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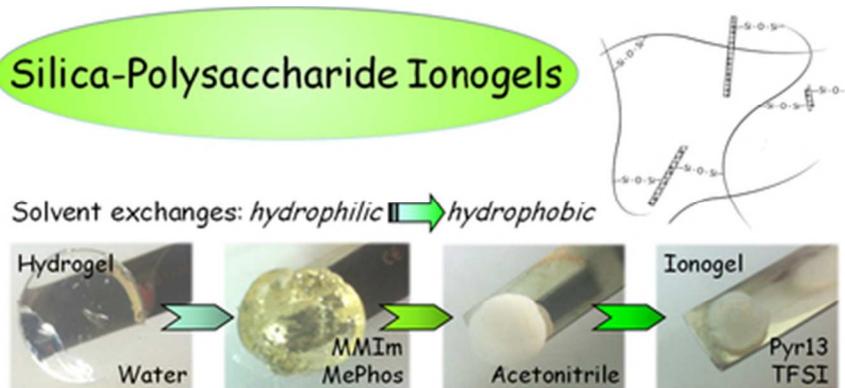
36x16mm (300 x 300 DPI)

ARTICLE TYPE

Biopolymer based nanocomposite ionogels: high performance, sustainable and solid electrolytes

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Ionogels based on a chemically cross-linked polysaccharide matrix and a hydrophobic ionic liquid offer a sustainable alternative to petrochemical-based polymer electrolytes. These newly obtained cellulose-based ionogels present the
10 **flexibility, thermal stability and high ionic conductivity of a liquid; this latter property can be further enhanced by adding silica nanofibers. As a result they can be used as a high-performance and eco-friendly electrolyte in the production of all-solid, sustainable devices.**

15 Ionogels are an original class of hybrid organic-inorganic materials in which a solid host network confines an ionic liquid, thereby retaining or enhancing its liquid dynamics.[1,2] Due to the negligible vapour pressure of ionic liquids (ILs), their confinement within a porous network results in a stable solid-like
20 material. Some of the ILs' interesting properties show good potential for use in material science (*e.g.* electrochemical devices)[3] and in the chemistry of bio-resources (*e.g.* as good biopolymer solvents).[4,5] The ionogel approach thus opens new opportunities for developing novel solid state devices.[6,7] When
25 compared to inorganic matrices, the polymer based ionogels present better mechanical properties. In addition bio-sourced polymers have an advantage over petroleum-based polymers when it comes to developing sustainable technologies. Various examples of biopolymer based ionogels can be found in the
30 literature. To date, however, there are only a few examples of physical ionogels based on a hydrophilic IL.[8-11]

Here we report a novel class of ionogels based on chemically cross-linked polysaccharide, *i.e.* silanized hydroxypropyl methylcellulose (Si-HPMC), and hydrophobic IL, N-propyl-N-
35 methylpyrrolidinium bis(trifluoromethylsulfonyl)imide (Pyr13 TFSI). These Si-HPMC ionogels are obtained via the facile route consisting of liquids exchanges, starting from Si-HPMC hydrogels.[12] The structure of the biopolymer and the scheme of the nanocomposite are presented in Scheme 1. The ionogel shows
40 a good ionic conductivity, which can be further greatly enhanced by adding mesoporous silica anisotropic nanofibers (NFs).

We firstly prepared Si-HPMC hydrogels as described elsewhere.[13] These hydrogels contained 2 wt% of polysaccharide cross-linked via Si-O-Si bridges, and 98 wt% of aqueous
45 solution. Then we exchanged the aqueous solution with the 1,3-dimethylimidazolium methylphosphonate (MMIm MePhos) by means of submersion of the hydrogels into the hydrophilic IL for 24 h. It is here worth to point out that if such an IL dissolves cellulose, it does not dissolve reticulated cellulose. After drying
50 (24 h, 50 °C and ambient atmosphere), this hydrophilic MMIm MePhos IL was subsequently exchanged with acetonitrile by placing the ionogels in a Soxhlet apparatus for 24 h. Then, the samples were immediately placed in a hydrophobic IL (Pyr13 TFSI) bath for 24 h, and then dried using the same technique as
55 above. This IL was absorbed, resulting in a homogeneous self-standing hydrophobic ionogel composed of a chemically cross-linked polysaccharide matrix confining the hydrophobic IL.

Fig. 1 Images of the samples obtained at each liquid exchange step; the weight percentages indicate the amount of the liquid present inside the sample, the
60 volume losses refer to Pyr13 TFSI ionogels *vs.* hydrogels.
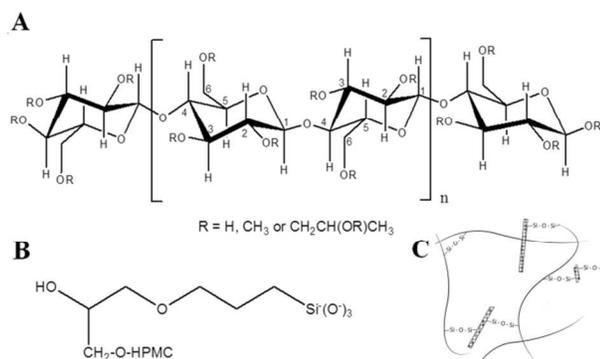
Scheme 1 Hydroxypropyl methylcellulose (HPMC) (A), silanized HPMC (Si-HPMC) (B), Si-HPMC / silica nanofibers composite (C).

The direct exchange of water for Pyr13 TFSI led to a dehydrated polysaccharide without swelling of the Pyr13 TFSI. Another series of exchange sequences to replace water by acetonitrile and then acetonitrile by Pyr13 TFSI, led to a non-homogeneous ionogel. Consequently, the progressive exchange from hydrophilic to hydrophobic ionic liquid (water / MMIm MePhos / acetonitrile / Pyr13 TFSI), appeared to be necessary. The same process was also carried out with Si-HPMC hydrogels containing 1 and 4 wt% of silica nanofibers (NFs) to obtain Si-HPMC-NFs nanocomposites ionogels which remained homogeneous. The covalent grafting of NFs onto the polysaccharide was ensured thanks to the pending siloxane groups. The silica NFs, which show form factor close to 10 (diameter $^{ca.}$50 nm, length $^{ca.}$500 nm), and the reinforced nanocomposite hydrogel were synthesized as already reported.[14,15] It was also already evidenced that the percolation of silica NFs network within the hydrogel occurred at a value of around 3 wt%.[15] For this reason we investigated 1 and 4 wt% of NFs content.

The images of our samples at each step are presented in Fig. 1. The volumes of the samples decreased from the hydrogel to the final Pyr13 TFSI based ionogels. Nevertheless, the shrinkage is less important with silica NFs: 67 % of volume loss for Si-HPMC-NFs ionogel with 4 wt% of NFs, while 93 % and 95 % of volume loss respectively with 1 wt% of NFs and without NFs. This ability of NFs' to preserve volume could be related to Si-O-Si linkages which bridge the silica NFs to the silanized biopolymer. Whatever the NFs amount, the material is stable and the IL does not leach out of the ionogels (Fig. 1 and Fig. 2) Moreover, Fig. 2 shows the good flexibility of the final Si-HPMC Pyr13 TFSI ionogel. The ionogels containing hydrophilic IL (MMIm MePhos) and hydrophobic IL (Pyr13 TFSI) were observed by scanning electron microscopy (SI, Fig. S1). FTIR spectroscopy was performed on this last ionogel and its spectrum was compared to that of pure Pyr13 TFSI and MMIm MePhos IL. The bands at 1575 cm^{-1} and 2310 cm^{-1} (Fig. 3, stars) in MMIm MePhos spectrum correspond *resp.* to imidazolium ring and P-H (anion).[16,17] These bands are not observed in Pyr13 TFSI IL nor in final Pyr13 TFSI based ionogel. On the other hand, we observe the bands at 1329 cm^{-1} (-SO$_2$ vibration)[18] and 1347 cm^{-1} (-CF$_3$ vibration)[19] (Fig. 3, arrows) in Pyr13 TFSI IL as well as in final Pyr13 TFSI based ionogel spectra. The solvent exchange is thus completed and

Fig. 2 Photography of Si-HPMC ionogel in flexion.

the polysaccharide based ionogel with pure hydrophobic Pyr13 TFSI IL is evidenced.

The quantity of liquid absorbed by the gel after each step in the exchange was evaluated by weight and expressed in wt% referring to total weight of matrix and liquid (Fig. 1). The amount of liquid introduced into the polymer matrix decreased in line with a rise in the hydrophobic character of the liquid. It can also be noted that the same weight percentage of MMIm MePhos (~95 wt%) and acetonitrile (~85 wt%) was introduced into ionogels with and without silica NFs. More specifically, it is worth pointing out that the amount of Pyr13 TFSI in Si-HPMC ionogel without NFs was lower (69 wt%) compared to that in Si-HPMC-NFs ionogels; this amount of Pyr13 TFSI increased in line with the NFs content (83 and 90 wt% with 1 and 4 wt% of NFs *resp.*). This is consistent with a smaller volume loss of the ionogel when the NFs content increased. Again, it appeared that Si-O-Si bonding between NFs and Si-HPMC prevented a collapse of the host network. Such a bonding between polysaccharide's pending silanol groups and silica NFs was evidenced, upon NFs addition, by the shortening of gel time and the increase of compressive Young modulus.[15]

Thermogravimetric analysis (TGA) was carried out on a pristine Si-HPMC polymer, Si-HPMC hydrogel and Si-HPMC Pyr13 TFSI ionogels, with and without NFs. The results are presented in Fig. 4. The Si-HPMC polymer (red) degradation occured at higher temperature when cross-linked in hydrogel (green) (240 °C *vs.* 210 °C), since in the pristine Si-HPMC polymer (not in the gel) the pending silanolates did not polycondense together. Once the water of the hydrogel was finally exchanged by the Pyr13 TFSI to form the ionogel (black), the thermal stability of polymer was enhanced (260 °C).
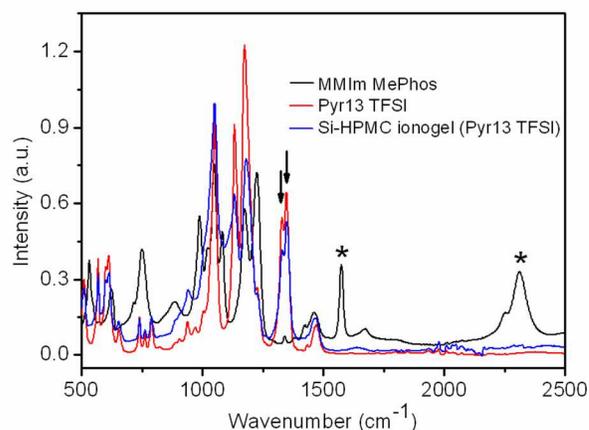
Fig. 3 FTIR spectra of MMIm MePhos, Pyr13 TFSI and Si-HPMC ionogel containing Pyr13 TFSI IL.
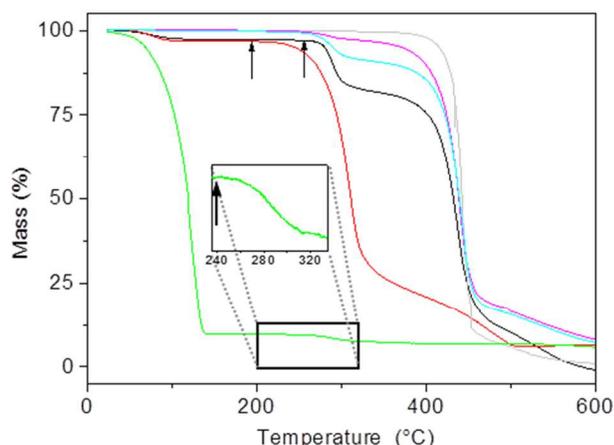
Fig. 4 TGA curves of Pyr13 TFSI IL and different Si-HPMC based samples: Pyr13 TFSI (grey), pristine Si-HPMC polymer (red), Si-HPMC hydrogel (green), Si-HPMC-Pyr13 TFSI ionogel (black), Si-HPMC-1wt% NFs ionogels (blue), Si-HPMC-4wt% NFs ionogels (pink); black arrows indicate the onset temperature of Si-HMPC polymer degradation.

As expected, confinement of Pyr13 TFSI did not change its thermal degradation, which occurred above 400 °C (grey, black, blue, pink). Moreover, the mass loss of Si-HPMC ionogel (black) between 370 °C and 470 °C (69 %) which corresponds to degradation of the IL correlates well with the weight percentage of Pyr13 TFSI IL as shown above (Fig. 1). We could also notice that the presence of silica NFs in Si-HPMC-NFs ionogels did not modify the thermal stability of the Si-HPMC (black, blue, pink).

Impedance spectroscopy was performed after each sample was carefully vacuum dried at 50 °C during 24 h. At room temperature (Table 1), the ionic conductivity of Si-HPMC Pyr13 TFSI ionogel without NFs is much lower than that of non confined IL. However, 0.7 mS cm⁻¹ is better or comparable to ionic conductivities of other polysaccharide based ionogels.[8,20] The addition of 1 wt% of silica NFs to the initial ionogel allowed an increase of the ionic conductivity. However, it has to be remembered that the amount of IL varies depending on NFs loading. Nevertheless, it has to be emphasised that increasing the NFs content up to 4 wt% allowed reaching an ionic conductivity of 4.5 mS cm⁻¹, which is higher than that of pristine IL. The Arrhenius plots for ionic conductivity of Si-HPMC - 4 wt% NFs ionogel and pristine Pyr13 TFSI are presented in Fig. 5. The activation energies were calculated between 20 °C and 90 °C and they are identical (0.3 eV) for both samples. Thus, the confined ionic liquid exhibits liquid-like dynamics. It is also worth pointing out that upon cooling the strong decrease (*i.e.* the slope break) of the ionic conductivity, due to liquid-to-solid transition, happens at lower temperature for the confined IL than for the pristine IL. In the whole range of temperature, the ionic conductivity of the Si-HPMC - 4 wt% NFs ionogel is higher than that of pristine Pyr13 TFSI.

Increased conductivity upon the addition of silica nanoparticles has been already reported elsewhere.[21-23] It is expected that a greater number of free ions are generated due to the preferential association of either IL cations with NFs pending silanolates or IL anions with NFs acidic silanols:

Table 1 Ionic conductivity of Pyr13 TFSI and different Si-HPMC Pyr13 TFSI ionogels at room temperature.

	Pyr13 TFSI	Si-HPMC ionogel	Si-HPMC-1wt% NFs ionogel	Si-HPMC-4wt% NFs ionogel
σ (mS.cm⁻¹)	2.8	0.7	1.5	4.5
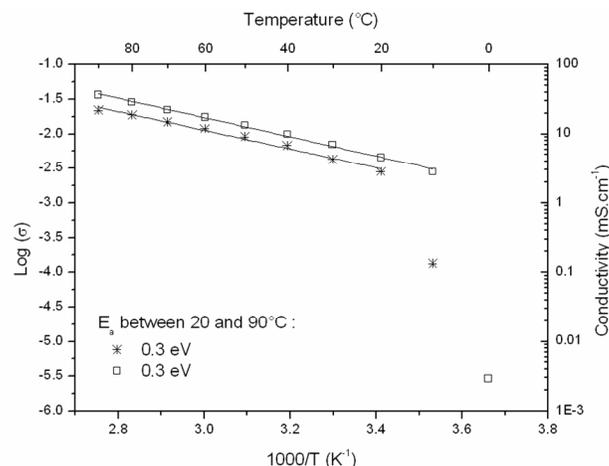
Fig. 5 Conductivity Arrhenius plot of pristine Pyr13 TFSI (*) and Si-HPMC–4wt% NFs ionogel containing Pyr13 TFSI (□). Inset: Activation energies for the above samples between 20 and 90 °C.

between both cases, it is difficult to know which really happens, since the surface's charge of the NFs in IL medium is hard to assert. Nevertheless, both enhance the free ions concentration in the double layer at the interface neighbourhood. Besides this, since the same activation energy was obtained for pristine Pyr13 TFSI and corresponding ionogel, the conduction pathway should occur in the same chemical environment, *i.e.,* in the ionogel, within the ionic double layer at the silica interface. The very strong increase of conductivity obtained here at a relatively low level of nanocharges is due to the anisotropy of the silica nanofibers which enables silica percolation as presented above:[15] this continuous IL/silica interface allows breakdown of strongly associated IL ions throughout the membrane, increasing the ionicity of the IL and consequently the conductivity.

We presented here a novel type of ionogels based on polysaccharide confining hydrophobic IL which were prepared via liquids exchanges. These homogeneous solids showed good thermal stability and unexpectedly largely upgraded ionic conductivity. The presence of silica NFs inside the ionogels enabled an increase in the IL load and raised the ionic conductivity to 4.5 mS cm⁻¹ at room temperature, which is one of the highest recorded for a solid electrolyte. These new ionogels offer high electrolytic performances for a solid while respecting sustainability.

Acknowledgment

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Notes and references

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† Electronic Supplementary Information (ESI) available: experimental details and SEM images of Si-HPMC ionogels. See DOI: 10.1039/b000000x/

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