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Abstract:

This paper reports the one-pot synthesis and characterization of functionalized mesoporous SBA-15 silica, containing two loadings of different acid groups ($-CO_2H$, $-PO(OH)_2$ and $-SO_3H$). The thermodynamic features of the water confined in these porous silicas is investigated by Differential Scanning Calorimetry (DSC). The results show that the melting behaviour of the confined water is mainly governed by the pore diameter and, as a consequence, indicate that the chemical "decoration" of the porous surface does not play any key role on water thermodynamics in that case. On the contrary, the proton conductivity of the hydrated mesoporous materials, examined in a wide range of temperatures (-100 to 70°C), turns out to be strongly dependent on both the physical state of the confined water and the acidity of the functions located at the porous surface. The proton conductivity is shown to be directly related to the pK_a and the density of the functional groups attached to the mesopore

surface. The high conductivity values obtained at low temperature when the confined water is frozen, let us think that the –SO$_3$H functionalized SBA-15 investigated here could be promising candidates for electrolyte solids applications in fuel cells.

Introduction

Organic-inorganic hybrid materials based on silica and obtained by sol-gel process have attracted considerable attention during the last decades, as they constitute a unique class of materials combining the properties of organic moieties and inorganic matrix.[1-3] Since the discovery of ordered mesoporous silicas,[4-7] many investigations have focused on their functionalization to render them suitable for applications such as catalysis, separation, chemical sensors etc. Two main approaches have been used to anchor organic groups onto the inner pore surface of mesoporous silicas: grafting method (post-synthesis) and co-condensation method (direct or one-pot synthesis). Post-synthesis grafting of an organotrialkoxysilane RSi(OR')$_3$ onto the inner pore surface of the mesoporous silica was the first method established for functionalization.[8-10] This method is generic and allows the incorporation of many R groups including bulky ones. However, neither the loading nor the surface distribution of the functional groups, which depend on several parameters such as the number of the residual silanol (SiOH) groups as well as their accessibility, are easily controllable by this synthesis route.[11,12] Furthermore, post-synthesis grafting makes also possible the functionalization of the outer surface of the materials. A one step alternative approach, overcoming the main restrictions of the post-synthesis method, has been developed.[11,13,14] It consists in the copolymerisation of tetraethylorthosilicate (TEOS) and an organotrialkoxysilane RSi(OR')$_3$ in the presence of a structure-directing agent. This method requires the R group to be sufficiently hydrophobic to enter the core of the micelle and not too bulky to disturb the self-assembly imposed by the structure-directing agent. The main advantage of this method is that the functional groups are necessarily located at the inner material surface, their density is very well controlled and they are homogeneously distributed along the pores.[3] The drawback is that the size of the micelle and consequently its pore

diameter are affected by the functional groups. Although the porous structure is maintained, the textural properties may then slightly vary from one sample to another.

Among the numerous mesoporous organic-inorganic hybrid solids, efforts have been done to prepare acid functionalized mesostructured porous silica materials which could be used as solid electrolytes.[15-22] Indeed, acid functionalized mesoporous materials (by grafting or co-condensation) could constitute a promising class of solid state intermediate-temperature proton conductors, dedicated to Proton Exchange Membrane Fuel Cells (PEMFCs), due to their high charge carrier concentration, adjustable acid group density, oxidation resistance, thermal stability and high water adsorption properties in relation with both their high surface area and porous volume. By analogy with the renowned Nafion proton conducting membrane, many studies were focalized on sulfonic acid functionalization.[15-19,22] Alternatively, mesoporous silica proton conductors based on phosphoric or phosphonic acids have also attracted attention.[20,21] Owing to the amphoteric features of the phosphoric/phosphonic acid, such solids can behave both like a proton donor (acidic) and like a proton acceptor (basic) to form dynamic hydrogen bond networks, so that protons can be readily transported by fast hydrogen bond breaking and forming,[20,23,24] even under low humidity and at intermediate temperatures (i.e. 100-150°C). If the proton conduction properties of each type of these materials have been clearly demonstrated, it remains difficult to highlight the most promising candidate for PEMFCs applications, since the comparison of their conductivity performances is not straightforward. Indeed, these materials not only differ by the nature of the acid group, but also by other parameters, such as the synthesis mode, the acid group density, the pore diameter etc...

In this study, we report the synthesis and the conductivity properties of mesoporous SBA-15 silica functionalized by different acid groups ($-CO_2H$, $-PO(OH)_2$ and $-SO_3H$), for two densities of functionalization. All materials were prepared by direct synthesis using P123 as

structure directing agent. The porous structure was characterized by nitrogen adsorption-desorption isotherms, small angle X-Ray Diffraction (XRD) and Transmission Electron Microscopy (TEM). The local structure of functionalized SBA-15 was checked by means of a Solid-State NMR study. ^{29}Si nucleus was used to probe the silica network whilst ^{13}C and ^{31}P allowed us to examine the local structure of the functional groups. Before addressing the conductivity properties of the hydrated samples, the thermodynamic properties of water molecules that are confined into the material mesoporosity were investigated using Differential Scanning Calorimetry (DSC). Then, the proton conductivity was measured by mean of Complex Impedance Spectroscopy and the data discussed according to the nature and the concentration of the protogenic group of the functionalized mesoporous silica. In this paper we chose to investigate functionalized SBA-15 samples prepared by the one-pot synthesis route, since it offers a much better control of the inner surface chemistry, i.e. the functionalization rate and the function accessibility and distribution, despite the lower quality of their textural properties compared with their "homologous" materials prepared by post-synthesis grafting. Moreover, dc conductivity of fully hydrated porous solid state materials is not necessarily related to the textural characteristics to their surface chemistry, i.e. the nature and the density of the functional groups. For these reasons, the one-pot synthesis route is more appropriate for a systematic investigation of the hydrated sample conductivity as a function of the nature and the loading of the acid groups.

Results and Discussion

Preparation and characterization of the acid functionalized SBA-15 silica materials

Unfunctionalized SBA-15: The unfunctionalized SBA-15 was prepared as previously described,[25] by hydrolysis and polycondensation of tetraethoxysilane (TEOS) in presence of

Pluronic 123 as structure directing agent. After aging and removing the surfactant, the solid product was dried and denoted as **SBA-15**.

Acid functionalized SBA-15: The propylphosphonic, propylsulfonic or propylcarboxylic acid functionalized SBA-15 were obtained by hydrolysis (refluxing in acid aqueous solution) of functionalized mesoporous materials containing respectively -$PO(OEt)_2$, -SH or -CN groups, which were previously prepared by one-pot co-condensation of the Pluronic 123 with a mixture of $[(EtO)_3Si(CH_2)_3-X]$ and TEOS, where -X = -$PO(OEt)_2$, -SH or -CN, respectively (see scheme 1). The $[(EtO)_3Si(CH_2)_3-X]/nTEOS$ (with n=9, 19) molar ratio was fixed to 1/9 or 1/19, in order to finally get materials with two different loadings of acid functions.[26,27,28] Samples were labeled **SBA-PO(OH)$_2$ (1/9)**, **SBA-PO(OH)$_2$ (1/19)**, **SBA-SO$_3$H (1/9)**, **SBA-SO$_3$H (1/19)** and **SBA-CO$_2$H (1/9)**. The functionnalization of these materials was checked by NMR.

X-Ray Diffraction

The small angle powder X-ray pattern of the unfunctionalized **SBA-15** is depicted in Figure 1. It exhibits one intense peak accompanied by two weak peaks, indexed to the (100), (110), and (200) diffractions plans in the *p6mm* space group, respectively. This X-Ray pattern is typically observed for materials characterized by an hexagonal ordered array of one dimensional channel structure.[29] For the functionalized SBA-15 samples (cf Figure 1), the main (100) peak remains, whilst the others are more or less pronounced, dependently on the nature and on the concentration of the functional group. However, it was shown that materials with a similar single reflection can still exhibit local hexagonal symmetry.[30] In addition, Transmission Electron Microscopy images (TEM) evidences the highly ordered hexagonal structure of the porous network (cf Figures 2 and Figure SI.1)

The d_{100} spacing and a unit cell parameter ($a = 2d_{100}/\sqrt{3}$) values are summarized in Table 1. When one compares the data of **SBA-15** to those of the acid functionalized SBA-15, the cell parameter decreases, except for the **SBA-CO₂H (1/9)**. Noteworthy this decrease is more pronounced when the functionalization degree increases. This implies that the precursors [(EtO)₃Si(CH₂)₃-PO(OEt)₂] and [EtO)₃Si(CH₂)₃-SH] slightly disturb the stability of the micelles during the one-pot synthesis of the functionalized silica, and that this perturbation follows the precursor concentration.

N₂ adsorption-desorption measurements

The N₂ adsorption-desorption isotherms of the dry unfunctionalized and functionalized SBA-15 samples are illustrated in Figure 3. According to the IUPAC classification, all samples (except **SBA-SO₃H (1/9)** (cf Figure SI.2)) exhibit a type IV isotherm. These typical isotherms are characterised by a hysteresis loop of H₁ type and by sharp adsorption and desorption branches in relation with a narrow pore size distribution. The position of the capillary condensation step is directly related to the pore diameter, which varies with the nature (size, polarity and lipophylic character) of the functional group, because of its influence on the micelle size during the one-pot synthesis. In the case of **SBA-SO₃H (1/9)** sample, the hysteresis loop is a composite of H₁ and H₂ types (cf Figure SI.2), suggesting some constrictions along the nanopore. As a consequence, the capillary condensation occurs in a broader domain of relative pressure and the desorption branch exhibits a step, due to the "pore-blocking" effect.[31-33] Such a complex porous structure is likely to result from the influence of the organosilicon precursor in terms of hydrophilicity and compatibility with the micellar structure.

Anyway, it can be concluded that the mesoporous structure is maintained whatever the functionalization. Compared to **SBA-15**, the nitrogen capillary condensation of the

functionalized samples is shifted towards lower relative pressure, meaning that the textural properties of the silica depend on the concentration as well as on the nature of the functionalization. The textural data, i.e. surface area and pore volume, obtained for all the studied samples are listed in Table 1. External surface areas and pore wall thicknesses are given in supporting information III (cf Table SI.3). Those of **SBA-15** are in good agreement with the ones already reported for silica exhibiting similar pore diameters.[29,34] In all cases, the microporosity (<0.05 cm^3.g^{-1}) is negligible compared to the pore volume. The pore diameter (D_{p1}) of the functionalized samples decreases with the increase of the concentration of the organic groups. By contrast, the evolution of the textural properties (specific area "S_{BET}", Porous volume "V_{pore}") with the nature of the functional group is relatively complex and no clear trend was observed. The different textural properties of the obtained materials are due to the different types of interactions between the molecular precursors and the micelles during the synthesis. Then, the comparison of the textural properties based on the nature of the functionalization cannot be straightforward. Moreover, the arrangement and the steric environment of the organic chains at the nanopore surface may also play a key role. This last point is clearly emphasized when one compares the pore diameter obtained from the BJH method (D_{p1}) with the one, labelled dynamic diameter (D_{p2}), which is extracted from the ratio of the pore volume (V_{pore}) and the specific area (S_{BET}), i.e. $D_{p2}=4V_{pore}/S_{BET}$. From Table 1, one notes a fairly good agreement between both diameter values, for **SBA-15** and **SBA-CO$_2$H (1/9)**, whereas a discrepancy occurs for the two other families of samples **SBA-PO(OH)$_2$** and **SBA-SO$_3$H**, the discrepancy being more marked as the organic chain concentration increases. For these two last samples, the cylindrical pore model is probably no more acceptable. This outcome is probably due to the chains orientation and/or assembly at the pore surface, via hydrogen bonds between either the functional groups or the functional groups and the surface.[35] However, for the hydrated samples, inter-functions and surface-functions bonds

are inhibited,[35] so that this point is not relevant in this study, i.e, when one analyzes the conductivity properties of hydrated functionalized SBA-15.

Solid-state NMR characterization

The ^{29}Si single pulse NMR spectra of the dry samples **SBA-15** and functionalized **SBA-15** are presented in Figure 4. Silicon atoms are located at the centre of oxygen tetrahedra connected by corners and the silica network can be described using the common nomenclature in terms of Q^n $Si(OSi)_n(OH)_{4-n}$; n = 0, 1, 2, 3 or 4 and T^m $RSi(OSi)_m(OH)_{3-m}$, m = 0, 1, 2 or 3 sites which differ in the number of organic radical and OH groups connected to the tetrahedron. Our samples evidence two line groups: organosiloxane T^m lines and siloxane Q^n lines that are spread in the -50 to -80 ppm and -80 to -120 ppm ranges, respectively. The positions, relative intensities and assignment of the lines are reported in Table 2. T^m lines can be observed only for functionalized samples. The T^3 line is always present and corresponds to silicon atoms connected to the propyl spacer of the functional groups.

Three distinct resonances for siloxanes are observed and are associated to Q^2, Q^3 and Q^4 sites. The relative integrated intensities of the lines indicate that the majority of the silicon atoms belong to Q^4 substructures (Table 2), which correspond to silicon atoms located in the walls. Q^2 and Q^3 sites indicate that silanol groups are mainly located at the surface of the porous samples. Q^2 sites are rarely present with a concentration of a few percent only. According to ^{29}Si NMR results, the presence of T^m peaks with T^3 sites predominant over T^2 confirms that the organosilane precursors are effectively condensed as a part of silica matrix.[36] For all the functionalized samples and from the relative integrated intensities of Q^n and T^m signals, the T^m/Q^n ratio was estimated to be 0.11 and 0.05 for the 1/9 and 1/19 loadings of acid functions (Table 2), respectively. These results are in very good agreement

with the molar composition of the initial mixtures [1(EtO)$_3$Si(CH$_2$)$_3$-X]/nTEOS (n=1, 19), where -X = -PO(OEt)$_2$, -SH or –CN.

NMR spectra of hydrated samples (not shown) were also recorded and do not exhibit significant differences, so that it can be concluded that the silica wall is not reactive to water in that case.

^{13}C CP/MAS NMR spectra of the dry samples presented in Figure 5 and NMR parameters reported in Table 3 allow us to check that the one-pot functionnalization as well as the hydrolysis of the so-obtained solids have been successfully achieved, for all the samples. Further, it is clearly demonstrated that there is no unreacted functional group left in the studied samples, as shown by the disappearance of the bands assigned to the carbon response of the -CN, -O-CH$_2$-CH$_3$ and -CH$_2$-SH functions for the **SBA-CO$_2$H (1/9)**, **SBA-PO(OH)$_2$ (1/9)** and **SBA-SO$_3$H (1/9)** samples, repectively. Moreover, the spectra of **SBA-CN (1/9)**, **SBA-PO(OEt)$_2$ (1/9)**, and **SBA-SH (1/9)** show a line at 59 ppm which is attributed to residual ethoxy groups of TEOS or precursor. This line is removed after the chemical modification (hydrolysis) of -CN, -PO(OET)$_2$ and -SH groups. The data obtained for the solids characterized by the lower function density present the same trends (not shown here). ^{13}C CP-MAS experiments were not acquired for hydrated sample, because the presence of water, cross polarization is much less efficient leading to noisy spectra.

^{31}P NMR spectra of **SBA-PO(OEt)$_2$** and **SBA-PO(OH)$_2$** are shown in Figure 6. On the one hand, for the dry **SBA-PO(OEt)$_2$**, the ^{31}P spectrum exhibits only one line, located at 34 ppm, indicating a homogeneous environment of the phosphonate groups.[35] On the opposite, the spectrum of **SBA-PO(OH)$_2$** shows two lines. According to Aliev et al,[35] the line at 33 ppm is attributed to free phosphonic acid groups and those at 23 ppm to phosphonic acid groups engaged in hydrogen bonds. For the hydrated **SBA-PO(OH)$_2$** sample, we observe an important line narrowing and a slight shift toward lower chemical shift values of the lines

positions compared to those reported for the dry **SBA-PO(OH)$_2$** . The line width narrowing emphasizes that the mobility of the functional groups increases upon water adsorption. Moreover, for the hydrated **SBA-PO(OH)$_2$** we observe that the line corresponding to phosphonic groups engaged in hydrogen is greatly reduced. This indicates that these hydrogen bonds are unstable when water molecules are adsorbed in the nanopores.

The data obtained for the solids with the lower function density presents the same trends (not shown here). These results and those obtained from ^{13}C NMR highlight that the hydrolysis of **SBA-PO(OEt)$_2$** was successfully achieved.

Properties of the confined water

The first step of our experimental investigation consisted in characterizing thermodynamics of the water molecules confined in the nanopore of our samples, since the conductivity properties of the functionalized samples are strongly dependant on the water physical state, as we will see later. Thermodynamics was characterized using Differential Scanning Calorimetry (DSC) measurements. DSC signals obtained upon heating are shown in Figure 7 for all the samples. As expected,[43,44] they exhibit two endothermic peaks. The first one, occurring below 0°C corresponds to the melting of the solid state water confined in the SBA-15 nanopores. The second one, located between 70 and 100°C, is related to the water desorption. In both cases, the peak position depends on the nature of the functionalized silica. As usually observed for confined fluids, both melting and desorption occur over a large temperature range. In agreement with previous works reported on functionalized SBA-15 or MCM-41,[43-49] melting occurs in a temperature range lower than that of bulk water, whatever the surface decoration. Table 1 lists the melting temperature shifts ΔT_m, with $\Delta T_m = T_m - 273$ K where T_m is the temperature at the peak extremum. As ΔT_m differs from one sample to another, one may

wonder if it is influenced either by the chemical nature of the functionalized surface or by the pore diameter. According to the Gibbs-Thompson equation (Equation 1), a linear relationship between ΔT_m and the inverse of the pore radius (R_p) is established:[50]

$$\Delta T_m = -C_{GT}/R_p \quad \text{with} \quad C_{GT} = 2T_0(\gamma_{WS} - \gamma_{WL}) \times v/\Delta h_{SL} \qquad \text{Equation 1}$$

C_{GT} is the Gibbs-Thompson constant, accounting for the surface free energies per unit area of the interfaces wall/solid (γ_{WS}) and wall/liquid (γ_{WL}), the molar melting enthalpy (Δh_{SL}) and the molar volume (v) of the liquid or solid phase, depending on which has the lower free energy at the wall surface. As reported,[51] Equation 1 can be expressed by Equation 2:

$$\Delta T_m = -C_{GT}/(R_s) \quad \text{with} \quad R_s = R_p - R_t \qquad \text{Equation 2}$$

where R_t represents the thickness of the liquid-like layer at the wall surface and at the relevant melting temperature. It would correspond to ca. two monolayers of water molecules[51,52] and was estimated equal to 0.6 nm. Therefore R_s can be seen as the solid core radius. S. Jähnert et al.[51] investigated unfunctionalized silica, thus excluding the potential role played by the chemical surface. In our case, the inner surface differs from one sample to another because of the presence of the functional groups. This chemical decoration might influence the fluid/pore interaction and hence the melting point of the confined fluid. Assuming that in our case R_p can be estimated from the nitrogen adsorption/desorption isotherms analysis via the BJH formalism, we plotted the experimental values of ΔT_m (see Table 1) as a function of R_s^{-1} in order to check whether Equation 2 is obeyed or not. As shown in Figure 8, the linear dependence of ΔT_m is evidenced and the corresponding C_{GT} parameter (C_{GT} = 33 K.nm) determined from the linear fitting procedure perfectly agrees with the one reported by Brun et al (32.33 K.nm).[53] Besides, it can be readily considered that the negligible deviation at the origin coordinate, i.e. 0.95 K, falls within the experimental error.

Therefore it can be assumed that Equation 2 accounts well for the experimental data and, hence, concluded that the effect of the chemical nature of the inner pore surface is rather negligible on the water solid/liquid transition process.[54]

Proton conductivity properties

Complex Impedance Spectroscopy (CIS) has been extensively used to address the dynamics of confined liquids.[55-57] In this work, we firstly studied the conductivity response of all the dehydrated SBA-15 samples since, as reported in Ref. [56], dynamics of silanol groups at the inner surface of the nanopores give rise to a dielectric relaxation, which was associated to the rotational motion of the polar O-H bond. However, for all our samples, neither dielectric relaxation nor *dc* conductivity has been observed in the temperature and frequency ranges considered here. These results show that i) reorientational motions of OH groups are too fast or too slow to be detected using our experimental conditions and ii) there is no electrical charge, either electrons or ions, diffusing into the core or at the surface of the dehydrated samples. On the contrary, all our hydrated samples exhibit both polarisation ($\sigma_{pol}(\omega)$) and *dc* conductivity (σ_{dc}) signals (cf Equation 7, experimental section). This is clearly illustrated in Figure 9, where we reported the global conductivity (σ_{ac}) recorded at different temperatures, as a function of the frequency of the applied electrical field, in the case of **SBA-PO(OH)$_2$ (1/9)**, which can be taken as a typical example. At the highest temperatures and lowest frequencies, one also observes that the hydrated samples exhibit a so-called Maxwell-Wagner-Sillars contribution ($\sigma_{MWS}(\omega)$) that is due to interfacial polarisation arising from the blocking of ionic charges at the sample/metallic electrode interface. By comparison with the behaviour of their dehydrated counterpart, it can be assumed that *ac* conductivity of the hydrated samples is due to the water confined inside the nanopores.

The values of *dc* conductivity which can be determined from the *ac* conductivity spectra (see Figure 9) are plotted as a function of the inverse temperature following the relation deduced from the Nernst-Einstein model for ionic diffusion:

$$\sigma_{dc}(T) = \frac{\sigma_0}{T} \cdot exp\left(-\frac{E_a}{kT}\right) \qquad \text{Equation 3}$$

where σ_0 is *dc* conductivity at infinite temperature, E_a the activation energy and k the Boltzmann constant. As shown in Figure 10, three regimes are identified within the corresponding temperature ranges: (I) -100°C < T < -10°C, (II) -10°C < T < 40°C, and (III) T > 40°C. These temperature domains correspond to the existence of the different phases of the confined water, which were identified from DSC experiments: the confined water is frozen in (I), in a liquid state in (II) and evaporates in (III). This close connection between the behaviour of *dc* conductivity and DSC experiments is further validated by the fact that the transition between the domains (I) and (II) occurs at a temperature very close to the melting temperature T_m obtained from DSC. This outcome, reported here for **SBA-PO(OH)$_2$ (1/9)**, has been observed for all samples. As already outlined, it undoubtedly suggests that *dc* conductivity of our mesoporous silica strongly depends on the presence of water and on its physical state. The *dc* conductivity decrease measured in domain (III), which corresponds to desorption of the confined water molecules, confirms this assumption. In domains (I) and (II), the system obeys Equation 3, as shown by the linear dependence seen in Figure 10. In domain (II), we observe a decrease of the slope, i.e. of the activation energy, compared to that of domain (I), in relation with the higher mobility of the charge carriers in the water liquid phase. Although Equation 3 appears to be valid in domain (II), no activation energy value can be reasonably determined, due to the narrowness of the temperature domain in which it is estimated. Calculation of the activation energy was made possible in domain (I) for all the investigated samples (Figure 10 and Table 4). It is not possible from the values of E_a obtained for the different samples to clearly distinguish the influence of the acid group nature and of its

density. Meanwhile, it can be emphasized that all these values fall within the same order of magnitude as the one reported for solid state water confined in MCM-41 (E_a= 0.6 eV)[56] or for bulk water (E_a= 0.6 eV).[57] This comparison strongly suggests that the conduction mechanism involved in our systems is connected to protons dynamics in frozen water[60,61] and led us to consider that *dc* conductivity is probably due to protons diffusion assisted by water molecules via a Grotthuss mechanism.[62-64] In this model, proton transport is caused by proton translocation from one water molecule to its neighbour, followed by a subsequent rotation of the water molecules. The later governs the conductivity mechanism and hence the activation energy. For the unfunctionalized **SBA-15** sample, the protons which participate to the Grotthuss mechanism probably originate from the water molecules themselves but also from the dissociation of the silanol groups present at the nanopore surface.[65] For the functionalized samples, a larger quantity of mobile protons can be generated by the dissociation of the acid functions. The Grotthuss mechanism is confirmed by the fact that E_a values of dc conductivity reported for all samples are almost independent on the origin and content of protons (Table 4). σ_{dc} is therefore more influenced by the intrinsic dynamics of water molecules than by the acidity of the surface and, hence, is not much dependent on the functional groups. This suggests that the proton transport in these fully hydrated samples is mainly governed by the water molecules dynamics at the mesopore center. The surface roughness thus plays a minor role, which would not be probably the case for dehydrated or weakly hydrated samples.

Although the conductivity mechanism is likely the same for all the considered samples, the Arrhenius plots reported in Figure 11 show that the level of *dc* conductivity is much more sensitive to the surface chemistry. At fixed temperature (e.g. T = -30°C), the samples can be classified according to their *dc* conductivity:

$$\sigma_{dc}(\text{SBA-SO}_3\text{H } (1/9)) > \sigma_{dc}(\text{SBA-SO}_3\text{H } (1/19)) > \sigma_{dc}(\text{SBA-PO(OH)}_2 (1/9)) > \sigma_{dc}(\text{SBA-}$$

$$\text{PO(OH)}_2 (1/19)) > \sigma_{dc}(\text{SBA-15}) > \sigma_{dc}(\text{SBA-CO}_2\text{H } (1/9))$$

Except for the **SBA-CO₂H (1/9)** sample, all functionalized silica exhibit higher value of *dc* conductivity, than that of **SBA-15**. This observation does not only follow the functionalization loading, but also depends on the nature of the acid groups. This suggests that the protons content into the water confined at the pore center, which depends on the functional group concentration as well as the strength of the acid functions, plays a key role in the level of *dc* conductivity. In fact, mobile protons which participate to the Grotthuss mechanism mainly arise from the dissociation of the weak acids of either the chain functions and/or the silanol groups. Basically, *dc* conductivity is expressed by :

$$\sigma_{dc} = n \times \mu \times q \qquad \text{Equation 4}$$

where *n, μ* and *q* are the density, the mobility and the electrical charge of the carrier, respectively. As emphasized from the values of activation energy (Table 4), the proton mobility, *μ*, governed by the Grotthuss mechanism can be considered as independent of the investigated sample. Therefore, providing that *q* is constant, it can be deduced that the magnitude of dc conductivity is mainly governed by *n*, the density of dissociated, i.e. mobile, protons in the water confined in the mesopores.

The density of mobile protons can be readily estimated from the Brönstedt theory, which gives for a "weak" acid:

$$-\log[\text{H}^+] = \frac{1}{2}\text{pK}_a - \frac{1}{2}\log[\text{A}]_0 \qquad \text{Equation 5}$$

where $[\text{A}]_0$ is the concentration of the weak acid and pK_a its strength. Finally, providing that $n \propto [\text{H}^+]$ and that $[\text{A}]_0$ is the same for all (1/9) samples, the combination of Equations 4 and 5 leads to:

$$-\log(\sigma_{dc}) \propto \text{pK}_a \qquad \text{Equation 6}$$

The evolution of $-\log(\sigma_{dc})$ recorded at -30°C as a function of the pK_a of the acid function decorating our sample nanopores is plotted in Figure 12. The pK_a values were collected from the literature,[66-68] except for the phosphonic acid groups, for which no data could be found in the literature. In that case, we used the pK_a value characterizing the first acidity of the free propylphosphonic acid,[69] as a first approximation. As demonstrated by the linear relationship observed in Figure 12, the experimental dc conductivity data perfectly agrees with Equation 6 and hence validates the assumption proposed here. Furthermore, this simple model allows us to explain i) the lower level of dc conductivity observed in the (1/19) samples whose the function loading is much lower than that of (1/9) and ii) the lower dc conductivity of **SBA-CO$_2$H (1/9)** compared to that of **SBA-15** in relation with its higher pK_a value. Noteworthy, the same trend was observed for all the temperatures of domain I.

Based on the dc conductivity values recorded at low temperature, i.e. -30°C (cf Figure 12), and keeping in mind that in that case the confined water is frozen, the investigated samples and more particularly **SBA-SO$_3$H (1/9)**, can be considered as reasonably good protonic conductors. In the later, the conductivity value recorded at -30°C ($\sigma_{dc} = 10^{-4}$ S.cm^{-1}), is even higher than that reported at 60°C ($\sigma_{dc} = 2.10^{-5}$ S.cm^{-1})[17] for a similar functionalized SBA-15, prepared via grafting, despite the fact that the operating conditions (i.e. temperature) are rather unfavourable in our case. In Ref. [17] data were recorded at 60°C, in a 100% water-rich atmosphere, meaning that the sample contains a large amount of liquid water. This may suggest that the higher ordering of the functional groups at the mesopore surface, resulting from the one-pot synthesized, strongly enhances dc conductivity. In addition, Figure 12 also indicates that the best way to improve dc conductivity of the functionalized **SBA-15**, consists in preparing solids with acid functions, characterized by pK_a values lower than that of **SBA-SO$_3$H (1/9)**. Thus, we shall propose to replace the propyl chain of this functionalized sample,

by the fluorinated or chlorinated counterpart. This should be favourable for making highly conductive solids, potentially suitable for PEMFCs applications.

Conclusion

Mesoporous SBA-15 samples with phosphonic, sulfonic or carboxylic acid functionalization have been synthesized by the co-condensation method. Although the nature and the loading of these chemical "decorations" do not impact the confined water thermodynamics, they significantly influence the level of proton conductivity of the fully hydrated solids. In this study, due to experimental limitations, *dc* conductivity was investigated, while the confined water was frozen (T < -25°C). It is clearly demonstrated that *dc* conductivity increases with the acidic strength, as well as with the loading of the functional groups. A further investigation for which the confined water is in the liquid state imposes to work in controlled water atmosphere, which is out of scope of the present study. However it can reasonably be predicted that dc conductivity will be much higher in that case. For these reasons, it is possible to consider that the *dc* conductivity values measured in the current work are high enough to make these materials very promising for solid electrolytes applications. *dc* conductivity measurements at higher temperature and under various relative humidity conditions will be presented in a future paper.

Experimental Section

Chemicals: Pluronic P123 ($EO_{20}PO_{70}EO_{20}$, M=5800g/mol) and Tetraethylorthosilicate (TEOS) were supplied by Aldrich and ABCR, respectively. 3-Mercaptopropylriethoxysilane [$(EtO)_3Si(CH_2)_3SH$] and 3-cyanopropyltriethoxysilane [$(EtO)_3Si(CH_2)_3CN$] were supplied

from Aldrich and used as received. Triethoxysilylpropyldiethylphosphonate [$(EtO)_3Si(CH_2)_3PO(OEt)_2$], was synthesized as previously described.[70]

Acid functionalized SBA-15:

8.0 g (1.38 mmol) of Pluronic P123 were dissolved in 320 mL of HCl aqueous solution (pH=1.5). Then, we introduced 16.8 g (80.77 mmol) of TEOS and the appropriate amount of the selected precursor [$(EtO)_3Si(CH_2)_3-X$], according to the nature and the function degree of the functionalized material we expected. This mixture was stirred until obtaining a clear solution and then 0.08 g of NaF was added. After aging under regular stirring for 3 days at 60 °C, the resulting powder was filtered off and the surfactant was removed by Soxhlet extraction with hot ethanol for 24 hours. The recovered solid was dried at 70°C under vacuum. The so-obtained samples were denoted as **SBA-PO(OEt)₂ (1/9)**, **SBA-PO(OEt)₂ (1/19)**, **SBA-SH (1/9)**, **SBA-SH (1/19) and SBA-CN (1/9)**.

Then 3.0 g of **SBA-PO(OEt)₂ (1/9)** (3.90 mmol) or **SBA-PO(OEt)₂ (1/19)** (2.18 mmol) were treated by refluxing with 50 mL of HCl aqueous solution (12N) under stirring at 100°C during 24 hours. The solid product was recovered by filtration, washed several times with water and ethanol, and finally dried at 70°C under vacuum.[27,70] The so-prepared samples were noted **SBA-PO(OH)₂ (1/9)** and **SBA-PO(OH)₂ (1/19)**.

For the propylsulfonic acid functionalized SBA-15 preparation, 4.0 g of **SBA-SH (1/9)** (5.99 mmol) or **SBA-SH (1/19)** (3.16 mmol) have been firstly stirred with a hydrogen peroxyde solution (33%) during 24 hours and successively with a sulfuric acid aqueous solution (2M), during 20 minutes. Then, the solid products **SBA-SO₃H (1/9) or SBA-SO₃H (1/19)** were recovered by filtration, washed several times with water and ethanol, and finally dried at 70°C under vacuum.[27]

Finally, the propylcarboxylic acid functionalized **SBA-CO₂H (1/9)** was prepared by refluxing 4g (6.1 mmol) of **SBA-CN (1/9)** with 100 mL of H_2SO_4 aqueous solution (50%) under stirring at 120°C during 12 hours. Then, the solid product **SBA-CO₂H (1/9)** was recovered by filtration, washed several times with water, ethanol, acetone and ether and finally dried at 70°C under vacuum.[27]

Sample hydration: The samples were first dehydrated at 80°C for 24h and then maintained into contact with a water saturated atmosphere for 24 hours at room temperature.

X-ray Diffraction (XRD) : Powder X-ray diffraction patterns were recorded on a X-PERT PRO II Philips diffractometer by using Cu Kα radiation (d = 1.54056 Å).

Transmission Electron Microscopy (TEM): TEM observations were carried out at 100 kV on a JEOL 1200 EXII microscope. Samples for TEM measurements were prepared using ultramicrotomy techniques and then deposited on copper grids.

Nitrogen adsorption and desorption isotherms: Nitrogen adsorption and desorption isotherms were measured at 77 K on a Micromeritics TRISTAR 3000 analyzer. Before these measurements, the samples were outgassed for 12 hours at 70 °C under a stable vacuum of 4×10^{-3} mbar. The Brunauer-Emmett-Teller (BET) specific surface area was evaluated using adsorption data in a relative pressure range from 0.04 to 0.20, where the BET equation is applicable.[71] The mesopore size distribution was calculated on the basis of desorption branches of nitrogen isotherms, using the Barrett-Joyner-Halenda method (BJH),[72] and the pore size (D_p) was obtained from the peak position of the distribution curve. The total pore volume was determined from the amount adsorbed at a relative pressure of about 0.97. The

micropore volumes was assessed by means of a t-plot analysis, for which Harkins and Jura's expression was used to calculate the adsorbed layer thickness.[73]

Solid-State NMR: Solid state NMR spectra were recorded on a Varian VNMRS 400 Solid spectrometer with a magnetic field strength of 9.4 T equipped with 7.5 mm, 3.2 mm MAS probe. 7.5 mm MAS probe was used for ^{29}Si and ^{13}C nuclei with a spinning rate of 5 kHz. For ^{31}P nucleus, 3.2 mm MAS probe was used with a spinning rate of 10 kHz. Single pulse sequences with continuous decoupling were used for ^{29}Si NMR experiment, with 5 μs π/2 pulse duration and a recycle delay of 60 s. It was checked that with a 200 s recycle delay the same spectra decomposition are obtained. This last point allows us to consider that in our materials the ^{29}Si experiments recorded with a recycle delay to 60 s, are quantitative. For ^{13}C nucleus, CP MAS experiments were acquired with a 5 s pulse sequence repetition delay, 5 μs π/2 (^{1}H) pulse duration, 3 ms contact time. Then single pulse sequences with tppm[74] decoupling were used for ^{31}P experiment, with 4 μs π/2 pulse duration and a recycle delay of 30 s. The ^{29}Si and ^{13}C nuclei were referenced to TetraMethylSilane (TMS). The ^{31}P was referenced to H_3PO_4. Solid state NMR spectra were fitted using the Dmfit program.[75]

Differential scanning calorimetry (DSC): A Netzsch DSC 204 F1 was used for the DSC measurements under N_2 flux, from -150°C to 425°C and with a heating rate of 2°C/min.

Complex Impedance Spectroscopy (CIS): The proton conductivity was measured by CIS. Isothermal conductivity measurements were performed in the 10^{-2}-10^{6} Hz frequency range, with a Novocontrol dielectric alpha analyzer. The temperature of the sample, ranging from -100°C to 70°C, was controlled by a Quatro Novocontrol system. In order to prevent any destruction of the silica porous structure under external pressure, conductivity measurements

were not carried out on pellets prepared from compressed powder. Instead, we employed a specific cell similar to that generally used for liquids. About 100 mg of the powder sample was poured on the lower electrode of the cell, and then very gently pressed by the upper metallic electrode. CIS gives access to the real part of the ac conductivity, which results, in many cases from the superposition of Maxwell Wagner Sillars, $\sigma_{MWS}(\omega,T)$, dc conductivity, $\sigma_{dc}(T)$, and polarization conductivity, $\sigma_{pol}(\omega,T)$, (see Equation 7).

$$\sigma_{ac}(\omega,T)=\sigma_{MWS}(\omega,T) + \sigma_{dc}(T) + \sigma_{pol}(\omega,T) \quad\quad \text{Equation 7}$$

Basically, dc conductivity corresponds to long-range redistribution of charges, i.e. ionic or electron transport, while the polarisation contribution arises from local rearrangement of charges or dipoles causing dipolar reorientation and thus resulting in the intrinsic bulk polarization. Maxwell Wagner Sillars polarisation is due to the accumulation of charges at the sample/electrodes interface and also depends on extrinsic parameters, such as the sample shape.

Supporting Information Available:

Additional information as noted in the text.

Captions

Table 1. Structural and textural properties of the dry **SBA-15** and the different acid functionalized silica samples. ΔT_m values obtained from DSC experiments are also added.

Table 2. Deconvolution data of the ^{29}Si NMR spectra, for the dry **SBA-15** and the different acid functionalized silica samples. δ and R.I. are the isotropic chemical shift and the relative integrated intensity, respectively.

Table 3: Attribution of the experimental chemical shifts values of the ^{13}C CP/MAS solid state NMR to specific chemical species, in the case of the **SBA-CN (1/9)**, **SBA-CO$_2$H (1/9)**, **SBA-PO(OEt)$_2$ (1/9)** , **SBA-PO(OH)$_2$ (1/9)**, **SBA-SH (1/9)** and **SBA-SO$_3$H (1/9)** samples.

Table 4. Activation energies of the diffusion part of the conductivity for the dry **SBA-15** and the different acid functionalized silica samples.

Scheme 1. Preparation of acid functionalized materials **SBA-CO$_2$H**, **SBA-PO(OH)$_2$** and **SBA-SO$_3$H**.

Figure 1. XRD patterns of the **SBA-15** and the different acid functionalized silica. (XRD patterns are shifted by a constant factor).

Figure 2. TEM micrographs of **SBA-CO$_2$H (1/9)**. **(a),** Horizontal and **(b),** perpendicular views.

Figure 3. Nitrogen adsorption/desorption isotherms of the **SBA-15** and the different acid functionalized silica. (Isotherms plots are shifted by a constant factor).

Figure 4. ^{29}Si single pulse solid state NMR spectra of **SBA-15** and functionalized **SBA-15**.

Figure 5. ^{13}C CP/MAS solid state NMR spectra of : **a) SBA-CN (1/9)** and **SBA-CO$_2$H (1/9)** ; **b) SBA-PO(OEt)$_2$ (1/9)** and **SBA-PO(OH)$_2$ (1/9)** ; **c) SBA-SH (1/9)** and **SBA-SO$_3$H (1/9)**.

Figure 6. ^{31}P single pulse solid state NMR spectra of the dry **SBA-PO(OEt)$_2$** and **SBA-PO(OH)$_2$** and the hydrated **SBA-PO(OH)$_2$** samples.

Figure 7. DSC scanning curves showing the melting and boiling peaks of water confined in the **SBA-15** and the different acid functionalized silica at complete pore filling. (DSC curves are shifted by a constant factor).

Figure 8. Melting point depression ΔT_m versus the inverse of the core radius R_s (see Eq. 2). The line shows the fit of the data to a R_s^{-1} relation. The point corresponding to the bulk water melting is also represented by the open square symbol indicated by the arrow.

Figure 9. Real part of the global conductivity σ_{ac} as a function of the frequency f, for water confined in **SBA-PO(OH)$_2$ (1/9)**, at different temperatures, ranging from -100 to -5°C, by step of 5°C.

Figure 10. Ln($\sigma_{dc} \times T$) versus $10^3/T$ for water confined in **SBA-15-PO(OH)$_2$ (1/9)**, The lines are fits with the Nernst–Einstein equation.

Figure 11. Ln($\sigma_{dc} \times T$) versus $10^3/T$ for water confined in **SBA-15** and the different acid functionalized silica, in the temperature range -70 to -25°C.

Figure 12. –log(σ_{dc}) recorded at -30°C versus pK$_a$, for the **SBA-15** and the different acid functionalized silica. The line shows the fit of the data to a direct pK$_a$ relation.

Tables

Table 1. Structural and textural properties of the dry **SBA-15** and the different acid functionalized silica samples. ΔT_m values obtained from DSC experiments are also added.

Sample	Textural data (N_2 adsorption-desorption)					Structural data (XRD)		DSC data
	S_{BET} $(m^2.g^{-1})$	$V_{\mu\text{-pore}}$ $(cm^3.g^{-1})$	V_{pore} $(cm^3.g^{-1})$	$D_{p1}(BJH_{des})$ (Å)	D_{p2} (4V/S) (Å)	d_{100} (Å)	a (Å)	ΔT_m (K)
SBA-15	634	0.02	1.30	82	82	119	137	-8.1
SBA-PO(OH)$_2$ (1/9)	540	0.01	1.03	66	76	109	126	-10.6
SBA-PO(OH)$_2$ (1/19)	518	0.01	1.23	79	95	116	134	-7.9
SBA-SO$_3$H (1/9)	770	0.04	0.49	51	25	103	119	-17.3
SBA-SO$_3$H (1/19)	830	0.002	0.91	66	44	112	129	-12.7
SBA-CO$_2$H (1/9)	625	0.001	1.32	80	84	119	137	-8.0

Table 2. Deconvolution data of the ^{29}Si NMR spectra, for the dry **SBA-15** and the different acid functionalized silica samples. δ and R.I. are the isotropic chemical shift and the relative integrated intensity, respectively.

Samples	Parameters	T^2	T^3	Q^2	Q^3	Q^4	Ratio T^m/Q^n
SBA-15	δ (ppm)			-93	-103	-112	0
	R.I (%)			1	37	62	
SBA-PO(OH)$_2$ (1/9)	δ (ppm)		-67	-92	-102	-112	0.11
	R.I (%)		10	1	15	74	
SBA-PO(OH)$_2$ (1/19)	δ (ppm)		-66	-92	-102	-111	0.05
	R.I (%)		5	3	25	67	
SBA-CO$_2$H (1/9)	δ (ppm)	-59	-67	-91	-101	-111	0.11
	R.I (%)	1	9	1	28	61	
SBA-SO$_3$H (1/9)	δ (ppm)	-58	-67	-93	-102	-111	0.11
	R.I (%)	2	8	1	34	55	
SBA-SO$_3$H (1/19)	δ (ppm)		-66	-92	-102	-111	0.05
	R.I (%)		4	2	38	56	

Table 3. Attribution of the experimental chemical shifts values of the ^{13}C CP/MAS solid state NMR to specific chemical species, in the case of the **SBA-CN (1/9)**, **SBA-CO₂H (1/9)**, **SBA-PO(OEt)₂ (1/9)** , **SBA-PO(OH)₂ (1/9)**, **SBA-SH (1/9)** and **SBA-SO₃H (1/9)** samples.

Sample	δ (ppm)	Species	Reference
SBA-CN (1/9)	11	Si-**CH₂**(CH₂)₂-CN	[37-40]
	16	Si-O-CH₂-**CH₃**	
	19	Si-CH₂-**CH₂**-CH₂-CN	
	59	Si-O-**CH₂**-CH₃	
	120	Si-(CH₂)₃-**CN**	
SBA-CO₂H (1/9)	11	Si-**CH₂**(CH₂)₂-CO₂H	
	19	Si-CH₂-**CH₂**-CH₂-COOH	
	36	Si-(CH₂)₂-**CH₂**-CO₂H	
	178	Si-(CH₂)₃-**CO₂H**	
SBA-PO(OEt)₂ (1/9)	10-20	Si-CH₂-CH₂-CH₂-P-	[26,35,41]
	10-20	Si-O-CH₂-**CH₃**	
	10-20	Si-(CH₂)₃-PO(OCH₂**CH₃**)₂	
	30	Si-(CH₂)₂-**CH₂**-P-	
	59	Si-O-**CH₂**-CH₃	
	63	Si-(CH₂)₃-PO(O**CH₂**CH₃)₂	
SBA-PO(OH)₂ (1/9)	10-20	Si-**CH₂**-**CH₂**-CH₂-P	
	30	Si-(CH₂)₂-**CH₂**-P-	
SBA-SH (1/9)	10	Si-**CH₂**(CH₂)₂-SH	[41,42]
	15-20	Si-CH₂-**CH₂**-CH₂-SO₃H	
	15-20	Si-O-CH₂-**CH₃**	
	26	Si-(CH₂)₂-**CH₂**-SH	
	59	Si-O-**CH₂**-CH₃	
SBA-SO₃H (1/9)	10	Si-**CH₂**(CH₂)₂-SO₃H	
	17	Si-CH₂-**CH₂**-CH₂-SO₃H	
	53	Si-(CH₂)₂-**CH₂**-SO₃H	

Table 4. Activation energies of the diffusion part of the conductivity for the dry **SBA-15** and the different acid functionalized silica samples.

Sample	$\Delta E_a \pm 0.02$ (eV)
SBA-15	0.75
SBA-PO(OH)$_2$ (1/9)	0.65
SBA-PO(OH)$_2$ (1/19)	0.62
SBA-SO$_3$H (1/9)	0.68
SBA-SO$_3$H (1/19)	0.69
SBA-CO$_2$H (1/9)	0.65

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