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Hybrid Electrolytes

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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 cells¹⁻⁴. 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 casting⁵⁻⁶, the spray-coating⁷, the extrusion⁸ and more recently the electrospinning⁶.

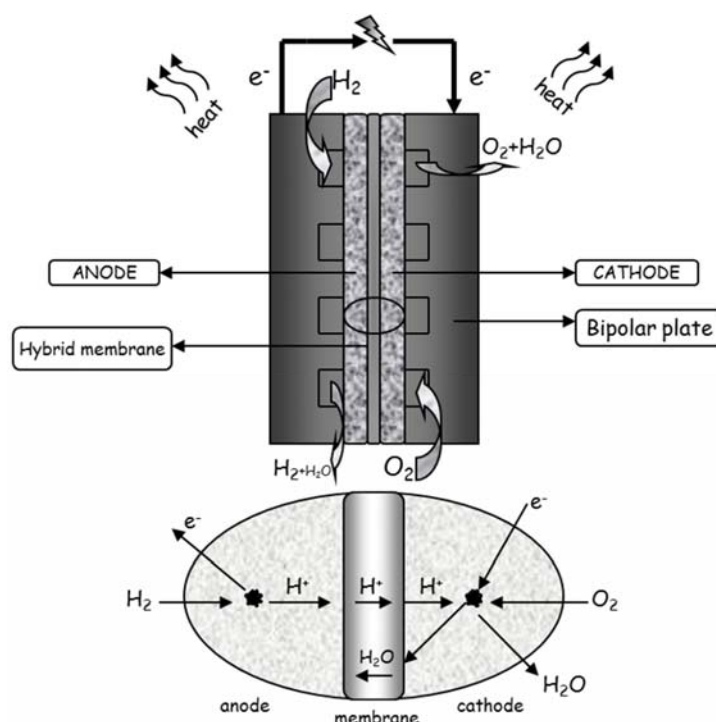


Figure 1: Synoptic layout of a fuel cell with a proton exchange membrane and, in the enlargement, at both electrode/membrane interfaces, the catalytic redox reactions.

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[®]-like perfluoroalkylsulfonic acid polymers (benchmark membranes)⁹⁻¹⁵, and sulfonated polyaromatic polymers¹⁶⁻¹⁷. These polymers include a second phase, (summarized in table 1) either an inorganic filler like mineral (laponite^{11, 16, 18}, montmorillonite¹²⁻¹⁴, zinc oxide (ZrO₂)¹⁹, Silica (SiO₂)²⁰, calcium hydrophosphonate¹⁰, titania (TiO₂)¹³) or a heteropolyacid (hydrophosphoric acid²¹, orthophosphoric acid²²⁻²³, phosphotungstic acid^{19, 24-28}, phosphomolybdic acid^{25-26, 29}, silicotungstic acid^{25, 27, 30}, phosphoantimonic acid³¹, zirconium phosphate sulfophenyl phosphate³², zirconium phosphate^{15, 27}, mesoporous acid silicate¹⁶).

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

Mineral fillers	Formulae or composition
Laponite ^{18, 33} (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 ¹² MontMorillonite (Na^+ -MMT) ¹⁸	$(\text{Na}, \text{Ca})_{0.3}(\text{Al}, \text{Mg})_2\text{Si}_4\text{O}_{10}(\text{OH})_2 \cdot n\text{H}_2\text{O}$
m-MMT ¹² modified MontMorillonite (dodecylamine-exchange montmorillonite)	as above
Zirconium isopropoxide ¹⁹ (Alfa Co. Ltd)	$[\text{Zr}(\text{OCH}(\text{CH}_3)_2)_4(\text{CH}_3)_2\text{CHOH}]$
Heteropolyacids	
hydrophosphoric acid ²¹	H_3PO_2
Orthophosphoric acid ²²⁻²³	H_3PO_4
12-PhosphoTungstic Acid (PTA or PWA) ^{19, 24-27}	$(\text{H}_3(\text{P}(\text{W}_3\text{O}_{10})_4) \cdot n\text{H}_2\text{O})$
Phosphomolybdic Acid (PMA or PMo_{12}) ^{25-26, 29}	$(12(\text{MoO}_3 \cdot 2\text{H}_2\text{O}) \cdot \text{H}_3\text{PO}_4 \cdot 4\text{H}_2\text{O})$
SilicoTungstic Acid (STA or SiWA) ^{25, 27, 30}	$(\text{H}_4(\text{Si}(\text{W}_3\text{O}_{10})_4) \cdot n\text{H}_2\text{O})$
Phosphatoantimonic acid (H_3) ^{31, 33-34}	$(\text{HSb}(\text{PO}_4)_2 \cdot n\text{H}_2\text{O})$
Zirconium Phosphate Sulfophenyl Phosphonate (ZrPSPPh1.5) ³²	$(\text{Zr}(\text{HPO}_4) \cdot (\text{O}_3\text{PC}_6\text{H}_4\text{SO}_3\text{H})_{1.5})$
Zirconium Phosphate (ZrP) ^{27, 35}	$(\text{Zr}(\text{HPO}_4)_2 \cdot n\text{H}_2\text{O})$

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 forth³⁶⁻³⁷. The obtained membranes are known to be chemically and electrochemically stable, with respect to the potential window of the applications³⁸.

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 temperatures¹⁵.

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 decrease¹² or increase³¹ conductivities while improving other properties. For heteropolyacids, there is often an optimal loading²⁷, around 7 weight-percent (wt.%), for example, for sulfonated polysulfones (SPS) /phosphoantimonic acid (H3)^{31, 34, 39}. The size and the shape of the fillers also have its importance³⁴ 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.

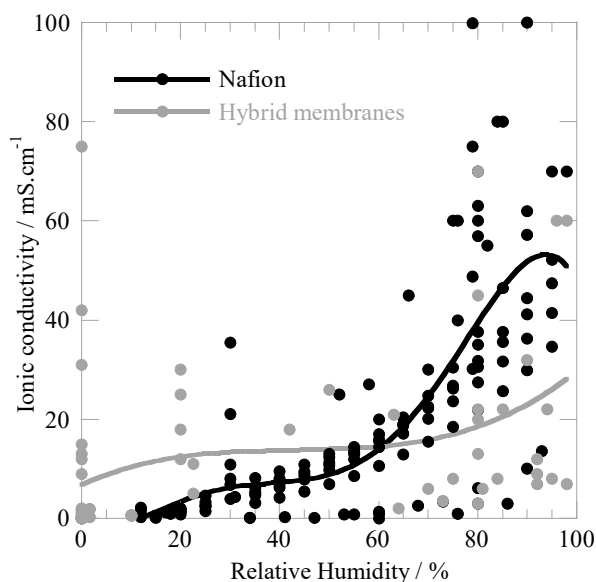


Figure 2: Ionic conductivity as a function of relative humidity ($T \in [0, 120^\circ\text{C}]$ for each relative humidity). The curves are the weighted average conductivities at each relative humidity between the different temperatures (i) for Nafion[®], and (ii) of the conductivities of the hybrid 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 questionable⁴⁰ since the literature reported contradictory results on the role played by the inorganic fillers¹³⁻¹⁵. It can be noticed that the improvement of the proton conductivity was low the last 20 years^{4, 14-16} 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^{9-10, 16}: (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^{12, 15}.

Mechanical properties

Improving effects of the mechanical properties at the local scale and the localization of the crystalline zones¹⁰ are invoked to explain this paradox. The ionic transport has been shown to be intimately linked with the local mechanical properties⁴¹ and the multiscale structure⁴²⁻⁴³.

The addition of heteropolyacids (Table 2) can reinforce the membrane, either with ionic charges (heteropolyacids) or not³³. This addition can also weaken the membrane in the case of weak interactions. The system with sodiated forms of heteropolyacids²⁵ 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 (σ)	Young Modulus/MPa (E)	Elongation at break/% (ϵ)
Nafion (23°C, 50%RH) ⁴⁴	23/28	288/281	252/311
NaSTA/Nafion [®] 117 ²⁵	14		45
NaPMA/Nafion [®] 117	8		70
NaPTA/Nafion [®] 117 (wet)	3		170
SPS 1.1 mol H ⁺ ·kg ⁻¹ 3.5/7.1/12 wt.% of H ₃ ³⁹		158/88/59	6.4/5.4/1.9
SPS 3/25 wt.% of H ₃ ³⁹		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 heteropolyacid⁴⁵. 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.

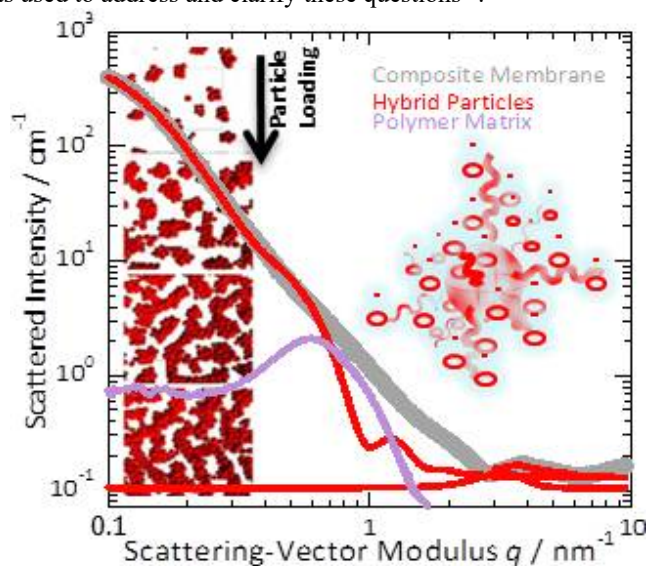
Table 3: Degradation temperatures at 5 wt.% of weight loss of hybrid membranes.

Hybrid ionomers/fillers	Degradation temperature/°C (Inert atmosphere 10°C·min ⁻¹)
Nafion/MMT(3/5/7 wt.%) ¹²	340/330/330
Nafion/m-MMT(3/5/7 wt.%)	340/340/350
Sulfonated PolyEtherEtherKetone/MMT(10 wt.%) ¹⁸	320
Sulfonated PolyEtherEtherKetone /Laponite(10 wt.%)	320
Hybrid polymers/mineral fillers/acids	
Al ₂ O ₃ (50 wt.%) + H ₂ SO ₄ (6 mol·L ⁻¹) + Poly(VinylideneFluoride)/15 mol.%HexaFluoroPropylene (PVdF-HFP) ⁴⁶	180
Zr/Polydimethylsiloxane/H ₃ PO ₄ ¹⁹	300
Hybrid ionomers/heteropolyacids	
NaSTA/ Nafion ^{®25}	300
phosphotungstic acid ²⁴	T>800
phosphotungstic acid/Sulfonated bisphenolsulfone (SPBS) 20/40/60 (6/4)	347/359/411
Polymer/heteropolyacids	
phosphotungstic acid/bisphenolsulfone ²⁴	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 description⁴⁷⁻⁴⁸. 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 investigated¹⁴⁷⁻⁴⁹.

A recent study of an original composite membrane composed of conducting polystyrenesulfonic acid-grafted silica particles (Figure 3) into a PVdF-HFP matrix³⁷ was used to address and clarify these questions⁴⁹.



*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^{4, 50-52}. In fact, it has been possible to locate and to control the inorganic phase (size, structure)^{6-7, 52-53}, even at the nanoscale⁶. The figure 4 shows the Small Angle Neutron Scattering (SANS) spectra (the absolute intensity as a function of the scattering-vector modulus q in nm^{-1}) of membranes obtained by electrospinning coupled to the sol-gel chemistry⁵⁴⁻⁵⁵ 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.

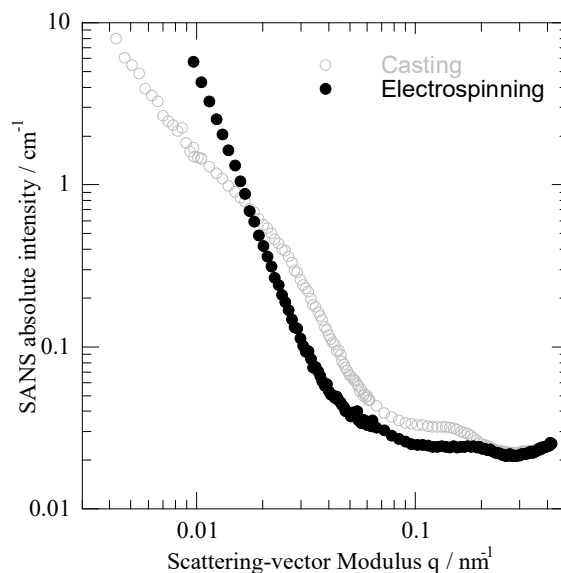


Figure 4: Scattered intensity versus scattering-vector modulus q of electrospun and casting membranes with 55 wt.% of inorganic phase.

The control of the ionic inorganic hybrid phase has significantly enabled to improve the ionic conductivity up to 80°C ⁵⁶ with values in the same order of magnitude as Nafion membranes. This innovative coupling has achieved notable mechanical properties⁵⁶. 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^{6, 43, 56}. 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^{43, 57}.

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°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^{6, 43, 56}.

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 payback⁵⁸. 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 (TiO₂) nanocrystals are an interesting alternative to conventional inorganic photovoltaic devices because of their high-efficiency and low-cost⁵⁹. But the presence of liquid electrolyte causes often sealing problems that impact the long term operation of the devices and raises safety issues⁶⁰. Therefore, different strategies to solidify the electrolyte have been explored⁶¹. The most studied ones are based on hole conductors (HTM) such as inorganic materials, conjugated polymers or small doped molecules⁶². Such cells are reaching performances of 7.2%⁶³ but are still limited by their naturally low electronic conductivity, by the insufficient penetration of solid electrolytes in the nanoporous electrodes⁶⁴ which can reduce the cell performances by 10 to 20%⁶⁵. Alternatively, the ionic conductor may play a role of solid electrolyte to obtain an efficiency up to 8.1%⁶⁶. 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 flammability⁶⁷. 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^-)⁶⁸. 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 window⁶⁹. 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/m² at 25°C perpendicular to the cell plane) [AM 1.5] illuminations⁷⁰. 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 specifications⁷¹. 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 properties⁷².

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 liquids⁷³⁻⁷⁴. 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 proposed⁷⁵. 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.

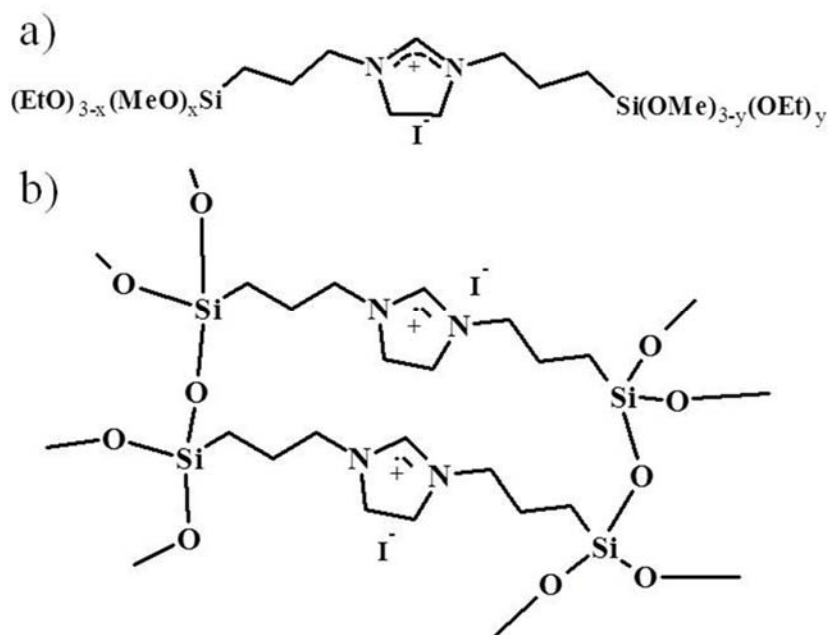


Figure 5: a) Example of an ionic liquid precursor: 1,3-di(3-trimethoxysilylpropyl)imidazolium iodide, and b) schematic of the organization of the imidazolium groups into the silica network.

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 DSSCs⁷⁶. 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 semiconductor⁷⁷, i.e. to induce the oxidation of iodide ions via a fast mechanism.

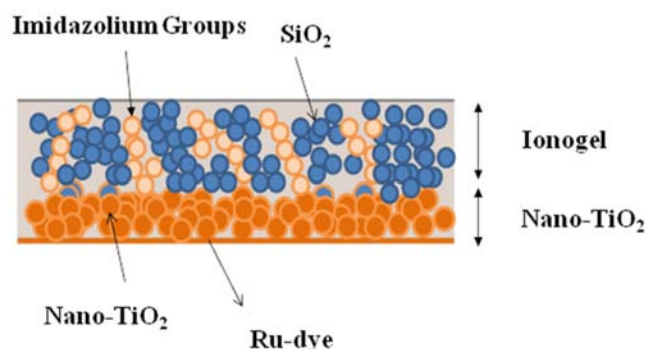


Figure 6: Schematic representation of the DSSC using an in-situ reaction of the ionic liquid precursor with silica precursor (Reproduced with permission from reference 78. Copyright [2013] [the Centre National de la Recherche Scientifique (CNRS) and the Royal Society of Chemistry]).

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 liquids⁷⁸⁻⁸⁰. Varying the concentration of diiodine directly alters the ratio of ion pairs⁸¹ 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).

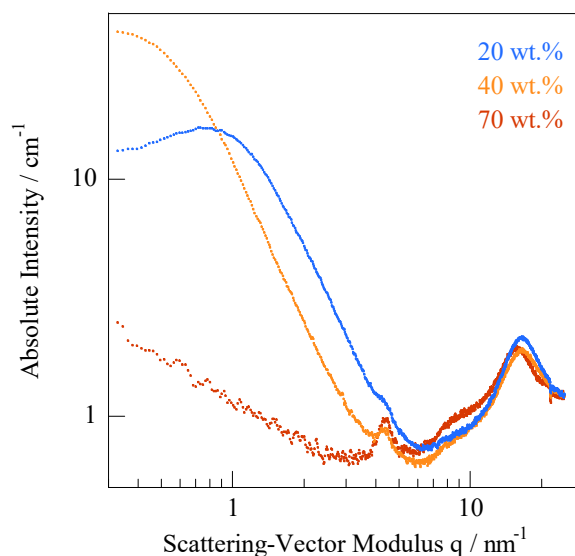


Figure 7: SWAXS absolute intensity as a function of the scattering-vector modulus q for different weight content of the ionic-liquid monomer (Reproduced with permission from reference 78. Copyright [2013] [the Centre National de la Recherche Scientifique (CNRS) and the Royal Society of Chemistry]).

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 unit⁸² as well as in the bulk liquid-like ionic liquid⁸³. A shoulder is also observed *ca.* 9 nm^{-1} . It corresponds to a correlation length of 0.7 nm, close to the one reported in literature for π stacking interactions⁸⁴⁻⁸⁶. 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 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 cells⁸⁷ 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"⁸⁸, co-condensed by sol-gel chemistry, called "soft chemistry"⁵⁴, also allows to propose a class of electrolytes using little energy resources and widespread molecules having lower toxicity than usual solvents⁸⁹⁻⁹⁰.

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 copolymers⁹¹⁻⁹³. Recently, the use of ionic liquids (ILs) as functional additives of thermosets as well as thermoplastics has

opened new horizons in polymer science⁹⁴⁻⁹⁸. In fact, ILs have been investigated as building blocks of polymer matrices and as ionic conducting agents of polymer electrolytes⁹⁹⁻¹⁰⁰.

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 batteries¹⁰¹⁻¹⁰². 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 conductivity¹⁰³⁻¹⁰⁴. Thus, different routes to design polymer electrolytes have been described: 1) impregnation of gel electrolytes with hydrophilic or hydrophobic ILs⁷¹ and 2) inclusion of polymers in ILs¹⁰⁵⁻¹⁰⁶.

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 obtained¹⁰⁷⁻¹⁰⁸. 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 properties¹⁰⁹⁻¹¹¹. 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 networks¹¹²⁻¹¹⁵. 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 networks¹¹²⁻¹¹³. 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 performances¹¹⁶⁻¹¹⁸. 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 matrices⁹⁹. 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 investigated⁹⁹. 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 μm) whereas phosphonium ionic liquid combined with iodide anion induced a “spider web” morphology (Figure 8).

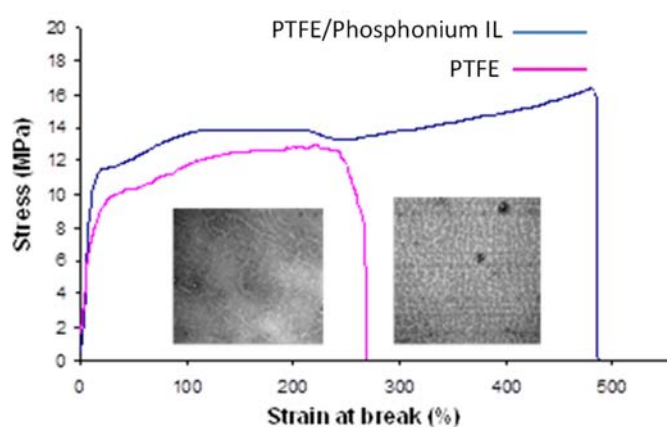


Figure 8: Mechanical curves and TEM micrographs of PTFE without and with phosphonium ionic liquids.

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 structures¹¹⁹⁻¹²⁰. 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)]¹²¹. In addition, the authors have highlighted that the addition of few percent of ILs induced more polar β -phase and more homogeneous distribution morphology as well as an excellent compromise between stiffness and strain to failure¹²¹. 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.

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