bonding interactions of between the BiSA molecules. For pure SPOD-SPT, the spectra show peaks at 3400-3200 cm⁻¹ which are related to the absorbed water and can be assigned to the OH stretch of the hydrogen-bonded groups (intra- and intermolecular, respectively). Between 3150 and 2300 cm⁻¹ a broad band complex appears, the weak peak at 2590 cm⁻¹, whose intensity increases with the content of BiSA, may be related to the proton transfer between the BiSA molecules and probably also from BiSA to the nitrogen atoms in the heterocyclic rings of SPOD-SPT.

The Region 1800-900 cm⁻¹: In the IR spectra of doped membranes (Fig. 3), the shoulders at 1620 cm⁻¹ and 1290, which grows when increasing the concentration of doping agent, may be assigned to C=N stretching in the heteroatomic ring (imidazole) of the doping agent; the shoulder at 1290 cm⁻¹, growing with the concentration of doping agent, can be assigned to CN stretching vibrations. The CN stretching vibrations are observed to produce intense bands at 1200-1310 cm⁻¹

¹, for BiSA should be the intense peak at 1278 cm⁻¹ [18]. The frequency range 1400-1000 cm⁻¹ comprises also absorptions due to the sulfonic groups [10, 16]. The peak at 1395 cm⁻¹ has been attributed to the SO₂ asymmetric stretching of the sulfonic group covalently bonded to the SPOD-SPT polymer, and show an increasing intensity with increasing amount of doping, probably the presence of the doping agent may interrupt the interactions between nitrogen atoms of oxadiazole and triazole rings and hydrogen atoms of the sulfonic group covalently bonded, and therefore increasing the amount of free sulfonic groups respect to the amount of them in the pure SPOD-SPT. This same effect may also be the reason for the increasing intensity of the peak at 1197 cm⁻¹ in the composite materials and it is attributed to the SO₂ symmetric stretching of the sulfonic group covalently bonded to SPOD-SPT. With increasing amounts of BiSA, the absorption intensity of the shoulder at 1147 cm⁻¹ also increases and it is relative to the SO₃ asymmetric stretching of the sulfonic group in BiSA, and the peaks at 1061-1067 cm⁻¹, with intensity increasing when increasing the doping level, has been assigned to SO₃ symmetric stretching of the sulfonic group in BiSA .

Dynamical mechanical relaxations of the doped materials have been investigated. The main goal of the mechanical characterization was to identify the relaxations of the pure SPOD-SPT and how they are affected by the dispersed doping agent. Figures 4 and 5 show plots of tan δ (mechanical damping) and E' (storage modulus) respectively versus temperature for each of the membranes; the results were obtained with dry membranes.

(Figure 4)

For the membrane from pure SPOD-SPT, the glass transition temperature (T_g) at 420 °C are related to α -transition of the polymer backbone. The bulky triazole side groups make the rotation difficult and contribute to the high temperature transition. Interactions between ionic groups and basic nitrogens of neighboring chains can additionally contribute to the high value. For the same membrane a T _{β} relaxation peak appears at 291 °C. This probably corresponds to the motion of the ether containing segment.

For the doped materials, the general trend is that both T_g and T _{β} decrease with increasing the concentration of doping agent, which is rationalized in terms of a plasticization of the chain backbone including the ether segments, since the interchain distance increases with the intercalation of the more mobile low molecular weight additive molecule. Also lower values of E' are observed for doped membranes (Fig. 5) reinforcing this affirmation.

(Figure 5)

The intrinsic transitions of the doping agent are other general characteristic of dynamical mechanical relaxations in the doped materials. It has been reported that imidazole molecule, with two protonation sites, assembles into a molecular clusters through intermolecular hydrogen-bonding [19]. Therefore we can assume that BiSA, with two protonation sites and a proton donor, may also form molecular assemblies, which would lead to fast proton transfer. The assembly is responsible for the broad transitions at 200 and 300°C when increasing the concentration of BiSA in the membranes, as can be seen in the plots of $\tan \delta$ and E' versus temperature (Fig. 4 and 5). The transition around 200°C could be probably due to changes in state of the imidazole-rich phase, like disassembling, what leads to a higher mobility system with dramatic decreases of E' module. The decrease starts just above 120°C, which is reported as the melting temperature for pure BiSA supplied by Aldrich. The transition at 300°C could be additionally related to significant weakening of the interaction (ionic and H-bond) between the additive and the polymer chain backbone. For low concentrations, the BiSA molecules do not form assemblies and no measurable changes could be seen at 200°C. The proton conductive measurements were performed up to 120°C and therefore below all the transitions at conditions at which mobility is quite low to significantly contribute to a vehicle mechanism. However it must be mentioned that still some water is present in the membrane and can play a role in the proton transfer.

The proton conductivities of the polymer at 120°C and very low relative humidity (5%) are plot as a function of the BiSA doping level and shown in Figure 6.

(Figure 6)

The proton conductivity increases with the content of the doping agent. These results suggest that the proton transport is mainly facilitated by the hydrogen bonds, being transferred between different acceptor and donor sites in the polymer and in the BiSA molecules. Figure 7 shows a proposed proton-conducting scheme in BiSA molecular crystals, in which proton hopping from sulfonic acid groups in BiSA to imidazole rings in neighboring molecules occurs, A similar mechanism has been proposed for sulfonated pyridine in the literature [13].

(Figure 7)

The protonated and non-protonated nitrogens in BiSA as well in SPOD-SPT can act as donors and acceptors in the proton-transfer reactions. In the protonation of the doping molecules, the neighboring sulfonic groups in SPOD-SPT could also be involved, like it has been exposed in the discussion of the infrared studies. The high conductivity values measured with increasing

concentration of BiSA, are in agreement with the assumed relation between the formation of the proton-conduction in a hydrogen bonding network practically without the need for liquid vehicular molecules at the intermediate temperature and low humidity conditions (Figure 7) [13].

Conclusions

Homogeneous membranes based on SPOD-SPT copolymer, bearing both acidic (-SO₃H group) and basic sites (basic nitrogen) in the main chain were doped with small molecules containing also both type of sites, BiSA, in order to improve the proton conductivity at high temperature and low relative humidity. The doped materials were studied with respect to their mechanical behavior and their proton conductivity. These membranes combine high thermal stability with the ability to form a hydrogen bonding network, facilitating the proton transfer between protonated (donors) and non-protonated (acceptors) nitrogens and sulfonic groups in BiSA and in the polymer.

Acknowledgments

The authors thank H. Böttcher for the DMTA characterization and the FCT foundation, Portugal, for the fellowship of M. Boaventura.

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Figures Caption

Figure 1. Molecular structures of (a) SPOD-SPT and (b) BiSA.

Figure 2. FTIR spectra of pure BiSA (e) and of SPOD-SPT/BiSA membranes in the region 4000-2000 cm^{-1} , for different doping levels (x): (a) x = 0, (b) x = 3 mol%, (c) x = 9 mol%, (d) x = 22 mol%.

Figure 3. FTIR spectra of pure BiSA (e) and of SPOD-SPT/BiSA membranes in the region 1800-900 cm^{-1} , for different doping levels: (x): (a) x = 0, (b) x = 3 mol%, (c) x = 9 mol%, (d) x = 22 mol%.

Figure 4. $\tan \delta$ versus T for SPOD-SPT/BiSA membranes with different doping levels (x): 0, 3, 9 and 22 mol%.

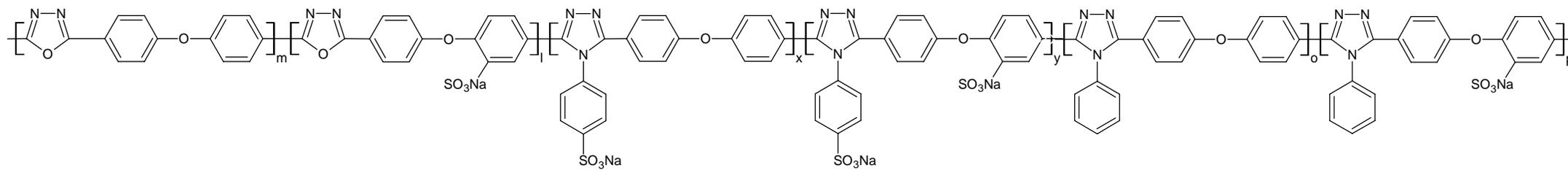
Figure 5. E' versus T for SPOD-SPT/BiSA membranes with different doping levels (x): (\diamond) = 0, (Δ) x = 3 mol%, (O) x = 9 mol%, (∇) x = 22 mol%.

Figure 6. Proton conductivity of SPOD-SPT/BiSA membranes as a function of the doping level at 120°C and 5% relative humidity.

Figure 7. Proposed proton-conducting mechanism in SPOD-SPT/BiSA membranes.

Figure 1.

(a)



(b)

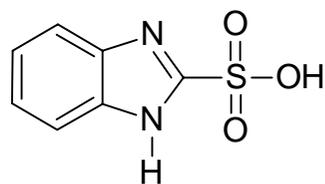


Figure 2.

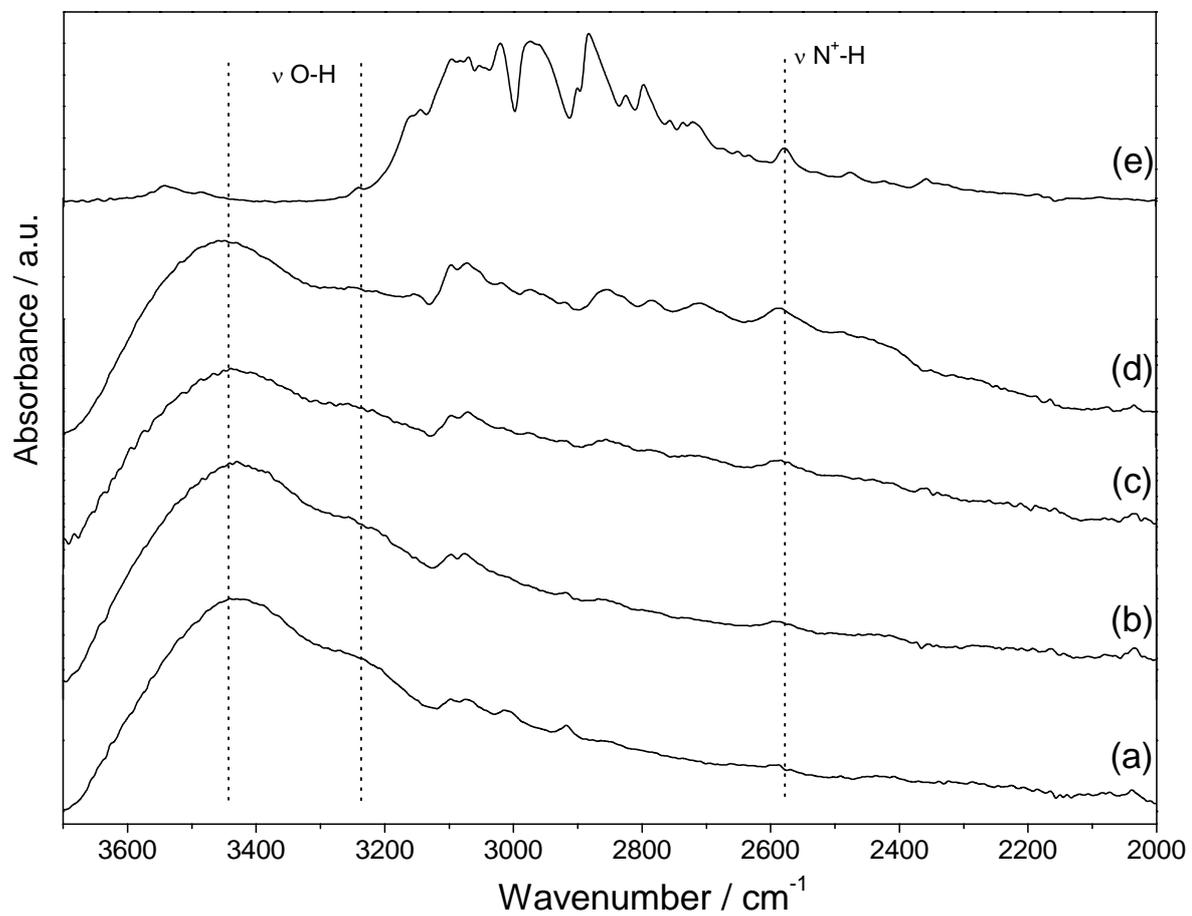


Figure 3.

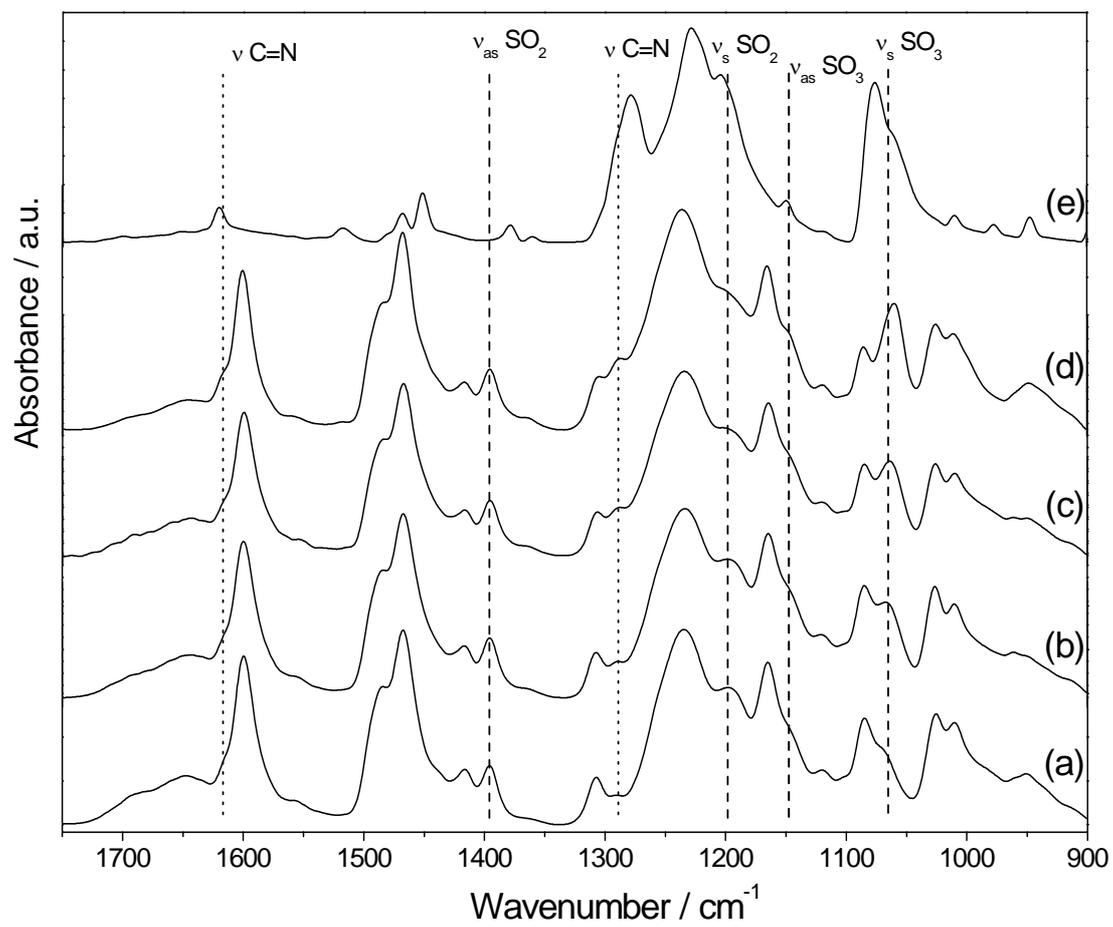


Figure 4.

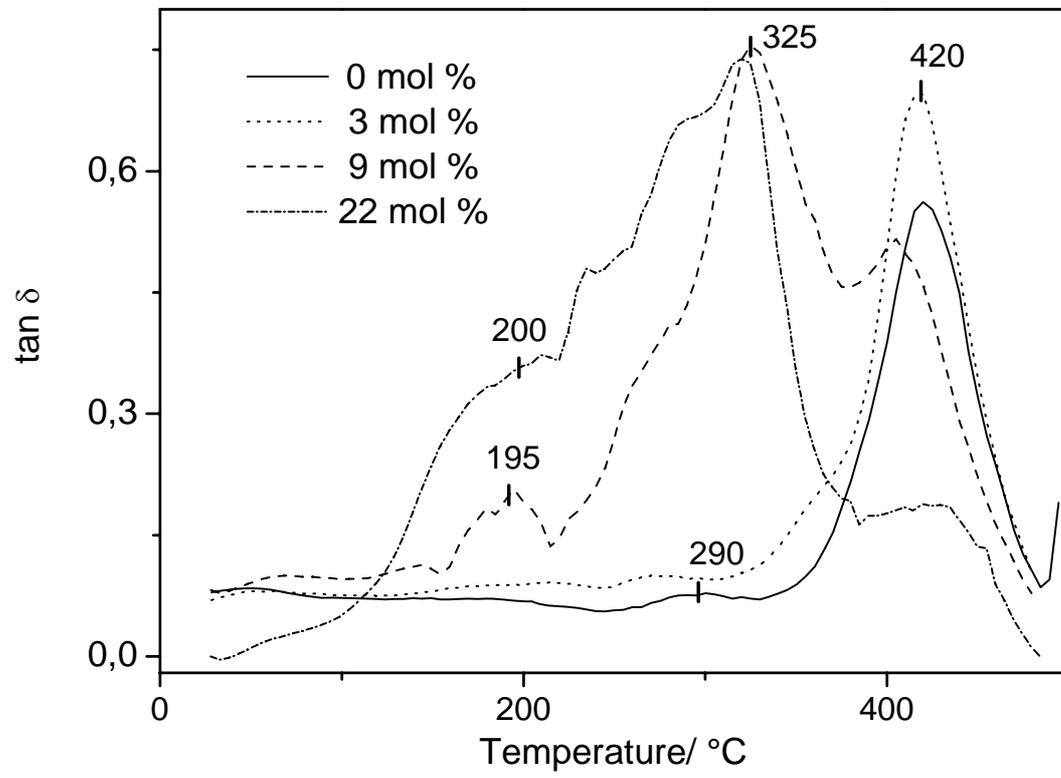


Figure 5.

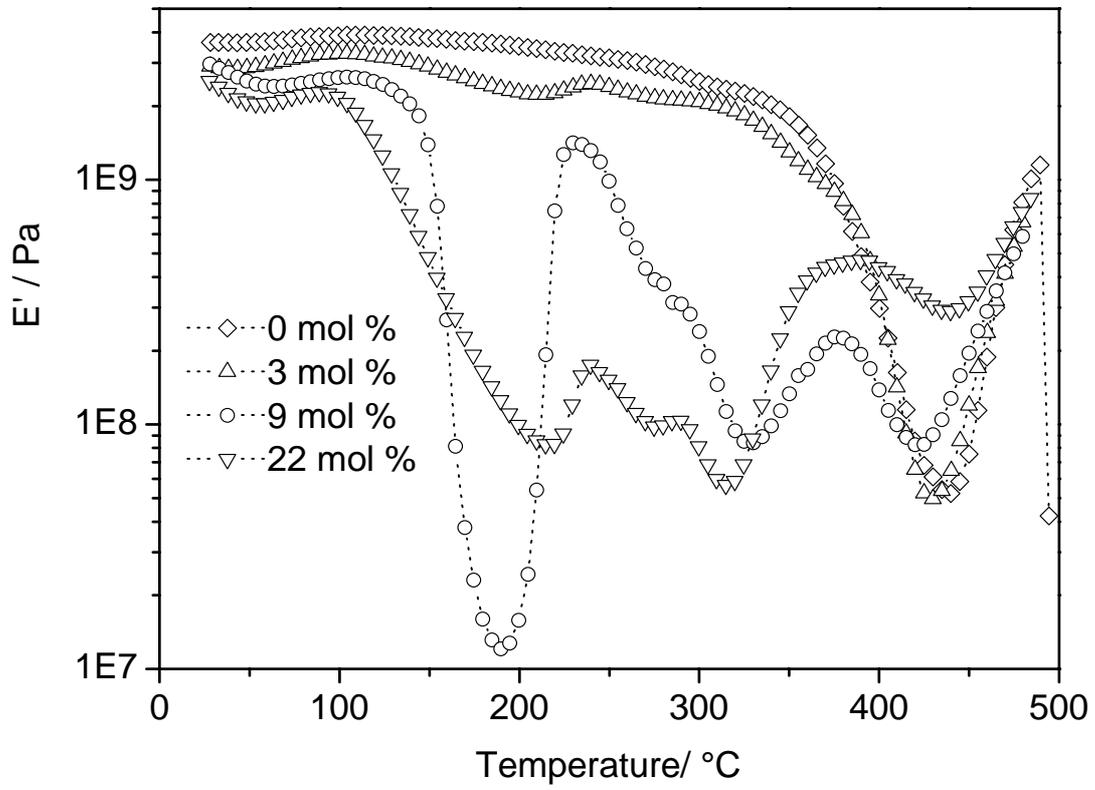


Figure 6.

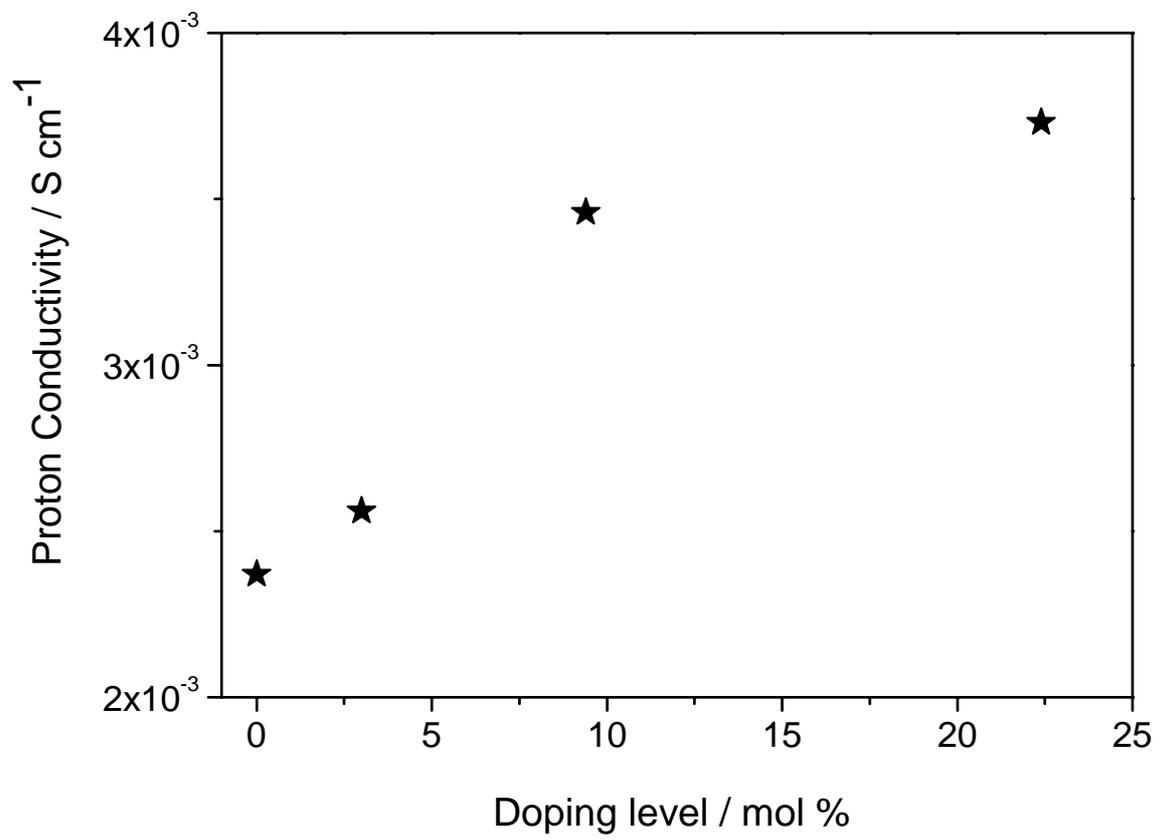


Figure 7.

