

# Proton-Conducting Nanocomposites and Hybrid Polymers

Y.D. Premchand<sup>1</sup>, M.L. Di Vona<sup>2</sup>, and P. Knauth<sup>1</sup>

## 1 Introduction

This chapter is about proton-conducting nanocomposites and hybrid polymers. Before beginning to treat the different examples from literature, we must first define what we understand by the terms ‘nanocomposite’ and ‘hybrid polymer’. Their definitions are neither simple nor unanimous. A useful criteria for hybrid materials classification is based on their chemical nature: Class I where organic and inorganic components are dispersed and held together only by weak forces, such as Van der Waals interactions, and Class II where the organic and inorganic moieties are linked through strong bonds, such as covalent bonds [1]. In this context, Van der Waals interactions are considered to include permanent dipole interactions (Keesom forces, including also hydrogen bonds), interactions between permanent and induced dipoles (Debye forces) and interactions between induced dipoles (London forces).

Class I hybrid materials and composites differ from each other in respect to the dimension of dispersion. However this difference is minimal when we consider ‘nanocomposites’. A nanocomposite is a material with nanometric domains of two coexisting phases without mutual solubility. In the following we will use the two terms, Class I and nanocomposite, as interchangeable.

To clarify our definition, let us take the example of the most widely employed proton-conducting polymer today: Nafion. Nafion at high degree of humidification is itself a fascinating material, presenting hydrophilic and hydrophobic nanodomains and could, in a sense, already be considered as a nanocomposite. Figure 1 shows this microstructure schematically: one observes nanometric channels in the structure containing water molecules and dissociated sulfonic acid groups. Polymer domains are situated between these hydrophilic regions, where the hydrophobic perfluorated alkane chains are placed. No strong bonds exist between the two regions giving a relatively labile structure. The water containing domains are

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<sup>1</sup> Université de Provence, UMR 6121 CNRS, Centre St Jérôme, F-13397 Marseille Cedex 20, France

<sup>2</sup> Università di Roma Tor Vergata, Dip. Scienze e Tecnologie Chimiche, I-00133 Roma, Italy

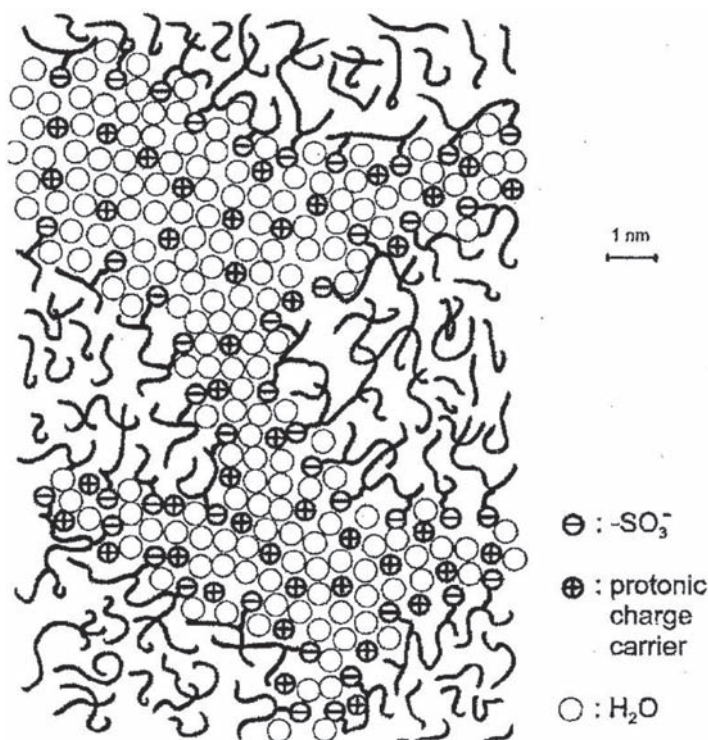


Fig. 1 Schematic representation of the microstructure of Nafion [3]

responsible for the relatively high conductivity of Nafion membranes under high humidification and at temperatures below 80°C. If one goes above this temperature, the conductivity drops sharply. There is still some debate about the origin of this effect: loss of water or change in polymer morphology [2, 3]. Whatever the origin, the technical need for permanent humidification and relatively low temperature of application for Nafion membranes is clearly established and limits the technological usefulness of these membranes, since fuel cell operation at higher temperature (typically 120°C) and under low relative humidity (such as 25% RH) is desirable.

An overview of recent literature in the domain of proton-conducting nanocomposite and hybrid materials shows mainly two categories of materials. The largest amount of literature has appeared on Nafion-related systems, initially with addition of binary oxides. The second largest group is hydrocarbon-based systems, generally aromatic but also some non-aromatic. This separation forms the basic structure of this chapter. It also includes an overview of synthesis and characterization procedures for these kinds of material as well as models used for microscopic description of transport phenomena. For further information on modeling of ionic conducting polymers, the reader is referred to the previous chapter of this book.

## 2 Synthesis

In the light of the general concepts described in the introduction, it may be presumed that the introduction of inorganic components within a polymer matrix intended for proton-conducting nanocomposite and hybrid membranes is accomplished through

1. Direct embedding
2. Covalent bonding directly to a polymeric matrix
3. Covalent bonding to supporting particles that can further bond covalently or embed physically into a polymer matrix.

### 2.1 Nanocomposites

Nafion is the widely preferred polymer component for the preparation of inorganic/organic nanocomposite membranes. Other polymers besides Nafion include aromatic hydrocarbon polymers, such as sulfonated polyetheretherketone (SPEEK), polybenzimidazole (PBI), non-aromatic hydrocarbon polymers like poly(ethylene oxide) (PEO) and many others. Solid inorganic components used are binary oxides such as  $\text{SiO}_2$ ,  $\text{TiO}_2$  and  $\text{ZrO}_2$ , or inorganic proton conductors like heteropolyacids. Recasting a bulk mixture of powdered or colloidal inorganic components with a polymer solution, and in-situ formation of inorganic components within a polymer membrane or in a polymer solution are the two preferred synthesis routes for achieving nanocomposite and hybrid proton-conducting polymer membranes using the above set of organic and inorganic components [4].

#### 2.1.1 Recasting

One of the simplest methods for the preparation of nanocomposite membranes is 'Solution-Casting' [5] using suitable organic solvents, preferably with high boiling point, followed by solvent elimination. It enables direct incorporation of nanosized inorganic materials into a polymer matrix and a number of nanocomposite membranes with Nafion and SPEEK as the backbone polymers have been prepared using this procedure [6]. In a typical experimental procedure, appropriate amount of inorganics are first mixed with the polymer solution under vigorous stirring. The membrane is then obtained by film casting and heated until all the solvent evaporates. For bulk mixing, the inorganic components should be prepared in the form of powders or dispersions. Silica, titania, zirconia, silicotungstic acid, phosphomolybdic acid, zirconium phosphate or phosphonate and silica supported inorganic acids are some of the inorganic components introduced by bulk mixing. The size and dispersion of the solid particles are of particular importance in this case to obtain uniform and nonporous membranes.

Major disadvantages of the recast procedure are possible in-homogeneities of the composite membrane and the formation of pores around the oxide particles, especially

for larger size additives. An appropriate method to avoid these difficulties is to use colloidal suspensions of inorganic additives; for example, a colloidal dispersion of hydrous oxides can be obtained by the hydrolysis of metal alkoxides in aqueous solution. According to this procedure, the aqueous dispersions of oxides are stratified over the polymer solution in the organic solvent. As water is evaporated, the oxide nano-particles transfer to the organic phase. This method differs from the conventional sol–gel technique in the sense that it does not involve condensation reactions that ultimately lead to the formation of an inorganic network within polymers. Instead the inorganic particles will remain as separate entities or as bulk in the resulting nanocomposite membranes. Parameters of interest are the type of inorganic filler, its surface area and size, and possible chemical surface treatment [7].

### 2.1.2 Sol–Gel

In situ generation of inorganic species within a polymer membrane by sol–gel process is a versatile strategy for the preparation of proton-conducting nanocomposite materials [8]. It enables the synthesis at nano- to sub-micrometer scales at low temperatures and the membranes obtained by this procedure are generally homogeneous. Ideally, the process begins with the infiltration of a molecular precursor solution into the polymer matrix at ambient temperatures. Hydrolysis of the infiltrated inorganic precursor then occurs due to the nucleophilic attack of the water present in the membrane on the inorganic atoms and the membranes are subsequently treated with necessary reactants to complete the condensation reactions. If the reaction is an acid-catalyzed hydrolysis, and the polymer happens to be ionomer like Nafion, the pendant  $\text{SO}_3^-\text{H}^+$  group will itself act as a catalyst, and the need for external reactants do not arise. The original morphology of unfilled polymer membranes will persist even after the invasion by sol–gel derived phase that is the membrane in itself will act as a template for the whole sol–gel process. Introduction of the ORMOSIL phase within monomer membranes are feasible through in-situ acid-catalyzed co-polymerization of tetraethylorthosilicate (TEOS) and organically modified silane monomers [9]. One major difficulty associated with the impregnation of polymer membranes with inorganic precursors is maintaining concentration gradient of precursor solutions; it virtually limits the incorporation of inorganic components into the polymer matrix to a certain level.

## 2.2 Hybrid Polymers

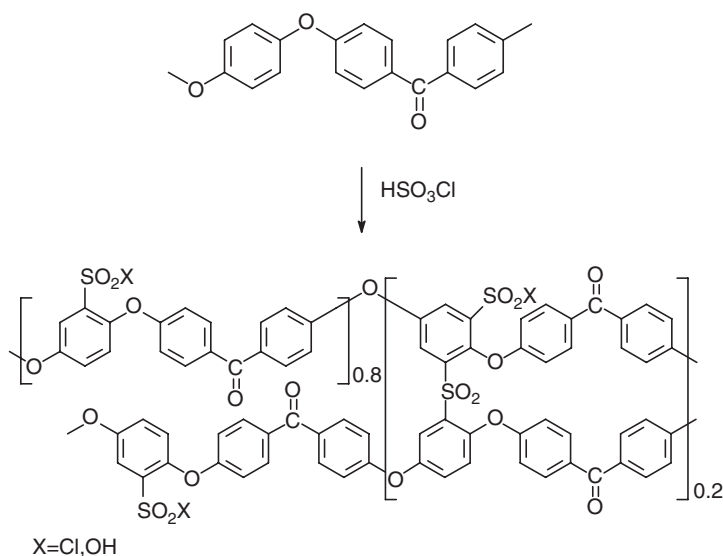
Synthesis of organic/inorganic hybrid polymers via the formation of covalent bonds between totally aromatic polymers and inorganic clusters is another effective approach in the development of proton-conducting membranes for fuel cell applications. This approach requires molecular precursors that contain a hydrolytically stable chemical bond between the element that will form the inorganic network during sol–gel processing and the organic moieties. Alternatively,

organic components can be chemically modified to covalently attach them to the inorganic network [10], e. g. silylation. The organic components after silylation are easily accessible to common hydrolysis and polycondensation reactions. This approach has been followed in the synthesis of an organic inorganic polymer known as Silylated-SPEEK (SiSPEEK) [11]; the primary aim is to synthesize a polymer containing both  $-\text{SO}_3\text{H}$  functions and silicon moieties. The order of the synthesis steps is

- Sulfonation
- Silylation
- Sol-gel process

A novel, efficient and experimentally simple method for the introduction of silicon functional groups into polymeric carbon frameworks is to combine in one macromolecule the features of a cross-linked polymer and the presence of covalent organic-inorganic, C-Si, bonds [12]. Cross-linking can be obtained during the sulfonation step by formation of  $\text{SO}_2$  bridges among the repeating unit of PEEK. The synthetic route takes the following steps:

- Direct sulfonation of PEEK with chlorosulfonic acid ( $\text{ClSO}_3\text{H}$ ); this will result in SOPEEK – sulfochlorinated PEEK (Scheme 1)
- Silylation – this will introduce covalently linked silicon moieties in SOPEEK
- Hydrolysis of sulfochlorinated PEEK in order to obtain the desired  $-\text{SO}_3\text{H}$  functions (SOSiPEEK, Scheme 2)



**Scheme 1** Synthesis of SOPEEK

Nanocomposites

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