Chapter 6

Hybrid Materials for High Ionic Conductivity

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Abstract  Organic–inorganic hybrid materials are a blending of two components where at least one of them is at the nanoscale. The sol-gel process is an interesting method to synthesize these materials because it allows a wide variation in compositions and inorganic/organic ratios, together with an excellent control of porosity (volume, size and connectivity) and functional groups. These features enable the design of hybrid materials with high ion conductivity for different applications as electrolytes for proton exchange membranes fuel cells (PEMFC) and lithium ion batteries. Two of the main constraints of PEMFC are the operation conditions, limited to maximum temperatures of 80°C and relative humidity near 100%. Increasing of operation temperature above 100°C is a highly desirable goal because it increases the electrochemical kinetics, improves CO tolerance, facilitates heat rejection, and reduces the problems associated with water management. Although some of the properties have been achieved separately, no system has been able to gather all the necessary requirements. In the case of application of hybrid materials as solid electrolytes for lithium ion batteries, the ion conductivity is only slightly improved compared with poly(ethylene oxide)-based polymer electrolytes and still far from values of organic liquids. Besides, in the field of microbatteries, the electrolyte thickness can be as low as one micron, and, in this configuration, ionic conductivities of $10^{-5} \text{S/cm}$ or higher would be enough for practical applications.
Keywords High temperature PEMFC • Hybrid electrolytes • Hybrid structure • Ionic conductivity • Li-ion batteries • Lithium ion conductivity • Mesoporous hybrids • Nafion®/inorganic membranes • Organic–inorganic interaction • Poly(ethylene oxide)/inorganic electrolytes • Proton conductivity • Proton Exchange Membrane Fuel Cell (PEMFC) • Sol-Gel • Water-free electrolytes

6.1 Introduction

Currently, the word “hybrid” is seen very often in our daily world. Some examples are the hybrid car, hybrid version of a computer software, hybrid type mobile phone, etc. The word “hybrid” has also been used in materials science and engineering. The dictionary meaning of the word “hybrid” is: “a thing made by combining two different elements”. Normally the terms “hybrid” and “hybrid materials” have been used to express materials produced by a combination of different materials. Therefore, an organic–inorganic hybrid is a combination of organic and inorganic materials. Also, the mixture of materials has been frequently called composites. In many cases, the difference between hybrid materials and composites is not so evident. It is widely accepted that conventionally known composites are mere mixtures of materials, and hybrid materials include at least one of the involved materials at either nanometer or molecular scale. Very interesting properties in these hybrid materials are expected that are not possible to find in organic polymer or inorganic material separately. For example, they can have features such as being flexible like plastic but have excellent mechanical strength and thermal stability. Inorganic–organic hybrids have received a great deal of attention from many different fields, and are a hot topic in materials science and engineering.

Yamada et al. [1] defined hybrid materials as mixtures of two or more materials with new properties created by new electron orbitals formed between each material, such as covalent bond between polymer and silanol. Makishima [2] categorized substances into three materials by their chemical-bond modes, i.e. metals, organic materials and their polymers, and ceramics. He also defined hybrid materials as mixtures of two or more materials with newly formed chemical bonds. His categorization of hybrid materials and their related materials were proposed as follows:

i. Composites Mixture of materials consisting of a matrix and a micron-level dispersion.
ii. Nanocomposites Sub-micron level mixture of similar kinds of materials.
iii. Hybrids Sub-micron level mixture of different kinds of materials with chemical bond between them.
iv. Nanohybrids Atomic or molecular level mixture of different materials with chemical bonds between their different materials.

Gómez-Romero and Sanchez [3] defined hybrid materials as organic–inorganic hybrid materials or inorganic biomaterials and classified them into two main kinds,
depending on the nature of the links and interactions existing at the hybrid interface (Fig. 6.1). Class I hybrids include all systems where there are no covalent or ionic-covalent bonds between the organic and inorganic components. Thus, only Van der Waals, hydrogen bonding or electrostatic forces are present. On the contrary, in Class II hybrids, at least parts of the inorganic and organic components are linked through strong covalent or ionic-covalent bonds. Hybrids can also be characterized by the type and size of the organic or the inorganic precursors. Precursors can be two separate monomers or polymers, or they can be covalently linked.

The above classifications were done from the viewpoint of chemical bonding between components and materials category. Their definitions of “hybrid materials” required an atomic or nanometer-level mixture of materials. Figure 6.2 shows a classification of hybrid materials and composites as a function of the scale level, as proposed by the Materials Science Society of Japan [4].

Suyama [5] proposed three inorganic–organic hybrids, categorizing them on the basis of structural differences of inorganic and organic materials. The first example of inorganic–organic hybrids is the organically modified silicates fabricated by sol-gel processing. The organic-modified silicates, as shown in Fig. 6.3a, have excellent mechanical properties due to strong covalent bonds between silica and organic molecules mixed in a molecular scale [5].

Hybrid materials fabricated in such a manner are characterized by the particular chemical bonds between silica and organic molecules, in contrast with traditional composites. Nowadays, there are many types of inorganic–organic hybrids. A clay/polymer hybrid is one example of another inorganic–organic hybrid material, as shown in Fig. 6.3b. Here, strong chemical bonds between silicate monolayers and polymer molecules offer much improved mechanical properties and lower gas permeability than those of polymer materials. On the other hand, the sol-gel approach is the preponderant one to obtain polymer-silica nanoparticles hybrid materials, as shown Fig. 6.3c. The method includes either the use of nanometer-size silica particles or their precipitation through hydrolysis and condensation reactions of silicon alkoxides. Silica is dispersed in the solution and then in situ polymerization of the monomer is carried out.

![Fig. 6.1 Scheme of different kinds of hybrid materials (Class I—weak forces and Class II—strong forces) by Gómez-Romero and Sanchez [3]](image-url)
The synthesis of hybrid materials using the sol-gel process allows the combination of different organic and inorganic precursors: alkoxides, organically modified alkoxides and monomers. The versatility of the method leads to a wide variation in compositions and inorganic–organic ratios, together with an excellent control of porosity (volume, size and connectivity) and functional groups. These characteristics allow the design of hybrid materials with high ion conductivity for different applications. The manufacturing of electrolytes for proton exchange membranes fuel cells (PEMFC) and lithium ion batteries are two of the most significant ones nowadays.

### 6.2 Proton Exchange Membrane Fuel Cells (PEMFC)

Proton exchange membrane (PEM) fuel cells are one of the most promising clean energy technologies currently under development [6–11]. The major advantages include: current prototype efficiency up to 60%, high energy densities (relative to

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**Fig. 6.2** Classification of hybrid materials and composites at different scale levels proposed by Materials Science Society of Japan [4]

**Fig. 6.3** Morphologies in inorganic–organic hybrid materials proposed by Suyama [5]: a polymer-modified silica, b clay-polymer layer and c silica particle—polymer matrix
batteries) and the ability to operate on clean fuels while emitting no pollutants. Despite these benefits, penetration of PEM fuel cells technology into the market place is being limited by cost and reliability issues. An immense worldwide effort to develop both catalyst and membrane and study the long-term behavior of fuel cells has so far met with moderate success. As a result, it is widely acknowledged that the goal of large scale fuel cell market penetration in areas including transport has moved from 2010 to 2015, and that there are still many technical and market issues to overcome. These challenges include: choosing the appropriate fuel source and infrastructure, industry regulation, safety and public acceptance.

Research into fuel cells has grown exponentially over the last 15 years [12–17]. In the case of the polymer fuel cell, the major breakthroughs in technology which have allowed a significant improvement in the overall performance of the PEM fuel cells, have been the modification of Nafion (Du Pont). In fact, Nafion is the benchmark by which all new materials are compared. A significant number of these modified derivatives of Nafion and other polymers (e.g. sulfonated polyetherketones or SPEK) are appearing in a wide range of the latest fuel cell prototypes. The history and current development of PEM fuel cells is linked to advantages and disadvantages of Nafion under different operating conditions.

Nafion and other perfluorinated PEMs have been widely used because of their excellent proton conductivity and electrochemical stability due to the PTFE backbone [18]. However, they are expensive, not as durable as desirable especially under cycling voltage, humidity, and freezing and thawing conditions, unstable at temperatures over 100°C, and effectively conduct protons only when they imbibe sufficient water, which limits operating temperatures of PEM fuel cells to around 80°C. A cell temperature above 100°C is a highly desirable goal. As the operation of fuel cells at higher temperature increases electrochemical kinetics, improves CO tolerance, facilitates heat rejection, and reduces the problems associated with water management [18–21], there have been extensive research efforts to find alternative membranes that are stable at higher temperatures. In fact, a desirable PEM must not only be highly proton conductive under hot and dry conditions, it should be thin for low resistance and high protonic conductivity, compliant to make a good contact with electrodes, but also rigid enough to provide support to the membrane electrode assembly (MEA), thermally and dimensionally stable, impervious to gaseous or liquid fuels, as well as to electrons, with a low electroosmotic drag, and mechanically strong enough to last several years. This is a tall order indeed, and it is small wonder that success at finding alternatives to Nafion has been limited despite a very large-scale research effort.

It is important to understand that high temperature operation is being prevented by three main barriers [22, 23]:

1. Loss of hydration of the PEM and instantaneous increase in membrane resistance.
2. Polymer membrane degradation above 120°C.
3. Lack of intermediate proton conductors in the range of 100–400°C with a unique proton ‘solvating’ species supporting conduction in the regime.
The factor that has the highest influence on conductivity of proton conducting electrolytes is the degree of hydration. Hence, to understand the design parameters for high temperature PEMs, it is important to have a fundamental understanding of water and proton transport mechanisms. On the other hand, there are many other significant issues that will need to be resolved before alternative membranes are used in PEM fuel cells. These issues include standard operating considerations such as mechanical strength and durability, cyclability, synthesis, and integration in addition to design issues including catalyst compatibility and scale up (or down). Finally, it is important to recognize potentially that the greatest barrier faced will be start-up and shut-down operation, as typically the low temperature and high temperature conductivity mechanisms vary greatly.

6.2.1 New Polymer Electrolytes for High Temperature PEMFC

There have been numerous candidates developed for higher temperature operation of PEM fuel cells, both by modifying Nafion membranes and also by developing completely new systems of membrane [24–31]. Two main types of polymer membranes have dominated research efforts: sulfonated aromatic polymers (e.g. sulfonated polyetheretherketone, SPEEK and polyetherketone, SPEK) and perfluorosulfonic acid membranes such as Nafion which have been the industry benchmarks. These membranes both exhibit phase separated domains consisting of an extremely hydrophobic backbone which gives morphological stability and extremely hydrophilic functional groups. These functional groups aggregate to form hydrophilic nanodomains which act as water reservoirs. However, the conductivity of sulfonated aromatic polymers is also heavily dependant on the degree of sulfonation. At reduced levels of sulfonation the aromatic polymers have lower water contents and reduced conductivity, lower than $10^{-2}$ S/cm, which is not acceptable for use in fuel cell membranes. Nevertheless, if the degree of sulfonation is increased to improve conductivity, the mechanical properties of the membrane deteriorate.

With the aim of looking for alternatives, many efforts are being made to develop organic–inorganic hybrid membranes. The aim here is to review a variety of strategies that authors have developed within each class of hybrids and give the reader an idea of the enormous effort that has been carried out in the development of alternative hybrid electrolytes, alternatives to Nafion, which can operate at high temperatures. In the literature we have found different strategies on hybrid membranes and can be classified into two categories: Class I and Class II hybrids.

6.2.2 Class I Hybrid Electrolytes for High Temperature PEMFC

The incorporation of inorganic materials to improve chemical and mechanical properties, and thermal stability of polymer organic materials is a new procedure
to get hybrid materials. Going from one extreme to another, organic components contribute to the formation of defect-free inorganic membranes and make it less brittle. The route followed in PEMFC field is based on the former type: modification of polymer matrix with an inorganic component. In the case of membranes for Direct Methanol Fuel Cells (DMFC), this kind of hybrid material is also of particular interest since it is a potential method for reducing methanol permeability and increasing proton conductivity. Examples of suitable polymer component are perfluorosulfonic matrix or alternative polymers that have been considered according to the following criteria: resistance to high temperatures, and presence along the backbone of an aromatic ring for sulfonation. The following polymers have therefore been checked as possible candidates for new proton conductive polymers: Polyamideimide (PAI), Polybenzimidazole (PBI), Polyetheretherketone (PEEK), Polyethersulfone (PES) and Polyimide (PI) [32–44].

There are several reviews in which different authors classified the state of the art in Class I hybrid membranes with different criteria: either taking into account the nature of the polymeric matrix (perfluorosulfonic or non-perfluorosulfonic), or the driving mechanism (water-based systems and alternative systems that use other solvents or heterocycles) [26–31, 45, 46].

The hydrophilic inorganic additive is added to retain water at higher temperatures and to increase acidity. However, there are two possibilities: adding the hydrophilic inorganic material into the perfluorinated membrane, or using the polymer as a binding medium for a large amount of inorganic proton conductors [47]. The inorganic component includes hygroscopic oxides such as SiO$_2$, TiO$_2$, SnO$_2$, ZrO$_2$, etc. These oxides do not have high intrinsic proton conductivity but increase the water retention of the membrane, especially at high temperature and/or low humidity conditions. Contents around 10 wt% are appropriate to improve these properties without limiting the conductivity properties of the polymer matrix. The method to incorporate the inorganic component has two main procedures: incorporation of oxide particles to the polymer before material consolidation, and precipitation from alkoxides through sol-gel reactions. The preparation of hybrid organic–inorganic materials using the sol-gel process has been a subject of growing interest because it leads to more homogeneous materials avoiding agglomeration and phase separation. Using this procedure, significant improvement in current–voltage response has been obtained at high temperature (130°C) when SiO$_2$-P$_2$O$_5$-ZrO$_2$ was in situ incorporated in a Nafion membrane [37, 48].

Examples of other inorganic additives are: (1) clays, formed with SiO$_4$ tetraedra and linked into two-dimensional networks [41], (2) zeolites, aluminosilicates enclosing cavities suitable for water molecules [49, 50], (3) hygroscopic layered-structures compounds as zirconium phosphate and other metal phosphates [42, 43], (4) heteropolyacids, clusters of tungsten, molybdenum, and others with high proton conductivity at low temperature because of the presence of protons and water molecules in the structure [39, 40] and (5) mesoporous inorganic micro or nanoparticles with pore sizes below 10 nm, sometimes ordered, that can be functionalized with protonic functions such as COOH, SO$_3$H or PO$_3$H$_2$ [51–53].
In the case of zeolites, exposing some inorganic oxides to water atmosphere at high temperature leads to oxygen vacancies in the oxides that are replaced by hydroxyl groups from the dissociation of water vapor, leaving protons to form covalent bonds with the lattice oxygen. The water uptake and the concentration of incorporated protons depend highly on the concentration of oxygen vacancies in oxides and the rate of water incorporation reactions. The diffusion of these incorporated protons in the lattice of oxides results in the high conductivity observed in these oxides. Among them, the highest proton conductivity was observed in oxides with perovskite-type structures (ABO$_3$) with cubic or slightly reduced symmetry [49, 50].

In regard to mesoporous hybrid systems, the very high and structured porosity of these new hybrid membranes obtained by sol-gel enhance the water storage, the intimate mixture of polymeric chains with inorganic phase, and mostly the exchange capacity (IEC) through a much larger surface area available for functionalization [51–53]. Indeed, this approach gathers together complementary essential properties: first, water uptake control due to the open mesoporosity; second, the enhancement of proton conductivity values when the membrane operates at high temperature and low relative humidity rate opening the possibility to graft sulfonic moieties in the silica phase; third, the mechanical property of the membrane, in which the formation of a finely dispersed mesostructured inorganic network leads to a flexible and non-swelling homogeneous material. Mesoporous silica/polymer hybrids can also be made through entrapping polymers in the nanochannels of mesoporous silica through the hydrogen bonding between the silanol groups on the silica surface and the groups in polymer chains. Hence, groups which can form hydrogen bonds with silanol groups are very necessary for a certain polymer if high loading of polymers has to be trapped. The hydrogen donating property of silanol moieties is so strong that organic polymers having hydrogen accepting groups such as amide moieties form hydrogen bonds with silanol groups. For polymers without hydrogen accepting groups, other methods should be used to graft hydrogen accepting groups onto polymer chain [54, 55].

Although this concept seems promising, the success so far seems limited and the interaction between the inorganic phase and proton conductor is not sufficiently understood. Further, the stability of the material in the polymer host is uncertain. Certain materials (e.g. heteropolyacids) dissolve in the water produced in the fuel cell leaching out if there is no chemical bond with the network.

Another approach is the replacement of water by a less volatile, non aqueous, and high proton conducting solvent developing the same function as water. Four relevant examples of such ‘water replacements’ are phosphoric acid, and systems that contain heterocycles such as imidazole, solid acids as CsHSO$_4$ and CsH$_2$PO$_4$, and ionic liquids. The compounds should have the ability to act as a Brönsted base, and have a high dielectric constant and a low volatility. Proton conducting species are mainly responsible for transporting protons in short and long ranges. From the atomic level, only oxygen and nitrogen are suitable for carrying protons in the PEMFC due to chemical stability and interaction of oxygen and nitrogen with protons. Possible proton conducting species with oxygen include water, oxygen
anion, hydroxyl anion, alcohol, ether, ester, carboxylic acid, inorganic oxoacid, and oxygen-containing heterocycles. For nitrogen, those include ammonia, amino groups, and nitrogen-containing heterocycles.

Phosphoric acid ($H_3PO_4$) is a highly viscous liquid and was first used in phosphoric Acid Fuel Cells (PAFCs), which were developed in the 1960s and also the first type of fuel cells to be commercialized. The operating temperature of PAFC is in the range of 150–220°C, indicating the excellent proton conductivity properties at high temperature. The estimated proton mobility of phosphoric acid at the melting point (42°C) is $2 \times 10^{-5}$ cm$^2$/s with a conductivity of $7.7 \times 10^{-2}$ S/cm [56]. In the case of PEMFC, the main application of phosphoric acid has been to dope polybenzimidazole (PBI)-based polymers. Wainright et al. [57] first proposed and developed PBI doped with $H_3PO_4$ for application as electrolyte in high temperature PEMFC. PBI provides enough mechanical strength, stability, and acid absorption ability to produce the composite membranes. Several methods have been used to incorporate phosphoric acid into the polymer: (1) the cast polymer membranes were immersed into the phosphoric acid solution, (2) PBI polymer and acid were directly cast from a solution of PBI and $H_3PO_4$ in trifluoroacetic acid solution, and (3) PBI was prepared in polyphosphoric acid (PPA) and directly cast to form membranes. Although the doping level is similar, the properties of membranes prepared by different methods are quite different. Comparing results, it seems that a higher content of phosphoric acid leads to an improved conductivity.

Among various nitrogen-containing species, some heterocycles are most likely to be the proton carriers applied for high temperature PEMFC because the high electron density on nitrogen is partially reduced by the conjugated aromatic system and the oxidative stability of nitrogen is improved. Kreuer et al. [58] first proposed heterocyclic compounds as imidazole and pyrazole like proton conducting groups. The proton conducting ability of imidazole was determined by measuring the conductivity of sulfonated PEEK doped with imidazole and pyrazole at elevated temperatures, and also by studying the proton mobility. Imidazole also acts as a proton donating groups through the dissociation of the proton from the –NH group in imidazole. The conductivity of liquid imidazole was reported to be as high as $10^{-3}$ S/cm at the melting point of 90°C. Later work has been focused on the study of (i) imidazole doped acidic perfluorosulfonic polymer such as Nafion and (ii) imidazole derivatives bonded to alternative polymers [56]. The imidazole grafted polymer shows noticeable proton conductivity at high temperatures without external humidification, which provides a potential way to design so-called “intrinsic proton-conductive” polymers for high temperature applications. By covalently tethering the proton carriers to the polymer backbones, the leaching or evaporation of these free-water proton conducting molecules can be avoided getting stabilized conductivity and performance of the membrane at high temperatures. However, the first fuel cell tests reported based on acidic polymers with imidazole doping or imidazole grafted polymers were not successful, possibly due to the poisoning effect of imidazole to the platinum catalysts [59]. Although the boiling point of imidazole is as high as 256°C, the slow evaporation or leaching of small imidazole molecules may still lower the conductivity of the imidazole doped membrane. For polymers with imidazole
tethered, the difficulty is in either very low conductivity or insufficient mechanical strength. Besides the low conductivity, the thermooxidative degradation of imidazole and other heterocyclic compounds may also be a difficulty for applying these materials for long-term high temperature-PEMFC applications.

Other typical inorganic proton conducting materials are acidic salts of oxoacids such as CsHSO₄ [60]. At temperatures around 140°C, there exists a first-order phase transition of CsHSO₄, and above this point the solid shows proton conductivity as high as 10⁻² S/cm, which results from the hydrogen transportation between sulfate groups. However, to apply these inorganic proton conducting materials to high temperature PEMFC, there are still some severe disadvantages: (1) the low conductivities at temperatures below 200°C, which may be even worse when it was doped into a polymer matrix due to the large interfacial resistance; (2) the instability of these oxides in liquid water; and (3) insufficient mechanical properties of these solid oxides and their composites with polymers.

Recently, a few groups [61, 62] reported that some kinds of ionic liquid, such as imidazolium bis-(trifluoromethanesulfonyl)imide (HImTFSI) and 2,3-dimethyl-1-octylimidazolium triflate, have proton conducting ability and may be applied in PEMFC at elevated temperature. However, only part of the high total conductivity is related to proton conduction in these systems. The stability, leaching, and electro-osmotic drag of ionic components in the membrane are disadvantages for these systems. Till now, there is no acceptable cell performance data reported for ionic liquid-based membranes. Unfortunately, all these water-free systems that use alternative solvents to transport protons are typically soluble in the water produced in the fuel cell and can eventually leach out.

### 6.2.3 Class II Hybrid Electrolytes for High Temperature PEMFC

The second approach involved to replace Nafion membrane is based on hybrid organic–inorganic materials with nano-sized phases and interfaces, where chemical bonds are created between the inorganic moieties and the polymer matrix. The synthesis of class II hybrid organic–inorganic materials using sol-gel technology has attracted the continuous attention of researchers from different fields. This method is part of the process of “soft chemistry” and allows the incorporation of organic molecules in inorganic matrices, an operation that cannot always be done by other methods without degradation of any component. This fact makes possible the incorporation of organic groups with a range of reactive functionalities on the inorganic network and may generate structures in which the two networks, one organic and the other inorganic, are mutually intertwined and interconnected. Such structures can be generated from different synthesis routes: (1) simultaneous synthesis of organic and inorganic networks, (2) sequential synthesis: inorganic polymerization followed by organic polymerization or organic polymerization and subsequent inorganic polymerization. Sol-gel processes are complex because during synthesis side effects and competitive reactions, including esterification and
transesterification depolymerisation, can be produced. It is essential a strict control of the organic and inorganic polymerization kinetics, controlling all the parameters that govern them and avoiding phase separation processes, to achieve the appropriate conversion degrees and maintain the desired organic/inorganic ratio. The presence of an organic group covalently bound to the inorganic network (alkylalkoxide) affects the kinetics of sol-gel reactions, since the degree of condensation of trifunctionalized silicon decreases when the size of alkyl organic group increases. Using a polymerizable alkylalkoxide unit as a precursor, organic polymerization shows strong steric hindrance, which affects the degree of polymerization of organic and inorganic, and the level of crosslinking. Therefore, it is necessary to control the kinetics of polymerization and the factors that govern them in order to develop both networks simultaneously for preparing homogeneous nanostructured membranes with no phase separation. The key factor to obtain hybrid structures with specific properties is the design of the synthesis, including the choice of precursors, the organic/inorganic ratio and the strategy of organic and inorganic synthesis. The main advantage of synthesized class II hybrid membranes by the combination of sol-gel technique and polymerization process is that the growth of inorganic and organic phases allows the improvement of the interface comparing with hybrids class I and enlarge the dispersion of the networks [3]. However, the success of the procedure depends on the molar ratio of organic and inorganic precursors, the kind of precursors used, and reaction kinetics [63, 64]. Moreover, if the process includes monomers, the possibilities of synthesis of organic–inorganic membranes with the desired properties grow exponentially. The incorporation of monomers also allows to define the organic/inorganic ratio in a large range of compositions [65, 66]. An adequate design of the hybrid structures should generate membranes with high thermal stability able to operate at temperatures up to 200°C, and enough chemical stability against water, hydrogen, oxygen, and methanol in this temperature range. The major problem associated with the incorporation of an inorganic network is the increase of brittleness, because this originates membranes with mechanical stability not enough to resist the preparation process of the Membrane-Electrode Assembly (MEA). For this reason, the precise design of the hybrid structure is very important to solve this problem, and an adequate organic–inorganic ratio, crosslinking and synthesis procedure is crucial. The membranes ought to have high proton conductivity to be applied in PEMFC. Two main alternatives are used to provide high proton conductivity in hybrid membranes: a high concentration of SO$_3^-$ groups, as in Nafion-type membranes, and incorporation of high proton conducting compounds. In general, silica structure coming from silicon alkoxides and organically modified alkylalkoxides fulfills these requirements. On the other hand, inorganic components can also contribute to reach higher proton conductivities through both hydroxyl groups and nanosized porosity that attract and retain water molecules.

The class II hybrid membranes prepared by sol-gel with high proton conductivity for application in high temperature PEMFC can be classified considering the organically modified alkoxide uses to bond the organic and inorganic components. Glycidoxypropyl trimethoxysilane (GPTMS) is an organically modified alkoxide that has been widely used in the design of class II hybrid membranes.
Its three methoxy groups allow inorganic polymerization with the formation of siloxane chains, while the opening of epoxy group results in the formation of a bridge between components. Membranes obtained through hydrolysis and condensation reaction of this precursor without any proton donor shows low proton conductivity at high relative humidity: $1 \times 10^{-4}$ to $4 \times 10^{-3}$ mS/cm. Some of the hybrids produced use Poly (vinyl alcohol) (PVA) for the formation of the organic structure connecting with the inorganic component through of GPTMS. PVA is a cheap polymer widely used in the formation of hybrid membranes for fuel cells. Specifically, PVA-based membranes, doped with strong acids such as phosphomolybdic and phosphotungstic acids, have been tested as proton conductors [67, 68]. Other inorganic precursors such as tetraethyl orthosilicate (TEOS) and additives as chitosan, a linear polysaccharide composed of randomly distributed $\beta$-(1-4)-linked D-glucosamine (deacetylated unit) and N-acetyl-D-glucosamine (acetylated unit), have been incorporated to improve permeability and selectivity [69, 70].

However, the proton conductivity is not sufficient for use in PEMFC, and it is necessary to introduce other precursors such as phenyl triethoxysilane (SPS) and proton conductor additives as phosphoric acid to achieve higher conductivity values ($2 \times 10^{-3}$ S/cm at 120°C and 15% RH), but still insufficient [71, 72]. Other proton donors have been analyzed in these GPTMS-based hybrid systems. The introduction of heteropolyacids, as PWA y SiWA, and $\alpha$-zirconium phosphate (ZrP) leads to membranes with high proton conductivities up to 20 mS/cm. The high proton conductivity of the composites is due to the proton conducting path through the GPTMS-derived 'pseudo-polyethylene oxide' [73]. One possibility to increase the proton conductivity is to incorporate Nafion on a covalently cross-linked network composed of 4,4-methylenedianiline (MDA) and GPTMS. The hybrid membranes present a high degree of bound water (87%), adequate proton conductivity (0.034 S/cm), low methanol permeability ($1.1 \times 10^{-8}$ cm$^2$/s) and an adequate oxidative stability [74].

Another organically modified alkoxide used in the design of class II hybrid membranes is the 3-aminopropyltriethoxysilane (APTS). Its combination with other precursors as 3-triethoxyisilylpropyl (TSPHI) and $p$-vinylphenylmethyldiethoxysilane (VFMES), and doping with 4,5-dihydroimidazol allows the synthesis of hybrid membranes with conductivities up to $10^{-2} \times$ S/cm at 130°C [75].

Several hybrid systems were synthesized using polysiloxanes, showing a low glass transition temperature and high thermal and oxidative stability, but are highly permeable to oxygen, decomposed into water, and are sensitive to acidic and alkaline medium grade [76]. The main drawbacks of these types of membranes are their poor mechanical properties, making it difficult to obtain freestanding membranes, but have the advantage of providing proton conductivity due to its special structure.

Other kinds of class II hybrid membranes are based on PEEK that gave such good results in pure polymeric membranes. In this case, a new synthetic approach is developed to synthesize a hybrid membrane, PhSiSPEEK, which includes phenylsilanol groups covalently bound to the aromatic backbone of sulfonated PEEK. These membranes exhibit conductivity around $10^{-3}$ S/cm at 120°C and 20% RH [77].
An alternative organically modified alkoxide used in the design of class II hybrid membranes is the hybrid precursor metacriloxy propyltrimethoxysilane (MPS). The hybrid structure is usually formed by silica-methacrylate, although only a few works are devoted to this network [78]. A combination of methacrylate and epoxy structures has been also studied to reach strong hybrid membranes with improved proton conductivity. For example, systems based on styrene (STY)—2-hydroxiethyl methacrylate (HEMA)—TEOS—PWA and GPTMS—TEOS—2-allylphenol (AP) have reached high proton conductivities, similar to Nafion, at temperatures higher than 100°C and 100% RH. The combination of sulfonation process with heteropolyacids that have been immobilised within the membranes through electrostatic interaction with inorganic component overcoming the leakage problem from membranes allows proton conductivity values of $10^{-3}$ S/cm at 40°C and 65% RH. This result can be considered a significant improvement considering the measurement conditions at low temperature and relative humidity [79, 80]. Smith et al. [81] used poly(3-sulfopropyl-methacrylate) and poly(styrenesulfonic acid) as precursors that can be attached to the nanopore surface getting a robust membranes. Proton conductivity was dependent on temperature and humidity, reaching a value of $2 \times 10^{-2}$ S/cm at 30°C and 94% RH. Sel et al. [82] studied several membranes that contain a termopolymer poly[vinyldenefluoride-ter-perfluoro(4-methyl-3,6-dioxaoc7-ene sulfonyl fluoride)-ter-vinyltriethoxysilane] [poly(VDF-ter-PFSVE-ter-VTEOS)]. Vinyltriethoxysilane (VTEOS) units of the terpolymer help to bind and assemble the inorganic network into a continuous medium and the perfluoro (4-methyl-3,6-dioxaoc7-ene) sulfonyl fluoride (PFSVE) chains are able to bridge the conduction paths in the hybrid membrane by way of their SO$_3$H-functionalized chain ends. The incorporation of terpolymer into the hybrid SiO$_2$–SO$_3$H/poly(VDF-co-HFP) copolymer membrane allows conductivity values of around 10 mS/cm up to 120°C.

So far, all described hybrid membranes are based on silica as inorganic precursor. However, other precursors were used in the synthesis of such hybrid membranes. For example, Kim et al. [83] studied several hybrid membranes using titaniam alkoxides as precursors and polydimethylsiloxane (PDMS). The hybrid membranes showed proton conductivities around $2 \times 10^{-3}$ S/cm at 150°C and maximum power values of 30 mW/cm$^2$ at 150°C and 100% RH.

The incorporation of mesopores through templates can be useful to increase the water retention capability of the hybrid membranes, especially at high temperature operation. An approach consists of creating a three-dimensional interconnected network of mesostructured hydrophilic materials in an inert/uncharged thermosable polymer, PVDF-HFP. Specifically, the hybrid membranes contain a mesostructured SiO$_2$ network with acidic functionality (–SO$_3$H) and the fluorinated polymer PVDF-HFP. The sulfonic acid functionality is introduced by co-condensation of TEOS with an organically modified silane containing sulfonic acid groups, 2-(4-chlorosulfonylphenyl) ethyltrimethoxysilane. The mesoporosity is generated by the use of structure-directing agents such as P123 [poly(ethylene oxide–propylene oxide–ethylene oxide)] block copolymers. Final hybrid membranes that containing hierarchical porosities, macro-, meso- and micro-scale
exhibit a proton conductivity of 50 mS/cm at 70°C under 100% relative humidity [84]. Also in this research line, hybrid membranes were fabricated by electrospinning nanofibers composed of a proton conducting polymer with proton conducting, water-retaining inorganic nanoparticles. Nanofibers are obtained from sulfonated poly(arylene ether sulfone) (S-PAE) to which sulfonated polyhedral oligomeric silsesquioxane (S-POSS) nanoparticles were added to improve water retention and proton conductivity [85, 86].

6.3 Secondary Lithium Ion Batteries

A lithium ion battery cell consists of a positive and a negative electrode (both sources of chemical reactions) separated by an electrolyte which enable ion transfer between the two electrodes. Rechargeable lithium batteries have been used as efficient energy storage devices in lightweight electronic appliances, cellular phones and laptop computers because of the high energy densities. There have been many efforts to make microscale lithium batteries for application in fields related to microsystems, such as microsensors, micromechanics, and microelectronics [87]. The electrolyte is usually a flammable and explosive solution containing dissociated salts. The use of solid electrolytes should permit development of batteries which increase safety and provide greater flexibility of battery shape.

Besides a large electrolyte window, the electrolyte should have a stable electrode/electrolyte interface during cycling, a Li-ion conductivity higher than $10^{-4}$ S/cm, an electronic conductivity lower than $10^{-10}$ S/cm, chemical stability with respect to the electrodes, thermal stability over ambient temperature ranges and temperatures in the battery under high power, and made of safety (nonflammable and non-explosive) and non-toxic materials [88]. Solid electrolytes could meet all of these requirements, especially those, stable electrode/electrolyte interface and safety, which are more difficult to obtain with liquid electrolytes. An exemplary solid polymer electrolyte is the poly(ethylene oxide) (PEO) system containing a lithium salt. They are low-cost, nontoxic, and have a good chemical stability. It is widely accepted that ion conduction occurs in the amorphous phase above the glass-transition temperature ($T_g$) by a liquid-like motion of the Li ions associated with the segmental reorientations of the neighboring polymer strands. However, the polymers in such systems tend to crystallize, resulting in low room temperature ionic conductivity ($<10^{-7}$ S/cm at 25°C) and Li$^+$ transference number (0.1–0.3) [89].

6.3.1 Class I Hybrid Electrolytes for Li-Ion Batteries

Most approaches to increase the ionic conductivity of PEO systems are based on lowering the degree of PEO crystallization or reducing the glass transition temperature. The introduction of inorganic fillers to PEO-based electrolytes improves
the conductivity and mechanical properties of the electrolytes. Although initial attempts sought to improve the conductivity of electrolytes through the use of conductive particles, the conductivity enhancement is commonly attributed to a decrease in polymer crystallinity, and an enlargement of the amorphous domains in the PEO matrix. Figure 6.4 displays a scheme of a polymer matrix electrolyte including oxide particles.

The surface hydroxyl groups of these particles interact with oxygen from polymer network. The inorganic component disrupts the organic structure opening new channels for the lithium ion diffusion. Reports show that smaller particles are the most effective, presumably because their high-surface area inhibits crystallization, and the result is an enhanced conductivity, but it is still not comparable to that of the carbonate electrolytes [90]. Almost all of these polymer-inorganic nanocomposites were prepared through mechanical blending of nanosize particles, polymer, and salt in a compatible solvent. Solid electrolytes of thickness around 100 μm were prepared by solution from acrylonitrile–methyl methacrylate–styrene (AMS) terpolymer, LiClO₄ in ethylene carbonate (EC)/dimethyl carbonate (DMC) and silica particles [91]. The capacity to retain electrolyte solution and the mechanical state of the polymer electrolyte film was found to be dependent on the molar composition. Ionic conductivity at room temperature was calculated to
be $5 \times 10^{-4}$ S/cm. Another example of composite polymer electrolyte uses poly(acrylonitrile-co-methyl methacrylate) as precursor. A maximum conductivity $(2 \times 10^{-3}$ S/cm at $25^\circ$C) was found for the electrolyte containing 10 wt% silica with EC–PC. The reduction in $T_g$ of the plasticizer-rich phase in the composite polymer electrolytes due to the interaction between the added silica and lithium cation seems to be a main reason for the initial increase of the ion conductivities with the increase in the silica content. It can be observed a decrease of ion conductivity at higher silica content, attributed to the increase of viscosity of the plasticizer-rich phase and the decrease in the charge carrier numbers [92]. However, both are known as “gel electrolytes” because they contain a large amount of liquid plasticizers, compromising the advantages looked for in a solid electrolyte.

### 6.3.2 Class II Hybrid Electrolytes for Li-Ion Batteries

Aggregation of nanoparticles is an inevitable event due to the high surface energy of small particles that undermines the efficacy of the ceramic fillers. A simple and effective method to overcome such a problem is the sol-gel process, wherein the nanosized ceramic fillers can be obtained in situ in the polymer matrix through a series of hydrolysis and condensation reactions of suitable precursors. Thus the ceramic fillers are uniformly distributed in the polymer and exhibit excellent properties. Considerable advance was gained recently by designing new electrolytes based on these organic–inorganic hybrids or nanocomposite systems, among which silica-based materials hold a prominent place. They are called ORMO-lytes (organically modified electrolytes) or ORMOCERs (organically modified ceramics) [89, 93, 94]. In contrast to hardly reproducible filling of polymer electrolytes with nanoparticles, the polycondensation of alkoxysilanes enables an extremely homogenised and reproducible distribution of the nano-sized oxidic units. On the other hand, the organic network is formed from reactive functional groups $R'$ of alkoxysilanes of the type $R'Si(OR)_3$, or by co-polymerizing reactive organic monomers with reactive functionalized alkoxysilanes. Figure 6.5 shows a scheme of a hybrid organic–inorganic electrolyte with chemical bonds between both components. Metal alkoxides and organically modified alkoxides produce the hybrid structure through inorganic condensation and polymerizable and non-polymerizable organic groups. The incorporation of reactive monomers allows a significant flexibility in the design of these materials.

Depending on the reactive organic functionalities and their thermal and uv-initiated organic crosslinking reactions, the materials can be adapted to meet all the electrolyte requirements. These inorganic–organic copolymers, synthesized by sol-gel processing, as host materials for ion conductors offer interesting properties: they are amorphous at room temperature, which causes comparatively high conductivities, and they provide higher thermal stability than pure organic matrices [95, 96]. Further, the inorganic–organic matrix enables mechanical and thermal stability of thin films/separators, even after the addition of plasticizers, fitting
perfectly for multi-layer technology and application in mini- and micro-batteries [97, 98].

Dahmouche et al. [99] have provided a comparative of organically modified sol-gel electrolytes producing chemical bonds between the organic (polymer) and inorganic (silica) phases, with others obtained from a mixture of tetraethoxysilane and poly(ethylene-propylene glycol) that are not chemically bonded. In the first case, lithium ion-conducting organic–inorganic nanocomposites based on poly(ethylene glycol) or poly-(propylene glycol) covalently attached to a silica network have been prepared using 3-isocyanatopropyltriethoxysilane, O,O′ Bis (2-aminopropyl)-polyethylene glycol (or O,O′ Bis (2-aminopropyl)-polypropylene glycol) and LiClO₄. The ionic conductivity is higher than $10^{-6}$ S/cm at room temperature. In the second family, prepared from tetraethoxysilane (TEOS), polyethylene glycol (PEG) and lithium salt, the organic and inorganic phases are not chemically bonded. Ionic conductivity has been studied as a function of the polymer chain length and concentration. Values up to $10^{-4}$ S/cm at room temperature have been obtained, that are strongly related to the connectivity of the two phases and the mobility of both the structural network and the active species. After, the same authors [100] present a higher room-temperature maximum conductivity ($6 \times 10^{-2}$ S/cm) for optimized hybrid electrolytes without covalent organic–inorganic chemical bonds (type II). This value was obtained for

Fig. 6.5 Scheme of a Class II hybrid electrolyte for Li-ion batteries based on metal (M) alkoxides and organically modified alkoxides with polymerizable ($R_1$) and non-polymerizable ($R_2$) organic groups, and monomers (P)
[O]/[Li] = 15 and PEG300/TEOS = 1.0 ratios. A similar hybrid ion conductor was prepared from a mixture of tetramethyl orthosilicate (TMOS), polyethylene glycol and lithium perchlorate (LiClO4) [101]. Again, ionic conductivity increases with decreasing molecular weight of polyethylene glycol because of the reduction of glass transition temperature ($T_g$), reaching a maximum of $10^{-5}$ S/cm at room temperature. Structural characterization by FTIR and NMR measurements confirm the presence of hydroxyl-free end groups bonded to carbon and silicon atoms. Although the ionic conductivity is attributed to lithium ions, proton diffusion cannot be rejected and both can coexist. In the absence of water, the diffusion mechanism of both ions is similar and would be observed in the same frequency range of impedance spectra. However, it is to be expected that without water, proton diffusion would be insignificant.

Chemical stability is an important issue, and some amorphous poly(ethylene oxide) (PEO)–SiO$_2$ composites have been prepared by sol-gel transformation based on the hydrolysis and condensation of TEOS, concurrent with ultraviolet (UV) irradiation of poly(ethylene glycol) dimethacrylate (PEGDMA) and methoxy poly(ethylene glycol) monomethacrylate (PEGMA) to produce the PEO network [102]. An alternative non-hydrolytic sol-gel route uses citric acid (CA), tetraethyl-orthosilicate (TEOS), ethylene glycol and Li$_2$CO$_3$ [103]. The hybrid conductor is shown to be fully amorphous at room temperature with an ionic conductivity above $10^{-5}$ S/cm. The incorporation of SiO$_2$ nanoparticles (5 nm) to the matrix without the presence of Li has a conductivity value of $10^{-6}$ S/cm at room temperature. This effect can be explained by the features of SiO$_2$ nanoparticles surface, which generally is hydrated, indicating that proton conductivity could be also presented.

Hybrid with other oxides different from silica have also been synthesized. For example, poly(ethylene oxide) –LiClO$_4$–TiO$_2$–Al$_2$O$_3$ organic–inorganic hybrids were synthesized using titanium (IV) and aluminum isopropoxides as inorganic precursors [104]. Ionic conductivity increased with oxides content up to 10 wt% ($3 \times 10^{-5}$ S/cm at room temperature) and then decreased above this amount. Infrared spectra show the formation of molecular scale PEO-oxide hybrids, although also the presence of free hydroxyl groups allowing some proton conductivity interference. Other authors, claiming that TiO$_2$ is more surface active than SiO$_2$, have prepared PEO/TiO$_2$ nanocomposite polymer electrolytes with an in situ uniform dispersion of TiO$_2$ particles in the polymer matrix [89]. The sol-gel process involves the hydrolysis and condensation reaction of titanium (IV) ethoxide in the presence of high MW PEO and LiBF$_4$. The room-temperature ionic conductivity of these polymer electrolytes ($10^{-6}$ S/cm) was an order of magnitude higher than that of the TiO$_2$-free sample. A high Li$^+$ transference number of 0.51 was recorded, and the nanocomposite electrolyte was found to be electrochemically stable up to 4.5 V versus Li$^+$/Li. The nanocomposites displayed enhanced ionic conductivity, in part because of the increase in the number of “active” charge carriers, as well as higher Li ion mobility. This behavior is attributed to the interaction between ceramic fillers, anions, and polymer chains.
The use of amino group is also an interesting approach to prepare hybrid electrolytes. Different chemically bonded hybrid electrolytes have been synthesized as an alternative to PEO from the reaction of diamino-terminated alkylene oxides with cyanuric chloride, followed by reaction with monoamino-terminated alkylene oxides and (3-aminopropyl) triethoxysilane [105]. The resulting films show improvements in both ionic conductivity and mechanical properties over PEO itself. The conductivity at 25°C for the optimum formulation is $4 \times 10^{-5}$ S/cm, although lithium conductivity decreases and film strength increases with increasing amounts of cross-linking agents. Slightly higher conductivities may be obtained with polymers having less than 25% (3-aminopropyl) triethoxysilane cross-linker. However, dimensional stability is compromised as the precursor percent approaches zero. The incorporation of ionic liquids at ambient temperatures to these structures increases the conductivity up to $10^{-3}$ S/cm at room temperature [106]. However, the presence of a liquid reduces some of the advantages of solid electrolytes as the greater flexibility of battery shape.

An extension to improve the performance of this class of electrolytes is the incorporation of nanoporosity in the microstructure by a surfactant templating sol-gel route. An example is the composite PEO-based electrolyte containing micro-sized nanoporous zirconium-oxide-sulfate filler [107]. Cetyltrimethylammonium bromide (CTAB), zirconium propoxide, ammonium sulfate and LiClO$_4$ were used for the synthesis of membranes. The presence of nanoporous filler favors the ion transport, enhancing the ion conductivity almost one order of magnitude compared with ceramic-free electrolyte. Authors claim that the fillers promote lithium conducting pathways as a result of the Lewis acid–base interactions occurring between the ceramic nanoporous surface and both the lithium salt ClO$_4^-$ anion and the PEO segments. Anyway, the maximum ionic conductivity at room temperature is around $10^{-5}$ S/cm, not enough for practical application. Only at temperatures higher than 70°C the conductivity value ($10^{-3}$ S/cm) is interesting for application in batteries.

The increase of mechanical, thermal and chemical stability of solid electrolytes when an inorganic component is incorporated to produce hybrid organic–inorganic materials has been demonstrated. However, lithium ion conductivity is only slightly improved compared with poly(ethylene oxide)-based polymer electrolytes and still far from values of organic liquids. On the other hand, it is necessary to consider the electrolyte thickness which in the case of organic liquid is usually higher than a hundred microns. In the field of microbatteries, the electrolyte thickness can be as low as one micron. In this configuration, ionic conductivities of $10^{-5}$ S/cm or higher would be enough for practical applications.

**Acknowledgments** The authors acknowledge the Spanish Science and Innovation Ministry under National Program ACI-PLAN E (project PLE2009-0074) for financial support.
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