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## **Hybrid Electrolytes**

**Manuel Maréchal<sup>a,\*</sup>, Christel Laberty-Robert<sup>b</sup>, Sébastien Livi<sup>c</sup>**

<sup>a</sup>CNRS, INAC-SPRAM, F-38000 Grenoble, France; Univ. Grenoble Alpes, INAC-SPRAM, F-38000 Grenoble, France; CEA, INAC-SPRAM, F-38000 Grenoble, France. manuel.marechal@cea.fr

<sup>b</sup>Sorbonne Universités, UPMC Univ. Paris 06, CNRS-UMR 7574, Collège de France, Laboratoire de Chimie de la Matière Condensée de Paris, 11 place Marcelin Berthelot, F-75005 Paris, France.

<sup>c</sup>Université de Lyon, F-69003, Lyon, France; INSA Lyon, F-69621, Villeurbanne, France; CNRS, UMR 5223, Ingénierie des Matériaux Polymères.

The need for clean, safe and efficient energy is a major societal issue that involves the development of new technologies for storage and energy production. The electrolytic media are at the center of the electrochemical devices like fuel cells, dye-sensitized solar cells, also called Grätzel, or supercapacitors or lithium-ion batteries. The finding of new electrolytes is rather challenging as it must fit certain constraints such as wide electrochemical windows, sufficient ionic conductivities, excellent thermal stability and sufficient mechanical properties. Many studies have converged towards the study of hybrid electrolytes consisting of organic and inorganic phases, or polymer-ionic liquid mixtures, to obtain solid electrolytes and to fulfill all these constraints. Controlling the structure at the nanoscale and understanding their properties at various length and space scales are crucial for their optimization. Recent and different ways were proposed to design hybrid electrolytes opening new perspectives in the energy field. The genesis and the presentation of these

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developments are presented through three main applications: the fuel cells, the organic photovoltaic cells and the energy storage.

### **Introduction**

The consumption of energy is continuously increasing and one of the answer is to improve the energy devices. Then the need to develop new advanced materials for the production and storage of energy in safe, efficient and environmentally friendly conditions is prominent. Electrolytes, at the center of the various devices, follow an incremental evolution together with breakthroughs.

Hybrid electrolytes have been widely investigated for various energy devices and fall into three broad types: (A) Hybrid membranes for Proton Exchange Membranes for Fuel Cells (PEMFCs) especially for temperatures up to 120 degrees Celsius (°C), (B) Hybrid ionic conductor xerogels for organic photovoltaic devices, and (C) Hybrid polymer/ionic liquid membranes for use in the energy storage. All these hybrid electrolytes have recently experienced new advances by controlling their structure at various length scales from macro- to nano-scales.

### **A - Hybrid Polymer Membranes for Proton Exchange Membranes for Fuel Cells**

The hybrid electrolytic polymer membranes have been extensively studied for fuel cells<sup>1-4</sup>. A scheme of fuel devices equipped with polymer membrane is presented in the figure 1. These membranes can be obtained by different processing routes after mixing the polymers and the inorganic components. The main processes are the casting<sup>5-6</sup>, the spray-coating<sup>7</sup>, the extrusion<sup>8</sup> and more recently the electrospinning<sup>6</sup>.

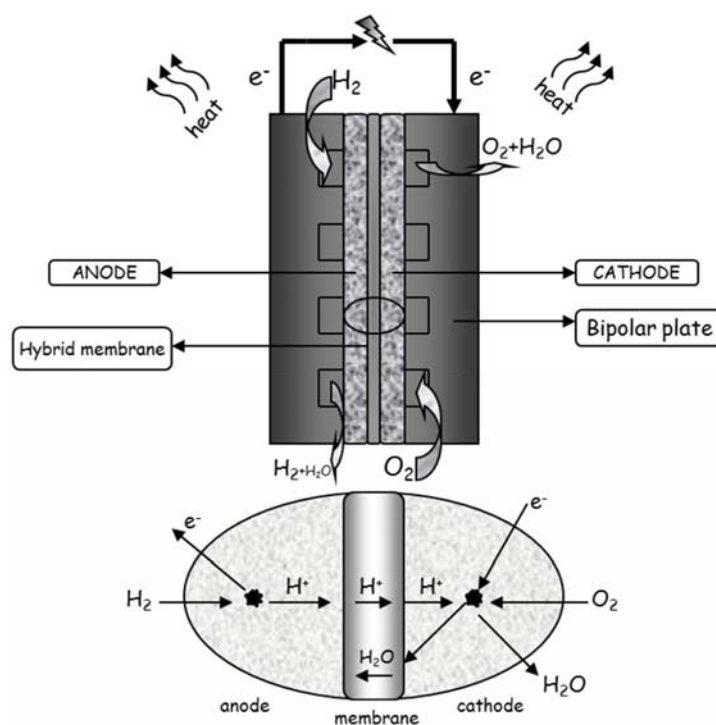


Figure 1: Synoptic layout of a fuel cell with a proton exchange membrane and, in the enlargement, at both electrode/membrane interfaces, the catalytic redox reactions.

### a - Hybrid polymer membranes with inorganic fillers

This family can be divided into several subfamilies depending on whether the polymer phase is an ionic conductor and whether the inorganic or hybrid phase contains ionic groups. One of the main families is constituted of membranes with a polymer electrolyte such as Nafion<sup>®</sup>-like perfluoroalkylsulfonic acid polymers (benchmark membranes)<sup>9-15</sup>, and sulfonated polyaromatic polymers<sup>16-17</sup>. These polymers include a second phase, (summarized in table 1) either an inorganic filler like mineral (laponite<sup>11, 16, 18</sup>, montmorillonite<sup>12-14</sup>, zinc oxide (ZrO<sub>2</sub>)<sup>19</sup>, Silica (SiO<sub>2</sub>)<sup>20</sup>, calcium hydrophosphonate<sup>10</sup>, titania (TiO<sub>2</sub>)<sup>13</sup>) or a heteropolyacid (hydrophosphoric acid<sup>21</sup>, orthophosphoric acid<sup>22-23</sup>, phosphotungstic acid<sup>19, 24-28</sup>, phosphomolybdic acid<sup>25-26, 29</sup>, silicotungstic acid<sup>25, 27, 30</sup>, phosphoantimonic acid<sup>31</sup>, zirconium phosphate sulfophenyl phosphate<sup>32</sup>, zirconium phosphate<sup>15, 27</sup>, mesoporous acid silicate<sup>16</sup>).

**Table 1: Mineral fillers and heteropolyacids used in the hybrid membranes for fuel cells.**

Mineral fillers	Formulae or composition
Laponite <sup>18, 33</sup> (Southern Clay Co.)	$(\text{Na}_{0.7}^{+}[(\text{Si}_8\text{Mg}_{5.5}\text{Li}_{0.3})\text{O}_{0.2}(\text{OH})_4]^{0.7-})$
MMT <sup>12</sup> MontMorillonite ( $\text{Na}^+$ -MMT) <sup>18</sup>	$(\text{Na}, \text{Ca})_{0.3}(\text{Al}, \text{Mg})_2\text{Si}_4\text{O}_{10}(\text{OH})_2 \cdot n\text{H}_2\text{O}$
m-MMT <sup>12</sup> modified MontMorillonite (dodecylamine-exchange montmorillonite)	as above
Zirconium isopropoxide <sup>19</sup> (Alfa Co. Ltd)	$[\text{Zr}(\text{OCH}(\text{CH}_3)_2)_4(\text{CH}_3)_2\text{CHOH}]$
Heteropolyacids	
hydrophosphoric acid <sup>21</sup>	$\text{H}_3\text{PO}_2$
Orthophosphoric acid <sup>22-23</sup>	$\text{H}_3\text{PO}_4$
12-PhosphoTungstic Acid (PTA or PWA) <sup>19, 24-27</sup>	$(\text{H}_3(\text{P}(\text{W}_3\text{O}_{10})_4) \cdot n\text{H}_2\text{O})$
Phosphomolybdic Acid (PMA or $\text{PMo}_{12}$ ) <sup>25-26, 29</sup>	$(12(\text{MoO}_3 \cdot 2\text{H}_2\text{O}) \cdot \text{H}_3\text{PO}_4 \cdot 4\text{H}_2\text{O})$
SilicoTungstic Acid (STA or SiWA) <sup>25, 27, 30</sup>	$(\text{H}_4(\text{Si}(\text{W}_3\text{O}_{10})_4) \cdot n\text{H}_2\text{O})$
Phosphatoantimonic acid ( $\text{H}_3$ ) <sup>31, 33-34</sup>	$(\text{HSb}(\text{PO}_4)_2 \cdot n\text{H}_2\text{O})$
Zirconium Phosphate Sulfophenyl Phosphonate (ZrPSPPh1.5) <sup>32</sup>	$(\text{Zr}(\text{HPO}_4) \cdot (\text{O}_3\text{PC}_6\text{H}_4\text{SO}_3\text{H})_{1.5})$
Zirconium Phosphate (ZrP) <sup>27, 35</sup>	$(\text{Zr}(\text{HPO}_4)_2 \cdot n\text{H}_2\text{O})$

The inorganic or hybrid fillers can also be embedded in non-ionic polymers, such as partially or perfluorinated polymers like Poly(Vinylidene Fluoride) (PVdF), Poly(Vinylidene Fluoride-co-HexaFluoroPropene) (P(VdF-HFP)), and so forth<sup>36-37</sup>. The obtained membranes are known to be chemically and electrochemically stable, with respect to the potential window of the applications<sup>38</sup>.

The overall objective of the hybrid approach is to decouple or couple the properties of the obtained membranes depending on the applications. For fuel cells, the properties include ionic conductivity, mechanical strength and/or water retention at elevated temperatures<sup>15</sup>.

### Proton conductivity

The addition of mineral fillers (layered silicates or metallic oxides) or heteropolyacids allows improving conductivities at low relative humidity (Figure 2). Most of the fillers/heteropolyacids has a substantial hydrophilicity and/or significant acidity, which explains the high water uptake. The addition of inorganic fillers may decrease<sup>12</sup> or increase<sup>31</sup> conductivities while improving other properties. For heteropolyacids, there is often an optimal loading<sup>27</sup>, around 7 weight-percent (wt.%), for example, for sulfonated polysulfones (SPS) /phosphoantimonic acid (H3)<sup>31, 34, 39</sup>. The size and the shape of the fillers also have its importance<sup>34</sup> since the different properties are highly dependent on the structuration of the fillers at the nanoscale and on the structuration of the organic components vs. inorganic ones at the various length scales.

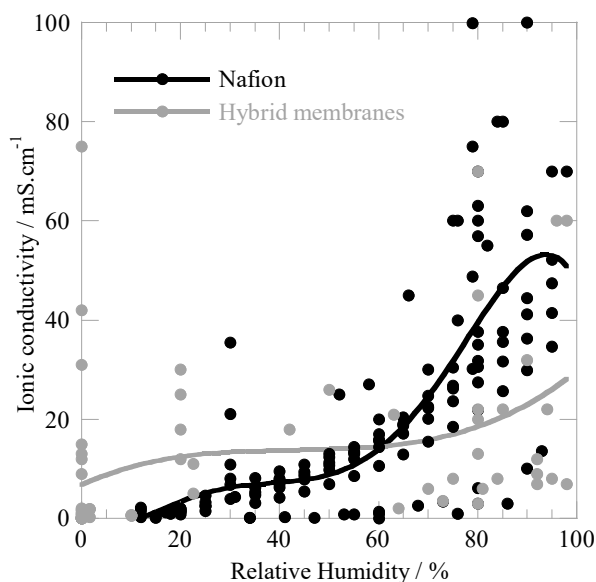


Figure 2: Ionic conductivity as a function of relative humidity ( $T \in [0, 120^\circ\text{C}]$  for each relative humidity). The curves are the weighted average conductivities at each relative humidity between the different temperatures (i) for Nafion<sup>®</sup>, and (ii) of the conductivities of the hybrid membranes previously cited.

The hydrophilic nature of these fillers should increase water uptakes and ionic conductivities in the final obtained composite membranes. The assumptions are questionable<sup>40</sup> since the literature reported contradictory results on the role played by the inorganic fillers<sup>13-15</sup>. It can be noticed that the improvement of the proton conductivity was low the last 20 years<sup>4, 14-16</sup> by using hybrid membranes in

the field of low/medium-temperature fuel cells. In the hybrid membranes, the interplay between the fillers and the polymer electrolytes is not clearly and definitely elucidated<sup>9-10, 16</sup>: (i) The water contained in the particles cannot easily be shared with the rest of the polymer electrolyte phase, and (ii) the conductivity of the inorganic/hybrid phase is in general at least one order lower than the one of the electrolytic organic phases. Nevertheless some composite membranes have worthwhile properties in the application uses<sup>12, 15</sup>.

### Mechanical properties

Improving effects of the mechanical properties at the local scale and the localization of the crystalline zones<sup>10</sup> are invoked to explain this paradox. The ionic transport has been shown to be intimately linked with the local mechanical properties<sup>41</sup> and the multiscale structure<sup>42-43</sup>.

The addition of heteropolyacids (Table 2) can reinforce the membrane, either with ionic charges (heteropolyacids) or not<sup>33</sup>. This addition can also weaken the membrane in the case of weak interactions. The system with sodiated forms of heteropolyacids<sup>25</sup> shows that, if the interaction is not strong enough, the network is weakened.

**Table 2: Mechanical properties of hybrid membranes.**

Hybrid membrane	Ultimate tensile strength/MPa ( $\sigma$ )	Young Modulus/MPa (E)	Elongation at break/% ( $\epsilon$ )
Nafion (23°C, 50%RH) <sup>44</sup>	23/28	288/281	252/311
NaSTA/Nafion <sup>®</sup> 117 <sup>25</sup>	14		45
NaPMA/Nafion <sup>®</sup> 117	8		70
NaPTA/Nafion <sup>®</sup> 117 (wet)	3		170
SPS 1.1 mol H <sup>+</sup> ·kg <sup>-1</sup> 3.5/7.1/12 wt.% of H <sub>3</sub> <sup>39</sup>		158/88/59	6.4/5.4/1.9
SPS 3/25 wt.% of H <sub>3</sub> <sup>39</sup>		370/340	48/60

### Degradation temperatures

The effect of heteropolyacids, which globally has high degradation temperatures, is not systematically studied (Table 3). In general, the obtained composites do not exhibit very different degradation temperatures from those of associated polymers. This observation seems logical since the degradation is always conditioned by the least stable component. For NaSTA/Nafion, the

degradation temperature is lower than that of Nafion alone. In the case of the composite made of phosphotungstic acid/SBPS, the addition of the mineral acid only reduces the degradation temperature of the low degrees of sulfonation (-44°C between 20 and 60 mol.% of sulfonation). This fact means that the acidic functional groups are more or less protected as the degree of sulfonation, the loading, the level of interaction (from repulsion to ionic crosslinking), and acid or alkaline forms of the heteropolyacid<sup>45</sup>. The ionic interactions of phosphotungstic acid/SBPS is such that the degradation temperature increases with the sulfonation rate instead of decreasing as for the pure ionomer(+64°C between 20 and 60 mol.% of sulfonation). The composites formed of non-ionic polymers and heteropolyacids have high degradation temperatures (>300°C). The combination of components having high degradation temperatures explains this observation. If all other characteristics are combined, they would be relevant candidates for "medium temperature" PEMFCs.

**Table 3: Degradation temperatures at 5 wt.% of weight loss of hybrid membranes.**

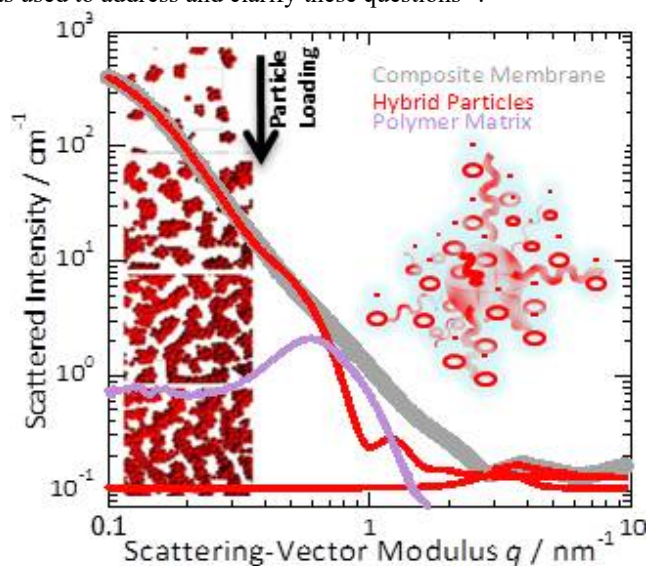
Hybrid ionomers/fillers	Degradation temperature/°C (Inert atmosphere 10°C·min <sup>-1</sup> )
Nafion/MMT(3/5/7 wt.%) <sup>12</sup>	340/330/330
Nafion/m-MMT(3/5/7 wt.%)	340/340/350
Sulfonated PolyEtherEtherKetone/MMT(10 wt.%) <sup>18</sup>	320
Sulfonated PolyEtherEtherKetone /Laponite(10 wt.%)	320
Hybrid polymers/mineral fillers/acids	
Al <sub>2</sub> O <sub>3</sub> (50 wt.%) + H <sub>2</sub> SO <sub>4</sub> (6 mol·L <sup>-1</sup> ) + Poly(VinylideneFluoride)/15 mol.%HexaFluoroPropylene (PVdF-HFP) <sup>46</sup>	180
Zr/Polydimethylsiloxane/H <sub>3</sub> PO <sub>4</sub> <sup>19</sup>	300
Hybrid ionomers/heteropolyacids	
NaSTA/ Nafion <sup>®25</sup>	300
phosphotungstic acid <sup>24</sup>	T>800
phosphotungstic acid/Sulfonated bisphenolsulfone (SPBS) 20/40/60 (6/4)	347/359/411
Polymer/heteropolyacids	
phosphotungstic acid/bisphenolsulfone <sup>24</sup>	313



### b - Polymer membranes with hybrid particles

Many associated properties still remain elusive, such as the sizes, the distribution and the structure of the inorganic or hybrid particles, the interactions and the interplay of structure/property relationships between these subsystems. The structural studies of such hybrid membranes are very rare, notably due to the presence of two subsystems. Despite this complexity, the investigation of multiscale materials using direct and reciprocal spaces allows reaching a thorough structural description<sup>47-48</sup>. Bulk and surface information are obtained in a large range of characteristic length scales ranging from the nanometer to angstrom scale. In the reciprocal space, the size, shape and interface effects can be discriminated between the different subsystems due to the large gaps between the related characteristic correlation lengths. The distribution and the size of the hybrid particles are notably investigated<sup>147-49</sup>.

A recent study of an original composite membrane composed of conducting polystyrenesulfonic acid-grafted silica particles (Figure 3) into a PVdF-HFP matrix<sup>37</sup> was used to address and clarify these questions<sup>49</sup>.



*Figure 3: SAXS absolute intensity as a function of the scattering-vector modulus  $q$  for (i) a swelled **composite membrane** with 50 wt.% of fillers at room temperature, (ii) a simulation of the form factor due to the **hybrid particles** with core-shell spheres having shell thicknesses equal to 70 nm distributed according a Schulz distribution ( $\sigma=0.5$ ) and a core radius equal to 60 nm as well as the contribution of the polyelectrolyte chains, and (iii) the experimental contribution of the **polymer matrix** (Reproduced with permission from reference 47. Copyright [2015][the Royal Society of Chemistry]).*

The structural variation of the various phases constituting the composite membranes i.e. the aggregates of particles, the polymer crystalline phase and their interactions, as a function of the amount of hybrid particles, were also described. The SAXS study, presented in the figure 3, shows the deconvolution of these different contributions. An incremental approach allowed to simulate the form factor of the hybrid particles with relevant parameters, to isolate the contribution of the polymer matrix, and to describe the polyelectrolyte chains of the hybrid particles. These results stress the possibility of a dichotomous interpretation leading to an overall quantitative and qualitative description of the nanostructure.

### **c - Nanostructured polymer membranes coupling electrospinning and sol-gel chemistry**

Understanding the relationship, between the nanostructure and the properties, is also highlighted by recent studies on hybrid membranes including silica sol-gel chemistry with precursors having sulfonic acid functions and PVdF-HFP<sup>4, 50-52</sup>. In fact, it has been possible to locate and to control the inorganic phase (size, structure)<sup>6-7, 52-53</sup>, even at the nanoscale<sup>6</sup>. The figure 4 shows the Small Angle Neutron Scattering (SANS) spectra (the absolute intensity as a function of the scattering-vector modulus  $q$  in  $\text{nm}^{-1}$ ) of membranes obtained by electrospinning coupled to the sol-gel chemistry<sup>54-55</sup> compared with the membrane having the same composition obtained by casting. These results clearly demonstrate the ability of the hybrid strategy to control the multiscale structure of these hybrid membranes particularly at the nanoscale. Thus, it is possible to modify the organization of ionic/hydrophilic domains (large  $q$ ), of the semi-crystalline phase of the polymer phase (intermediate  $q$ ), and at longer distances (small  $q$ ), which describes the characteristic correlation lengths of the fibers.

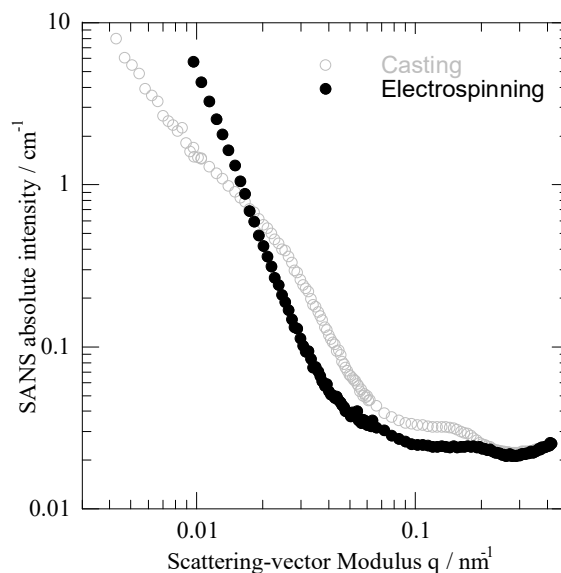


Figure 4: Scattered intensity versus scattering-vector modulus  $q$  of electrospun and casting membranes with 55 wt.% of inorganic phase.

The control of the ionic inorganic hybrid phase has significantly enabled to improve the ionic conductivity up to  $80^{\circ}\text{C}$ <sup>56</sup> with values in the same order of magnitude as Nafion membranes. This innovative coupling has achieved notable mechanical properties<sup>56</sup>. Beyond the macroscopic properties, this family has deepened the understanding of proton transport in an ionic multiscale host matrix. Indeed the original nanostructure is made of fibers with cylindrical hybrid "mille-feuille" structure<sup>6, 43, 56</sup>. This system allowed to increase knowledge in the field of multiscale transport in such membranes. By various techniques, the dynamics of the proton have been then described from the nano- to the macro-scales<sup>43, 57</sup>.

The hybrid membranes for fuel cells have been widely studied in the past 50 years. Renewed interest has also been held to increase the operation temperature up to  $120$  or even  $150^{\circ}\text{C}$ . But these membranes are struggling to replace the benchmark perfluorinated membranes. Hybrid membranes are evolved from polymer blended with inorganic materials to nanostructured hybrid membranes. This complexity, both with the choice of components, such as hybrid particles, and with different process and chemistry options, shows the importance of the obtained multiscale structures to improve the performance of electrolytes. The control of these structures at different scales including the nanoscale seems to be a key to their evolution towards an application. Indeed recent studies present

results distinguished from those of the previous families by coupling sol-gel chemistry and electrospinning as elaboration process<sup>6, 43, 56</sup>.

## **B - Electrolytic Xerogels for Organic Photovoltaic Cells**

Among the technologies available to the global energy mix, photovoltaic conversion appears as a key player. This renewable and inexhaustible energy is mainly based on silicon technology. Its interesting performances helped the photovoltaic industrialization. However, the manufacturing cost of silicon photovoltaic cells remains a real drawback to its development. Described for the first time in the seventies, organic photovoltaic materials are an interesting alternative to inorganic materials. Specifically, the new flexible photovoltaic devices with photosensitized dyes have great potential due to their low cost, low weight, flexibility and ability to large scale implementation. Recent studies point to their high potential energy payback<sup>58</sup>. However, to become a true complement to the inorganic technology, several challenges must be overcome, particularly in relation to the conversion efficiency, which is still extremely low. Indeed, the best yields reported in the literature for organic cells are nearly 11-13% in the laboratory against 15-25% for silicon cells.

### **a - Organic Solar cells**

Dye-sensitized solar cells DSSCs made of a mesoporous network of interconnected titania (TiO<sub>2</sub>) nanocrystals are an interesting alternative to conventional inorganic photovoltaic devices because of their high-efficiency and low-cost<sup>59</sup>. But the presence of liquid electrolyte causes often sealing problems that impact the long term operation of the devices and raises safety issues<sup>60</sup>. Therefore, different strategies to solidify the electrolyte have been explored<sup>61</sup>. The most studied ones are based on hole conductors (HTM) such as inorganic materials, conjugated polymers or small doped molecules<sup>62</sup>. Such cells are reaching performances of 7.2%<sup>63</sup> but are still limited by their naturally low electronic conductivity, by the insufficient penetration of solid electrolytes in the nanoporous electrodes<sup>64</sup> which can reduce the cell performances by 10 to 20%<sup>65</sup>. Alternatively, the ionic conductor may play a role of solid electrolyte to obtain an efficiency up to 8.1%<sup>66</sup>. An original approach is the use of quasi-solid electrolytes like gels. But electrolyte gels do not achieve the objectives of security and stability required by the technology for a sustainable industrial development. Indeed organic solvents are trapped in the matrix and have a high risk of instability at high temperatures, due to the increase of their volatilities, and flammability<sup>67</sup>. Moreover, these liquid electrolytes can "corrode" electrodes and dyes.

In Grätzel cells, the electrolyte contains a redox couple which carries electrons from the cathode to the molecules of the photosensitized dye. The most

promising redox couple discovered to date is the iodide/triiodide ( $I^- / I_3^-$ )<sup>68</sup>. Ionic liquids (ILs), which are organic salts having a melting temperature below 100°C, have key advantages over organic solvents: thermal and chemical stability, low volatility, non-flammability, and wide electrochemical window<sup>69</sup>. Among the various existing ionic liquids, imidazolium salts have been extensively tested as electrolytes for Grätzel cells. However, pure imidazolium iodide/triiodide ( $I^-/I_3^-$ ) exhibit high viscosity, which often yield DSSCs with poor performance. Therefore, the search for alternative electrolytes remains a strategic issue for practical applications. Recently, eutectic ternary mixtures of iodide ionic liquids as electrolyte, combined with nano-crystalline  $TiO_2$  particles as photo-electrode, lead to DSSCs with efficiency close to 8% under spectra (of 1 sun, 1000 W/m<sup>2</sup> at 25°C perpendicular to the cell plane) [AM 1.5] illuminations<sup>70</sup>. However, the long-term stabilities of such DSSCs have not been reported.

### **b - Ionogels**

The development of ionogels, solid or semi-solid electrolytes, containing ionic liquids is an original way to overcome the limitations of certain electrolytes or to meet new specifications<sup>71</sup>. The ionogels are composed of an ionic liquid and an organic network, constraining the liquid within a solid system, to provide a physical barrier between the electrodes and thereby prevent any short circuits. Accordingly, electrolytic ionogels should be safer and more suitable for the design of flexible devices. But some articles also disclose the use of electrolytes based on ionic liquids, including silica nanoparticles or networks to improve the performance of the obtained systems. Cells containing ionogels as electrolytes reached a yield of 7% in a Grätzel cell, and ionogels based on protic ionic liquids have shown significant transport properties<sup>72</sup>.

An alternative method for producing ionogels relies on the synthesis, in one step by sol-gel chemistry, of a silica network immobilizing in-situ ionic liquids<sup>73-74</sup>. But the ionic liquids are only trapped in the silica network and are not bound to the silica network leading to problems of leakage and therefore long-term stability. A modification of these strategies with silica nanoparticles, preformed and assembled with ionic liquids modified with silane groups, has been proposed<sup>75</sup>. The control of the “chemistry” allows obtaining powders in which the silica nanoparticles are connected to each other via imidazolium functions.

### **c - Mono-ionic xerogels**

An original and innovative route is to obtain an ionogel by a simple elaboration in one step, while (i) maintaining the main properties of gels trapping ionic liquids, and while (ii) mitigating their prohibitive functional drawbacks. Indeed, the approach is to co-condense a silica precursor with a functionalized ionic liquid with a trialkoxysilane function in acidic conditions to form a silica network wherein the cation or the anion of the ionic liquid is bonded to the silica network via covalent bonds (Figure 5). This approach is well positioned relative

to technological constraints of safety and efficiency, and uses the advantages of ionic liquids while avoiding the usual drawbacks during operation of a cell.

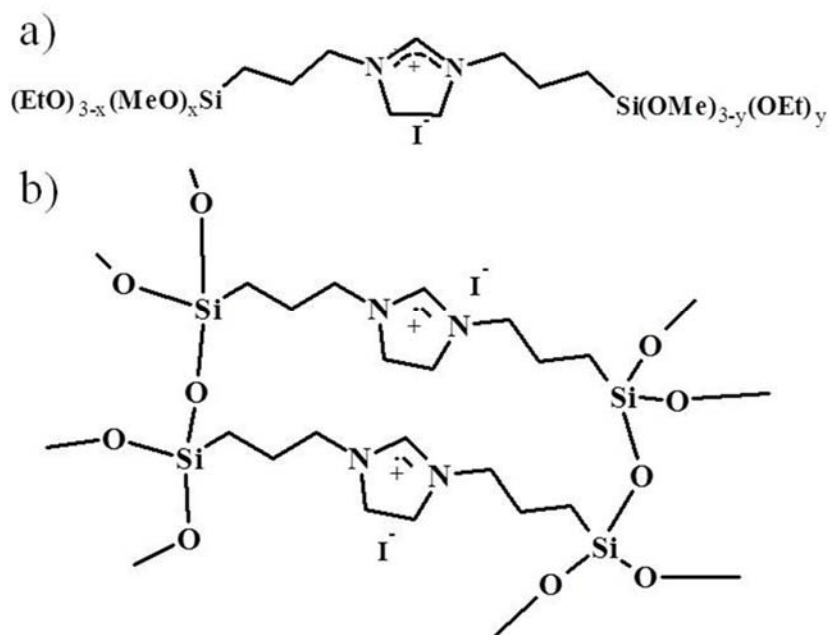


Figure 5: a) Example of an ionic liquid precursor: 1,3-di(3-trimethoxysilylpropyl)imidazolium iodide, and b) schematic of the organization of the imidazolium groups into the silica network.

In particular, this approach is interesting because the synthesis of the ionogels occurs directly into the DSSCs (see figure 6) and, as a consequence, a better control of the electrolyte/electrode interfaces may be achieved, enhancing the performances of the DSSCs<sup>76</sup>. More precisely, the DSSCs are filled with the liquid electrolyte that becomes gel with time. Thus, the electrode/electrolyte interfaces will be enhanced and then the reaction with the hole and the iodide will be facilitated, avoiding electron/hole ( $e^-$ /hole) recombination. The presence of covalent bonds between silica and ionic liquids may avoid leaks or volatilization of ionic liquids and prevent electrolyte losses. These conditions are more favorable for long term performances. Furthermore this cation immobilization strategy may have the same effect as its absorption on the semiconductor<sup>77</sup>, i.e. to induce the oxidation of iodide ions via a fast mechanism.

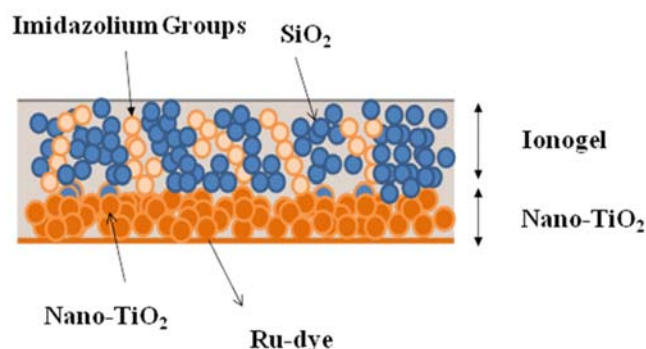


Figure 6: Schematic representation of the DSSC using an in-situ reaction of the ionic liquid precursor with silica precursor (Reproduced with permission from reference 78. Copyright [2013] [the Centre National de la Recherche Scientifique (CNRS) and the Royal Society of Chemistry]).

This concept of new materials immediately removes some critical limitations such as the penetration of semiconductor pores, volatility and exudation. The wide selection of precursors of the sol-gel chemistry, the nature (lengths, ionic groups, and functionality) of ionic liquid precursors and additives will create a model family and will be a relevant lever to evaluate and optimize the performance of the obtained gels. To adjust the concentrations, volumes and steric flexibility of ionic functions will indeed have a decisive influence on the transport properties and the structure of the ionic liquid xerogels. As it was ascertained, it is possible to obtain ionic mobilities identical to those obtained in the corresponding pure ionic liquids<sup>78-80</sup>. Varying the concentration of diiodine directly alters the ratio of ion pairs<sup>81</sup> and therefore the conduction mechanisms. Various parameters impact the diffusion coefficient of  $I_3^-$ .

#### **d - Description of the nanostructure by Small and Wide Angle X-rays scattering (SWAXS)**

The ionic liquid subunits influence the nanostructure of the ionogels as observed by SWAXS performed on ionogels with various wt.% of the ionic-liquid monomer (Figure 7).

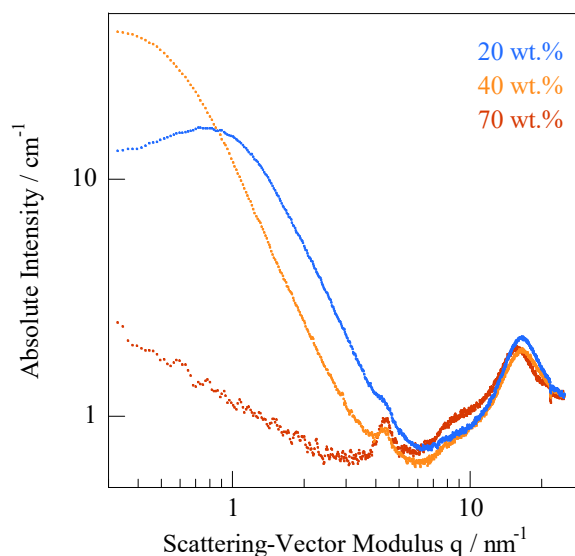


Figure 7: SWAXS absolute intensity as a function of the scattering-vector modulus  $q$  for different weight content of the ionic-liquid monomer (Reproduced with permission from reference 78. Copyright [2013] [the Centre National de la Recherche Scientifique (CNRS) and the Royal Society of Chemistry]).

All the xerogels exhibit a broad peak at  $q \sim 16.5 \text{ nm}^{-1}$  that is characteristic of the silica tetrahedrons within the amorphous silica network. For xerogels containing more than 60% in weight of the ionic-liquid monomer, a peak is also observed at  $q = 4.4 \text{ nm}^{-1}$ . This distance is related to the length of the ionic liquid subunits, and is very close to the lengths found in ionic silica nanoparticle networks including ligands with one imidazolium chloride unit<sup>82</sup> as well as in the bulk liquid-like ionic liquid<sup>83</sup>. A shoulder is also observed *ca.*  $9 \text{ nm}^{-1}$ . It corresponds to a correlation length of 0.7 nm, close to the one reported in literature for  $\pi$  stacking interactions<sup>84-86</sup>. Accordingly, this distance was attributed to the correlation length between the aromatic units in between the ionic liquid backbones. Additionally, the curves profile at low  $q$  is highly dependent on the quantity of ionic liquid precursor in the ionogels. For ionogel with more than 60% of the ionic liquid, the flat profile at low  $q$  indicates that no aggregate and no domain, up to a size of 100 nm, are present in the xerogels. The system appears homogeneous at this scale. Conversely, the intensity increases toward low  $q$  values for xerogels containing less ionic-liquid precursor. This would correspond to the existence of small cross-linked domains in the 20 nm range. The broad peak between 0.8 and 0.9  $\text{nm}^{-1}$  indicates a correlation length of  $\sim 8 \text{ nm}$  for ionogels containing up to 25 wt.% of ionic-liquid monomers. Xerogels with 30



and 40 wt.% of ionic-liquid monomer exhibit an upturn at low  $q$ . Correlation length of about 1 nm was obtained. The observed results clearly show that the presence of functionalized ionic liquid dramatically influence the nanostructure of the resulting ionogels.

The knowledge gained on the ionic transport, multi-scale structure and their correlation in these mono-ionic ionogels allow developments in other applications such as in energy storage systems or fuel cells operating to over 100°C. Indeed, an understanding of mechanisms of gelation with ionic-liquid precursors and the involvement of the structure on ion transport will support the choice of the precursors according to the intended applications and theoretical developments of the ion dynamics in an ionic confined medium. To take few examples, modulate or change the  $I_2$  concentration in a Grätzel cell has a direct implication on the role of the Grotthuss mechanism. In a fuel cell, the choice of the mobile cation is essential for the electrode reactions. In general, the expected benefits go beyond Grätzel cells, since this approach by immobilization is also relevant in fuel cells<sup>87</sup> and batteries.

The history of electrolytes for DSSCs showed the possibility to lift the various scientific and technological challenges. These latest results, including solid electrolytes without liquid phases, especially make possible to solve a large part of these obstacles. This evolution is possible through the structuring of the host matrix in a wide range of spatial and temporal scales in these inorganic/organic hybrid environments, which are ionic and confined. Furthermore, to control the nanostructure of these systems allows an improvement of their properties. Indeed this new generation of electrolytes for application in future Grätzel cells permits to correlate the ion transport properties and the diffusion of species. The use of ionic liquid precursors, regularly cited for use in "green chemistry"<sup>88</sup>, co-condensed by sol-gel chemistry, called "soft chemistry"<sup>54</sup>, also allows to propose a class of electrolytes using little energy resources and widespread molecules having lower toxicity than usual solvents<sup>89-90</sup>.

## **C – Polymer/Ionic Liquid Electrolytes for Energy Storage**

In the last few years, academic and industry research have had to overcome many challenges in the fields of environment, production, storage and conversion of energy but also in the reduction of costs in the transportation. Thus, polymer materials scientists have focused on the design and development of new functional polymer materials with unprecedented physical properties via the introduction of ionomers, nanoparticles or block copolymers<sup>91-93</sup>. Recently, the use of ionic liquids (ILs) as functional additives of thermosets as well as thermoplastics has

opened new horizons in polymer science<sup>94-98</sup>. In fact, ILs have been investigated as building blocks of polymer matrices and as ionic conducting agents of polymer electrolytes<sup>99-100</sup>.

### **a - Gel-like electrolytes**

For several years, “gel” electrolytes based on the combination of polar organic solvents and electrolyte salts have been widely studied in the fields of ionic devices, sensors and secondary batteries<sup>101-102</sup>. However, their volatility and their toxicity have led researchers to a new alternative through the use of ILs known for their excellent thermal stability, their low vapor pressure and their high ionic conductivity<sup>103-104</sup>. Thus, different routes to design polymer electrolytes have been described: 1) impregnation of gel electrolytes with hydrophilic or hydrophobic ILs<sup>71</sup> and 2) inclusion of polymers in ILs<sup>105-106</sup>.

Many polymer matrices have been also investigated such as poly(acrylonitrile) (PAN), poly(ethylene oxide) (PEO), poly(methylmethacrylate) (PMMA) and fluorinated polymers (polytetrafluoroethylene (PTFE) and poly(vinylidene fluoride) (PVDF)) where good ionic conductivities, high mechanical strength and transparency are obtained<sup>107-108</sup>. Very recently, research has focused on the development of solid or quasi-solid polymer electrolytes requiring a good confinement of the organic salts in the “host” polymer matrix as well as the high thermal-mechanical properties<sup>109-111</sup>. Thus, different authors have investigated the influence of the chemical nature (pyridinium, phosphonium, imidazolium) of the ILs on the structuration and the final properties of thermosets based on epoxy networks<sup>112-115</sup>. They have highlighted that the decomposition of pyridinium or imidazolium salts induces the formation of imidazole and pyridine which act as catalyst of the homopolymerization of epoxy networks<sup>112-113</sup>. In addition, the use of a small amount of ILs in epoxy-amine networks led to an increase of the storage modulus combined with a plasticizer effect by a decrease of the glass transition temperature ( $T_g$ ). Then, Livi and coworkers highlighted that phosphonium ionic liquids associated with phosphinate, dicyanamide or phosphate counter anions, could be used as curing agents of epoxy prepolymer composed of diglycidylether of bisphenol A (DGEBA). Thus, nanostructured thermosets based on epoxy-IL mixtures have been designed with glass transition temperature included between 80 °C and 140 °C coupled with excellent mechanical performances<sup>116-118</sup>. Nevertheless, improving the ionic conductivity of these new systems remains a real challenge.

### **b - Nanostructured polymer/ionic liquid electrolytes**

Another way was to develop nanostructured polymer/ionic liquid electrolytes with enhanced mechanical, thermal and barrier properties. Thus, ionic liquids were used in small amounts as building blocks in fluorinated matrices<sup>99</sup>. The influence of the chemical nature of the counter anion as well as the cation on the

morphology and on the final properties of polymer matrices has been also investigated<sup>99</sup>. For the first time, pyridinium, imidazolium and phosphonium ILs have been synthesized and used as functional additives in PTFE matrix. The authors have demonstrated that imidazolium and pyridinium salts led to the phase separation characterized by the presence of ionic clusters (nm to  $\mu\text{m}$ ) whereas phosphonium ionic liquid combined with iodide anion induced a “spider web” morphology (Figure 8).

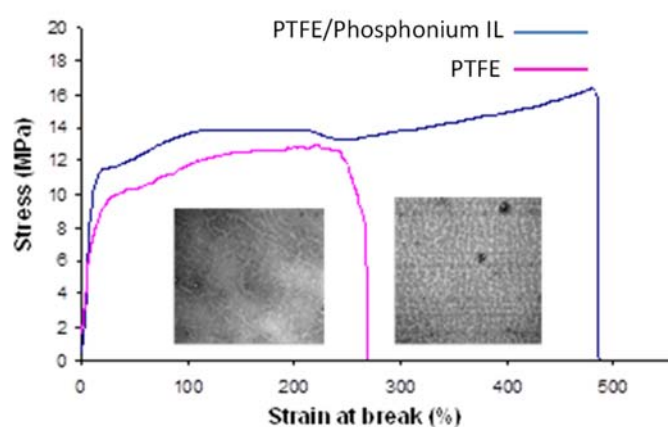


Figure 8: Mechanical curves and TEM micrographs of PTFE without and with phosphonium ionic liquids.

The behavior of the ionic liquid is very similar to ionomers where interactions between the polymer matrix and the cation-anion pairs are the key parameter of the phase separation inducing by the formation of multiplet structures<sup>119-120</sup>. Moreover, the mechanical performances were significantly improved with increases in the Young's modulus (E) of 160 % coupled with an exceptional increase of the strain at break (+ 190 %). Very recently, Yang et al. have also demonstrated that phosphonium ILs are excellent nanostructuring agents on a semicrystalline copolymer denoted Poly(Vinylidene Fluoride-ChloroTriFluoroEthylene [P(VdF-CTFE)]<sup>121</sup>. In addition, the authors have highlighted that the addition of few percent of ILs induced more polar  $\beta$ -phase and more homogeneous distribution morphology as well as an excellent compromise between stiffness and strain to failure<sup>121</sup>. These early results showed the feasibility of creating efficient polymer electrolytes based on epoxy networks or fluorinated matrices. Nevertheless, the challenge to overcome is to introduce the electrolyte salts in these membranes without changing the final properties of the materials obtained.

In conclusion, these different approaches based on endless ionic liquids combinations open up new horizons in the development of high-performance polymer electrolytes. However, a lot of work is required to obtain good mechanical strength and excellent ionic conductivity.

### Conclusion and Brief Summary

Hybrid electrolytes with improved properties were obtained for three energy devices (Fuel Cells, Organic Photovoltaic and energy storage). These new family of electrolytes, in their respective applications, tend to lessen the disadvantages of liquid phases present in the conventional electrolytes while improving their properties. These evolutions were possible thanks to an elucidation of the multiscale complex structure of the hybrid electrolytes and then the control of their nano-structuration. Beyond these improvements, this overall comprehension gives an opportunity to better understand various related properties including the mechanical properties and the transport mechanisms.

1. Jones, D. J.; Rozière, J. Advances in the Development of Inorganic–Organic Membranes for Fuel Cell Applications. *Adv. Polym. Sci.* **2008**, *215*, 219-264.
2. Alberti, G.; Casciola, M. Composite membranes for medium-temperature PEM fuel cells. *Annu. Rev. Mater. Res.* **2003**, *33*, 129-154.
3. Zhang, H. W.; Shen, P. K. Recent Development of Polymer Electrolyte Membranes for Fuel Cells. *Chem. Rev.* **2012**, *112* (5), 2780-2832.
4. Laberty-Robert, C.; Valle, K.; Pereira, F.; Sanchez, C. Design and properties of functional hybrid organic-inorganic membranes for fuel cells. *Chem. Soc. Rev.* **2011**, *40* (2), 961-1005.
5. Belieres, J. P.; Maréchal, M.; Saunier, J.; Alloin, F.; Sanchez, J. Y. Swollen polymethacrylonitrile urethane networks for lithium batteries. *J. Electrochem. Soc.* **2003**, *150* (1), A14-A20.
6. Maneeratana, V.; Bass, J. D.; Azais, T.; Patissier, A.; Valle, K.; Maréchal, M.; Gebel, G.; Laberty-Robert, C.; Sanchez, C. Fractal Inorganic–Organic Interfaces in Hybrid Membranes for Efficient Proton Transport. *Adv. Funct. Mater.* **2013**, *23* (22), 2872-2880.
7. Sel, O.; Azais, T.; Maréchal, M.; Gebel, G.; Laberty-Robert, C.; Sanchez, C. Sulfonic and Phosphonic Acid and Bifunctional Organic–Inorganic Hybrid Membranes and Their Proton Conduction Properties. *Chem. - Asian J.* **2011**, *6* (11), 2992-3000.
8. Sanchez, J. Y.; Chabert, F.; Iojoiu, C.; Salomon, J.; El Kissi, N.; Piffard, Y.; Marechal, M.; Galiano, H.; Mercier, R. Extrusion: An environmentally friendly process for PEMFC membrane elaboration. *Electrochim. Acta* **2007**, *53* (4), 1584-1595.
9. Ramani, V.; Kunz, H. R.; Fenton, J. M. Effect of particle size reduction on the conductivity of Nafion/phosphotungstic acid composite membranes. *J. Membr. Sci.* **2005**, *266* (1-2), 110-114.

10. Park, Y. S.; Yamazaki, Y. Low water/methanol permeable Nafion/CHP organic-inorganic composite membrane with high crystallinity. *Eur. Polym. J.* **2006**, *42* (2), 375-387.
11. Bebin, P.; Caravanier, M.; Galiano, H. Nafion/clay-SO<sub>3</sub>H membrane for proton exchange membrane fuel cell application. *J. Membr. Sci.* **2006**, *278* (1-2), 35-42.
12. Jung, D. H.; Cho, S. Y.; Peck, D. H.; Shin, D. R.; Kim, J. S. Preparation and performance of a Nafion/montmorillonite nanocomposite membrane for direct methanol fuel cell. *J. Power Sources* **2003**, *118* (1-2), 205-211.
13. Mura, F.; Silva, R. F.; Pozio, A. Study on the conductivity of recast Nafion/montmorillonite and Nafion/TiO<sub>2</sub> composite membranes. *Electrochim. Acta* **2007**, *52* (19), 5824-5828.
14. Lee, W.; Kim, H.; Kim, T. K.; Chang, H. Nafion based organic/inorganic composite membrane for air-breathing direct methanol fuel cells. *J. Membr. Sci.* **2007**, *292* (1-2), 29-34.
15. Yang, C.; Srinivasan, S.; Bocarsly, A. B.; Tulyani, S.; Benziger, J. B. A comparison of physical properties and fuel cell performance of Nafion and zirconium phosphate/Nafion composite membranes. *J. Membr. Sci.* **2004**, *237* (1-2), 145-161.
16. Karthikeyan, C. S.; Nunes, S. P.; Prado, L. A. S. A.; Ponce, M. L.; Silva, H.; Ruffmann, B.; Schulte, K. Polymer nanocomposite membranes for DMFC application. *J. Membr. Sci.* **2005**, *254* (1-2), 139-146.
17. Zhang, Y.; Zhang, H. M.; Zhai, Y. F.; Zhu, X. B.; Bi, C. Investigation of self-humidifying membranes based on sulfonated poly(ether ether ketone) hybrid with sulfated zirconia supported Pt catalyst for fuel cell applications. *J. Power Sources* **2007**, *168* (2), 323-329.
18. Chang, J. H.; Park, J. H.; Park, G. G.; Kim, C. S.; Park, O. O. Proton-conducting composite membranes derived from sulfonated hydrocarbon and inorganic materials. *J. Power Sources* **2003**, *124* (1), 18-25.
19. Kim, J. D.; Honma, I. Proton conducting polydimethylsiloxane/zirconium oxide hybrid membranes added with phosphotungstic acid. *Electrochim. Acta* **2003**, *48* (24), 3633-3638.
20. Zoppi, R. A.; deCastro, C. R.; Yoshida, I. V. P.; Nunes, S. P. Hybrids of SiO<sub>2</sub> and poly(amide-6-b-ethylene oxide). **1997**, *38* (23), 5705-5712.
21. Vargas, R. A.; Zapata, V. H.; Matallana, E.; Vargas, M. A. More thermal studies on the PVOH/H<sub>3</sub>PO<sub>2</sub>/H<sub>2</sub>O solid proton conductor gels. *Electrochim. Acta* **2001**, *46* (10-11), 1699-1702.
22. Li, S. W.; Liu, M. L. Synthesis and conductivity of proton-electrolyte membranes based on hybrid inorganic-organic copolymers. *Electrochim. Acta* **2003**, *48* (28), 4271-4276.
23. Tadanaga, K.; Yoshida, H.; Matsuda, A.; Minami, T.; Tatsumisago, M. Inorganic-organic hybrid films from 3-glycidoxypropyltrimethoxysilane and

- orthophosphoric acid for medium temperature fuel cells. *Electrochem. Commun.* **2003**, *5* (8), 644-646.
24. Kim, Y. S.; Wang, F.; Hickner, M.; Zawodzinski, T. A.; McGrath, J. E. Fabrication and characterization of heteropolyacid (H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>)/directly polymerized sulfonated poly(arylene ether sulfone) copolymer composite membranes for higher temperature fuel cell applications. *J. Membr. Sci.* **2003**, *212* (1-2), 263-282.
  25. Tazi, B.; Savadogo, O. Effect of various heteropolyacids (HPAs) on the characteristics of Nafion/HPAS membranes and their H<sub>2</sub>/O<sub>2</sub> polymer electrolyte fuel cell parameters. *J. New Mater. Electrochem. Syst.* **2001**, *4* (3), 187-196.
  26. Zaidi, S. M. J.; Mikhailenko, S. D.; Robertson, G. P.; Guiver, M. D.; Kaliaguine, S. Proton conducting composite membranes from polyether ether ketone and heteropolyacids for fuel cell applications. *J. Membr. Sci.* **2000**, *173* (1), 17-34.
  27. He, R. H.; Li, Q. F.; Xiao, G.; Bjerrum, N. J. Proton conductivity of phosphoric acid doped polybenzimidazole and its composites with inorganic proton conductors. *J. Membr. Sci.* **2003**, *226* (1-2), 169-184.
  28. Park, M. W.; Yang, J. C.; Han, H. S.; Shul, Y. G.; Lee, T. H.; Cho, Y. I. Heteropolyacid (H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>) incorporated solid polymer electrolyte for PEMFC. *Denki Kagaku* **1996**, *64* (6), 743-748.
  29. Asensio, J. A.; Borros, S.; Gomez-Romero, P. Enhanced conductivity in polyanion-containing polybenzimidazoles. Improved materials for proton-exchange membranes and PEM fuel cells. *Electrochem. Commun.* **2003**, *5* (11), 967-972.
  30. Tazi, B.; Savadogo, O. Parameters of PEM fuel-cells based on new membranes fabricated from Nafion, silicotungstic acid and thiophene. *Electrochim. Acta* **2000**, *45* (25-26), 4329-4339.
  31. Baradie, B.; Poinsignon, C.; Sanchez, J. Y.; Piffard, Y.; Vitter, G.; Bestaoui, N.; Foscallo, D.; Denoyelle, A.; Delabouglise, D.; Vaujany, M. Thermostable ionomeric filled membrane for H<sub>2</sub>/O<sub>2</sub> fuel cell. *J. Power Sources* **1998**, *74* (1), 8-16.
  32. Bonnet, B.; Jones, D. J.; Roziere, J.; Tchicaya, L.; Alberti, G.; Casciola, M.; Massinelli, L.; Bauer, B.; Peraio, A.; Ramunni, E. Hybrid organic-inorganic membranes for a medium temperature fuel cell. *J. New Mater. Electrochem. Syst.* **2000**, *3* (2), 87-92.
  33. Poinsignon, C.; Amodio, I.; Foscallo, D.; Sanchez, J.-Y. Low cost filled thermostable ionomer membrane for PEMFC. *Mater. Res. Soc. Symp. Proc.* **1999**, *548*, 307-312.
  34. Genova-Dimitrova, P.; Baradie, B.; Foscallo, D.; Poinsignon, C.; Sanchez, J.-Y. Ionomeric membranes for proton exchange membrane fuel cell (PEMFC): sulfonated polysulfone associated with phosphoantimonic acid. *J. Membr. Sci.* **2001**, *185*, 59-71.

35. Yoshiji, K. EP 04110352, 1992.
36. Di Noto, V.; Piga, M.; Giffin, G. A.; Negro, E.; Furlan, C.; Vezzu, K. New Nanocomposite Hybrid Inorganic-Organic Proton-Conducting Membranes Based on Functionalized Silica and PTFE. *ChemSusChem* **2012**, *5* (9), 1758-1766.
37. Niepceron, F.; Lafitte, B.; Galiano, H.; Bigarre, J.; Nicol, E.; Tassin, J. F. Composite fuel cell membranes based on an inert polymer matrix and proton-conducting hybrid silica particles. *J. Membr. Sci.* **2009**, *338* (1-2), 100-110.
38. Maréchal, M.; Wessel, R.; Diard, J. P.; Guindet, J.; Sanchez, J. Y. Study of PEMFC ionomers through model molecules mimicking the ionomer repeat units. *Electrochim. Acta* **2007**, *52* (28), 7953-7963.
39. Poinsignon, C.; Sanchez, J.-Y.; Piffard, Y.; Vitter, G.; Baradie, B.; Denoyelle, A. EP 97401613.1, 1997.
40. Kreuer, K. D.; Paddison, S. J.; Spohr, E.; Schuster, M. Transport in proton conductors for fuel-cell applications: Simulations, elementary reactions, and phenomenology. *Chem. Rev.* **2004**, *104* (10), 4637-4678.
41. Zapata, P.; Mountz, D.; Meredith, J. C. High-Throughput Characterization of Novel PVDF/Acrylic Polyelectrolyte Semi-Interpenetrated Network Proton Exchange Membranes. *Macromolecules* **2010**, *43* (18), 7625-7636.
42. Lyonnard, S.; Gebel, G. Neutrons for fuel cell membranes: Structure, sorption and transport properties. *Eur. Phys. J.-Spec. Top.* **2012**, *213* (1), 195-211.
43. Dos Santos, L.; Maréchal, M.; Guillermo, A.; Lyonnard, S.; Moldovan, S.; Ersen, O.; Sel, O.; Perrot, H.; Laberty-Robert, C. Proton Transport in Hybrid Organic-Inorganic Membrane: An Illuminating Paradox. *Adv. Funct. Mater.* **2015**, Submitted.
44. DuPont, Nafion® Membranes NR-111, NR-112. 2001; pp 1-5.
45. Sanchez, J.-Y.; Iojoiu, C.; Mercier, R.; Maréchal, M.; El Kissi, N.; Galiano, H.; Chabert, F. PCT WO 000830, 2006.
46. Navarra, M. A.; Materazzi, S.; Panero, S.; Scrosati, B. PVDF-Based Membranes for DMFC Applications. *J. Electrochem. Soc.* **2003**, *150* (11), A1528-1532.
47. Truffier-Boutry, D.; De Geyer, A.; Guetaz, L.; Diat, O.; Gebel, G. Structural study of zirconium phosphate-nafion hybrid membranes for high-temperature proton exchange membrane fuel cell applications. *Macromolecules* **2007**, *40* (23), 8259-8264.
48. Rubatat, L.; Gebel, G.; Diat, O. Fibrillar structure of Nafion: Matching Fourier and real space studies of corresponding films and solutions. *Macromolecules* **2004**, *37* (20), 7772-7783.
49. Maréchal, M.; Niepceron, F.; Gebel, G.; Mendil-Jakani, H.; Galiano, H. Inside the structure of a nanocomposite electrolyte membrane: how hybrid particles get along with the polymer matrix. *Nanoscale* **2015**, *7* (7), 3077-3087.

50. Hogarth, W. H. J.; da Costa, J. C. D.; Drennan, J.; Lu, G. Q. Proton conductivity of mesoporous sol-gel zirconium phosphates for fuel cell applications. *J. Mater. Chem.* **2005**, *15* (7), 754-758.
51. Sel, O.; Soules, A.; Ameduri, B.; Boutevin, B.; Laberty-Robert, C.; Gebel, G.; Sanchez, C. Original Fuel-Cell Membranes from Crosslinked Terpolymers via a "Sol-Gel" Strategy. *Adv. Funct. Mater.* **2010**, *20* (7), 1090-1098.
52. Valle, K.; Belleville, P.; Pereira, F.; Sanchez, C. Hierarchically structured transparent hybrid membranes by in situ growth of mesostructured organosilica in host polymer. *Nat. Mater.* **2006**, *5* (2), 107-111.
53. Sanchez, C.; Boissiere, C.; Cassaignon, S.; Chaneac, C.; Durupthy, O.; Faustini, M.; Grosso, D.; Laberty-Robert, C.; Nicole, L.; Portehault, D.; Ribot, F.; Rozes, L.; Sassoie, C. Molecular Engineering of Functional Inorganic and Hybrid Materials. *Chem. Mat.* **2014**, *26* (1), 221-238.
54. Nicole, L.; Laberty-Robert, C.; Rozes, L.; Sanchez, C. Hybrid materials science: a promised land for the integrative design of multifunctional materials. *Nanoscale* **2014**, *6* (12), 6267-6292.
55. Sanchez, C.; Rozes, L.; Ribot, F.; Laberty-Robert, C.; Grosso, D.; Sassoie, C.; Boissiere, C.; Nicole, L. "Chimie douce": A land of opportunities for the designed construction of functional inorganic and hybrid organic-inorganic nanomaterials. *C. R. Chim.* **2010**, *13* (1-2), 3-39.
56. Dos Santos, L.; Rose, S.; Sel, O.; Maréchal, M.; Perrot, H.; Laberty-Robert, C. Electrospinning a Versatile Tool for Designing Hybrid Proton Conducting Membrane. **2015**, Submitted.
57. Dos Santos, L.; Laberty-Robert, C.; Maréchal, M.; Perrot, H.; Sel, O. Proton Diffusion Coefficient in Electrospun Hybrid Membranes by Electrochemical Impedance Spectroscopy. *Langmuir* **2015**, under press.
58. Espinosa, N.; Hosel, M.; Angmo, D.; Krebs, F. C. Solar cells with one-day energy payback for the factories of the future. *Energy Environ. Sci.* **2012**, *5* (1), 5117-5132.
59. Hagfeldt, A.; Boschloo, G.; Sun, L. C.; Kloo, L.; Pettersson, H. Dye-Sensitized Solar Cells. *Chem. Rev.* **2010**, *110* (11), 6595-6663.
60. Grätzel, M. Corrigendum to "Conversion of sunlight to electric power by nanocrystalline dye-sensitized solar cells" [vol 164, pg 3, 2004]. *J. Photochem. Photobiol., A* **2004**, *168* (3), 235-235.
61. Li, B.; Wang, L. D.; Kang, B. N.; Wang, P.; Qiu, Y. Review of recent progress in solid-state dye-sensitized solar cells. *Sol. Energy Mater. Sol. Cells* **2006**, *90* (5), 549-573.
62. Hsu, C. Y.; Chen, Y. C.; Lin, R. Y. Y.; Ho, K. C.; Lin, J. T. Solid-state dye-sensitized solar cells based on spirofluorene (spiro-OMeTAD) and arylamines as hole transporting materials. *Phys. Chem. Chem. Phys.* **2012**, *14* (41), 14099-14109.



63. Burschka, J.; Dualeh, A.; Kessler, F.; Baranoff, E.; Cevey-Ha, N. L.; Yi, C. Y.; Nazeeruddin, M. K.; Gratzel, M. Tris(2-(1H-pyrazol-1-yl)pyridine)cobalt(III) as p-Type Dopant for Organic Semiconductors and Its Application in Highly Efficient Solid-State Dye-Sensitized Solar Cells. *J. Am. Chem. Soc.* **2011**, *133* (45), 18042-18045.
64. Yang, L.; Cappel, U. B.; Unger, E. L.; Karlsson, M.; Karlsson, K. M.; Gabrielsson, E.; Sun, L. C.; Boschloo, G.; Hagfeldt, A.; Johansson, E. M. J. Comparing spiro-OMeTAD and P3HT hole conductors in efficient solid state dye-sensitized solar cells. *Phys. Chem. Chem. Phys.* **2012**, *14* (2), 779-789.
65. Planells, M.; Abate, A.; Hollman, D. J.; Stranks, S. D.; Bharti, V.; Gaur, J.; Mohanty, D.; Chand, S.; Snaith, H. J.; Robertson, N. Diacetylene bridged triphenylamines as hole transport materials for solid state dye sensitized solar cells. *J. Mater. Chem. A* **2013**, *1* (23), 6949-6960.
66. Komiya, R.; Han, L. Y.; Yamanaka, R.; Islam, A.; Mitate, T. Highly efficient quasi-solid state dye-sensitized solar cell with ion conducting polymer electrolyte. *J. Photochem. Photobiol., A* **2004**, *164* (1-3), 123-127.
67. Kay, A.; Grätzel, M. Low cost photovoltaic modules based on dye sensitized nanocrystalline titanium dioxide and carbon powder. *Sol. Energy Mater. Sol. Cells* **1996**, *44* (1), 99-117.
68. Oregan, B.; Grätzel, M. A Low-Cost, High-Efficiency Solar-Cell Based on Dye-Sensitized Colloidal TiO<sub>2</sub> Films. *Nature* **1991**, *353* (6346), 737-740.
69. Armand, M.; Endres, F.; MacFarlane, D. R.; Ohno, H.; Scrosati, B. Ionic-liquid materials for the electrochemical challenges of the future. *Nat. Mater.* **2009**, *8* (8), 621-629.
70. Bai, Y.; Cao, Y. M.; Zhang, J.; Wang, M.; Li, R. Z.; Wang, P.; Zakeeruddin, S. M.; Gratzel, M. High-performance dye-sensitized solar cells based on solvent-free electrolytes produced from eutectic melts. *Nat. Mater.* **2008**, *7* (8), 626-630.
71. Neouze, M. A.; Le Bideau, J.; Leroux, F.; Vioux, A. A route to heat resistant solid membranes with performances of liquid electrolytes. *Chem. Commun* **2005**, (8), 1082-1084.
72. Delahaye, E.; Gobel, R.; Lobbicke, R.; Guillot, R.; Sieber, C.; Taubert, A. Silica ionogels for proton transport. *J. Mater. Chem.* **2012**, *22* (33), 17140-17146.
73. Sharp, K. G.; Scherer, G. W. Interaction of formic acid with the silica gel network. *J. Sol-Gel Sci. Technol.* **1997**, *8* (1-3), 165-171.
74. Dai, S.; Ju, Y. H.; Gao, H. J.; Lin, J. S.; Pennycook, S. J.; Barnes, C. E. Preparation of silica aerogel using ionic liquids as solvents. *Chem. Commun.* **2000**, (3), 243-244.
75. Litschauer, M.; Neouze, M. A. Nanoparticles connected through an ionic liquid-like network. *J. Mater. Chem.* **2008**, *18* (6), 640-646.

76. Nogueira, A. F.; Longo, C.; De Paoli, M. A. Polymers in dye sensitized solar cells: overview and perspectives. *Coord. Chem. Rev.* **2004**, *248* (13-14), 1455-1468.
77. Pelet, S.; Moser, J. E.; Grätzel, M. Cooperative effect of adsorbed cations and iodide on the interception of back electron transfer in the dye sensitization of nanocrystalline TiO<sub>2</sub>. *J. Phys. Chem. B* **2000**, *104* (8), 1791-1795.
78. Goebel, R.; Hesemann, P.; Weber, J.; Moller, E.; Friedrich, A.; Beuermann, S.; Taubert, A. Surprisingly high, bulk liquid-like mobility of silica-confined ionic liquids. *Phys. Chem. Chem. Phys.* **2009**, *11* (19), 3653-3662.
79. Lunstroot, K.; Driesen, K.; Nockemann, P.; Van Hecke, K.; Van Meervelt, L.; Gorller-Walrand, C.; Binnemans, K.; Bellayer, S.; Viau, L.; Le Bideau, J.; Vioux, A. Lanthanide-doped luminescent ionogels. *Dalton Trans.* **2009**, (2), 298-306.
80. Fontaine, O.; Toudjine, A.; Maréchal, M.; Bonhomme, C.; Ribot, C.; Geffroy, B.; Jousset, B.; Sanchez, C.; Laberty-Robert, C. One-pot Route To Class II Hybrid Ionogel Electrolytes for DSSC. *New J. Chem.* **2014**, *38*, 2008-2015.
81. Call, F.; Stolwijk, N. A. Impact of I<sup>-2</sup> Additions on Iodide Transport in Polymer Electrolytes for Dye-Sensitized Solar Cells: Reduced Pair Formation versus a Grotthuss-Like Mechanism. *J. Phys. Chem. Lett.* **2010**, *1* (14), 2088-2093.
82. Martinelli, A.; Maréchal, M.; Ostlund, A.; Cambedouzou, J. Insights into the interplay between molecular structure and diffusional motion in 1-alkyl-3-methylimidazolium ionic liquids: a combined PFG NMR and X-ray scattering study. *Phys. Chem. Chem. Phys.* **2013**, *15* (15), 5510-5517.
83. Clement, S.; Tizit, A.; Desbief, S.; Mehdi, A.; De Winter, J.; Gerbaux, P.; Lazzaroni, R.; Boury, B. Synthesis and characterisation of pi-conjugated polymer/silica hybrids containing regioregular ionic polythiophenes. *J. Mater. Chem.* **2011**, *21* (8), 2733-2739.
84. Pichon, B. P.; Scampini, S.; Bied, C.; Moreau, J. J. E.; Man, M. W. C. The Influence of Arylene and Alkylene Units on the Structuring of Urea-Based Bridged Silsesquioxanes. *Eur. J. Inorg. Chem.* **2012**, (32), 5312-5322.
85. Fernandes, M.; Nobre, S. S.; Xu, Q.; Carcel, C.; Cachia, J. N.; Cattoen, X.; Sousa, J. M.; Ferreira, R. A. S.; Carlos, L. D.; Santilli, C. V.; Man, M. W. C.; Bermudez, V. d. Z. Self-Structuring of Lamellar Bridged Silsesquioxanes with Long Side Spacers. *J. Phys. Chem. B* **2011**, *115* (37), 10877-10891.
86. Litschauer, M.; Peterlik, H.; Neouze, M.-A. Nanoparticles/Ionic Linkers of Different Lengths: Short-Range Order Evidenced by Small-Angle X-ray Scattering. **2009**, *113* (16), 6547-6552.
87. Lee, S. Y.; Ogawa, A.; Kanno, M.; Nakamoto, H.; Yasuda, T.; Watanabe, M. Nonhumidified Intermediate Temperature Fuel Cells Using Protic Ionic Liquids. *J. Am. Chem. Soc.* **2010**, *132* (28), 9764-9773.

88. Anastas, P.; Eghbali, N. Green Chemistry: Principles and Practice. *Chem. Soc. Rev.* **2010**, *39* (1), 301-312.
89. Zhao, D. B.; Liao, Y. C.; Zhang, Z. D. Toxicity of ionic liquids. *Clean: Soil, Air, Water* **2007**, *35* (1), 42-48.
90. Ranke, J.; Molter, K.; Stock, F.; Bottin-Weber, U.; Poczobutt, J.; Hoffmann, J.; Ondruschka, B.; Filser, J.; Jastorff, B. Biological effects of imidazolium ionic liquids with varying chain lengths in acute *Vibrio fischeri* and WST-1 cell viability assays. *Ecotoxicol. Environ. Saf.* **2004**, *58* (3), 396-404.
91. Maiez-Tribut, S.; Pascault, J. P.; Soule, E. R.; Borrajo, J.; Williams, R. J. J. Nanostructured epoxies based on the self-assembly of block copolymers: A new miscible block that can be tailored to different epoxy formulations. *Macromolecules* **2007**, *40* (4), 1268-1273.
92. Vermogen, A.; Masenelli-Varlot, K.; Seguela, R.; Duchet-Rumeau, J.; Boucard, S.; Prele, P. Evaluation of the structure and dispersion in polymer-layered silicate nanocomposites. *Macromolecules* **2005**, *38* (23), 9661-9669.
93. Krishnamoorti, R.; Vaia, R. A.; Giannelis, E. P. Structure and dynamics of polymer-layered silicate nanocomposites. *Chem. Mater.* **1996**, *8* (8), 1728-1734.
94. Livi, S.; Duchet-Rumeau, J.; Gerard, J.-F. Nanostructuring of ionic liquids in fluorinated matrix: Influence on the mechanical properties. *Polymer* **2011**, *52* (7), 1523-1531.
95. Yousfi, M.; Livi, S.; Duchet-Rumeau, J. Ionic liquids: A new way for the compatibilization of thermoplastic blends. *Chem. Eng. J* **2014**, *255*, 513-524.
96. Livi, S.; Duchet-Rumeau, J.; Gerard, J.-F.; Thi Nhan, P. Polymers and Ionic Liquids: A Successful Wedding. *Macromol. Chem. Phys.* **2015**, *216* (4), 359-368.
97. Livi, S.; Gérard, J.-F.; Duchet-Rumeau, J., Ionic Liquids as Polymer Additives. In *Applications of Ionic Liquids in Polymer Science and Technology*, Mecerreyes, D., Ed. Springer Berlin Heidelberg: 2015; pp 1-21.
98. Shaplov, A. S.; Marcilla, R.; Mecerreyes, D. Recent Advances in Innovative Polymer Electrolytes based on Poly(ionic liquid)s. *Electrochim. Acta* **2015**, *175*, 18-34.
99. Livi, S.; Gerard, J.-F.; Duchet-Rumeau, J. Ionic liquids: structuration agents in a fluorinated matrix. *Chem. Commun.* **2011**, *47* (12), 3589-3591.
100. Gray, F. M.; Maccallum, J. R.; Vincent, C. A.; Giles, J. R. M. Novel polymer electrolytes based on A-B-A block copolymers. *Macromolecules* **1988**, *21* (2), 392-397.
101. Hapiot, P.; Lagrost, C. Electrochemical reactivity in room-temperature ionic liquids. *Chem. Rev.* **2008**, *108* (7), 2238-2264.
102. Southall, J. P.; Hubbard, H. V. S. A.; Johnston, S. F.; Rogers, V.; Davies, G. R.; McIntyre, J. E.; Ward, I. M. Ionic conductivity and viscosity correlations in liquid electrolytes for incorporation into PVDF gel electrolytes. *Solid State Ionics* **1996**, *85* (1-4), 51-60.

103. Kim, K. S.; Choi, S.; Demberelnyamba, D.; Lee, H.; Oh, J.; Lee, B. B.; Mun, S. J. Ionic liquids based on N-alkyl-N-methylmorpholinium salts as potential electrolytes. *Chem. Commun.* **2004**, (7), 828-829.
104. Simone, P. M.; Lodge, T. P. Phase Behavior and Ionic Conductivity of Concentrated Solutions of Polystyrene-Poly(ethylene oxide) Diblock Copolymers in an Ionic Liquid. *ACS Appl. Mater. Interfaces* **2009**, 1 (12), 2812-2820.
105. Ohno, H. Molten salt type polymer electrolytes. *Electrochim. Acta* **2001**, 46 (10-11), 1407-1411.
106. Noda, A.; Watanabe, M. Highly conductive polymer electrolytes prepared by in situ polymerization of vinyl monomers in room temperature molten salts. *Electrochim. Acta* **2000**, 45 (8-9), 1265-1270.
107. Susan, M. A.; Kaneko, T.; Noda, A.; Watanabe, M. Ion gels prepared by in situ radical polymerization of vinyl monomers in an ionic liquid and their characterization as polymer electrolytes. *J. Am. Chem. Soc.* **2005**, 127 (13), 4976-4983.
108. Singh, B.; Sekhon, S. S. Polymer electrolytes based on room temperature ionic liquid: 2,3-dimethyl-1-octylimidazolium triflate. *J. Phys. Chem. B* **2005**, 109 (34), 16539-16543.
109. Maka, H.; Szychaj, T. Epoxy resin crosslinked with conventional and deep eutectic ionic liquids. *Polimery* **2012**, 57 (6), 456-462.
110. Maka, H.; Szychaj, T.; Pilawka, R. Epoxy Resin/Ionic Liquid Systems: The Influence of Imidazolium Cation Size and Anion Type on Reactivity and Thermomechanical Properties. *Ind. Eng. Chem. Res.* **2012**, 51 (14), 5197-5206.
111. Kowalczyk, K.; Szychaj, T. Ionic liquids as convenient latent hardeners of epoxy resins: Rapid communications. *Polimery* **2003**, 48 (11-12), 833-835.
112. Soares, B. G.; Livi, S.; Duchet-Rumeau, J.; Gerard, J.-F. Synthesis and Characterization of Epoxy/MCDEA Networks Modified with Imidazolium-Based Ionic Liquids. *Macromol. Mater. Eng.* **2011**, 296 (9), 826-834.
113. Guenther Soares, B.; Livi, S.; Duchet-Rumeau, J.; Gerard, J. F. Preparation of epoxy/MCDEA networks modified with ionic liquids. *Polymer* **2012**, 53 (1), 60-66.
114. Soares, B. G.; Silva, A. A.; Livi, S.; Duchet-Rumeau, J.; Gerard, J.-F. New Epoxy/Jeffamine Networks Modified with Ionic Liquids. *J. Appl. Polym. Sci.* **2014**, 131 (3).
115. Soares, B. G.; Silva, A. A.; Pereira, J.; Livi, S. Preparation of Epoxy/Jeffamine Networks Modified With Phosphonium Based Ionic Liquids. *Macromol. Mater. Eng.* **2015**, 300 (3), 312-319.
116. Thi Khan Ly, N.; Livi, S.; Pruvost, S.; Soares, B. G.; Duchet-Rumeau, J. Ionic Liquids as Reactive Additives for the Preparation and Modification of Epoxy Networks. *J. Polym. Sci., Part A: Polym. Chem.* **2014**, 52 (24), 3463-3471.

117. Silva, A. A.; Livi, S.; Netto, D. B.; Soares, B. G.; Duchet, J.; Gérard, J.-F. New epoxy systems based on ionic liquid. *Polymer* **2013**, *54* (8), 2123-2129.
118. Livi, S.; Silva, A. A.; Thimont, Y.; Thi Khanh Ly, N.; Soares, B. G.; Gerard, J.-F.; Duchet-Rumeau, J. Nanostructured thermosets from ionic liquid building block-epoxy prepolymer mixtures. *RSC Adv.* **2014**, *4* (53), 28099-28106.
119. Nyrkova, I. A.; Khokhlov, A. R.; Doi, M. Microdomains in block-copolymers and multiplets in ionomers - Parallels in behavior. *Macromolecules* **1993**, *26* (14), 3601-3610.
120. Eisenberg, A.; Hird, B.; Moore, R. B. A new multiplet-cluster model for the morphology of random ionomers. *Macromolecules* **1990**, *23* (18), 4098-4107.
121. Yang, J.; Pruvost, S.; Livi, S.; Duchet-Rumeau, J. Understanding of Versatile and Tunable Nanostructuring of Ionic Liquids on Fluorinated Copolymer. *Macromolecules* **2015**, *48*, 4581-4590.