Preface

Nanocomposite organic/inorganic materials are a fast expanding area of research, part of the growing field of nanotechnology. The term "nanocomposite" encompasses a wide range of materials mixed at the nanometer scale, combining the best properties of each of the components or giving novel and unique properties, unknown in the constituent materials, with great expectations in terms of advanced applications. Significant effort is focused on the ability to control the nanoscale structures via innovative synthetic approaches. The properties of nanocomposite materials depend not only on the properties of their individual components but also on their morphology and interfacial characteristics.

Experimental work has shown that virtually all types and classes of nanocomposite materials lead to new and improved properties, when compared to their macrocomposite counterparts: they tend to drastically improve the electrical conductivity, specifically the ionic conductivity, and thermal conductivity of the original material as well as the mechanical properties, e. g., strength, modulus, and dimensional stability. Other properties that might undergo substantial improvements include decreased permeability to gases, water and hydrocarbons, thermal stability and chemical resistance, surface appearance and optical clarity. Therefore, nanocomposites promise new applications in many fields such as mechanically reinforced lightweight components, nonlinear optics, battery cathodes and solid state ionics, nanowires, sensors, and many others. Much effort is going on to develop more efficient combinations of materials and to impart multifunctionalities to the nanocomposites.

In previous volumes of this book series, we have reported on the properties and applications of materials with characteristic dimensions in the nanometer scale. These reports were however mainly devoted to inorganic single phase materials. Recent years have seen a widespread development of polymer and hybrid organic/inorganic systems, which improve the variability of the materials properties and give supplementary freedom for realization of hitherto unattainable combination of properties.

In this book, we want to review some recent advances in composite materials with domain sizes in the nanometer range, emphasizing polymeric and hybrid systems, which have advanced spectacularly. Given the scientific background of the editors, most of the chapters are devoted to ionic conducting materials; some emphasis is put

on materials potentially useful in fuel cells and lithium ion batteries, including polymer nanocomposites with clay and other plate-shaped particles as second phase.

The first chapter sets the general frame for the investigation of composite polymeric electrolytes. This chapter is especially devoted to lithium ion conducting solid electrolytes for lithium batteries, with polyethylene-oxide-based systems playing a central role. But theoretical models of electrical properties and ionic conduction in polymers are discussed in depth and various scenarios for conductivity enhancement effects are outlined, including space charge and Lewis acid–base model. These concepts are useful for any kind of polymer electrolyte.

On the basis of these foundations, the second chapter addresses proton-conducting nanocomposite and hybrid polymers used as electrolyte membranes in proton exchange membrane fuel cells. An overview of recent literature in this domain is given: besides traditional Nafion, polyaromatic polymers play an increasingly prominent role in the field. Models used for description of the structure, stability, and transport properties of proton-conducting polymer nanocomposites are also outlined.

Thin-film metal–polymer and metal oxide–polymer nanocomposites are the subject of the third chapter: they are prepared by vacuum phase codeposition of metal and polymer, using *para*-xylylene as monomeric unit, and subsequent oxidation. The vacuum deposition technique might be applicable for related materials; relevant properties are reported, including adhesion and electrical resistance. These composite films can be used in different domains, such as microelectronics and Li-ion battery electrodes.

The mechanical properties of polymer nanocomposites with rod- and plate-shaped nanoparticles are described in the fourth chapter. The anisotropy plays a central role for improvement of mechanical properties. The materials preparation and analysis are described, including specific techniques such as dynamical mechanical analysis or moisture diffusion measurements. Modeling of mechanical properties is also treated.

The fifth chapter presents a small outlook on the vast and rapidly growing domain of computer simulation of materials. Relevant methods, quantum mechanics, Monte-Carlo simulations, and molecular dynamics, are briefly introduced. Cationic and anionic clay–polymer nanocomposite materials attract great attention as they offer enhanced mechanical, thermal, and catalytic properties as compared to conventional materials. They are also studied as possible solid electrolytes for batteries and fuel cells. Simulations of structure and dynamics of clay–polymer nanocomposites are presented, including Li-ion conduction and catalytic properties.

The last three chapters present specific structural spectroscopies, which were extensively applied to the domain of nanocomposites and have brought significant advances in the understanding of these systems. In all these chapters, the specific techniques are first introduced briefly; the advantages of the technique, the information available and significant examples are then presented again with particular emphasis on ionic conducting systems.

X-ray absorption spectroscopy studies of nanocomposites can provide information on the local environment and oxidation state of an atom, the technique being element specific, usable at low concentrations of target atom, and not restricted to crystalline

systems. The case of nanoparticles dispersed in an inorganic matrix or a polymer matrix and nanoparticle/nanoparticle composites are examined.

Nuclear magnetic resonance (NMR) is a valuable tool for studying ionic diffusion in materials and dynamical aspects of nanocrystalline ceramics and composites. This technique is particularly useful to differentiate alternative transport mechanisms, like fast interfacial vs. slower bulk diffusion, via the NMR relaxation rates. In this chapter, F- and Li-ion conducting nanostructured materials are particularly discussed.

Mössbauer spectroscopy is another nonconventional technique, which has proven to be of great relevance for the investigation of electrode materials for Li-ion batteries. The mechanism of lithium insertion/deinsertion during cycling of the battery can be followed in situ during the cycles. The local structure and oxidation state of ions can also be deduced from Mössbauer spectra.

The sum of these eight contributions should give a broad range of readers from solid state chemistry, solid state physics, and materials science an outlook on the status of research and development in the domain of nanostructured composites. The emphasis on ionic conducting materials makes this book particularly attractive for the solid state ionics and electrochemistry community. Given the particular impact of these materials for environmental and energy applications, readers interested in these topics should also profit from this book.

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Proton-Conducting Nanocomposites and Hybrid Polymers

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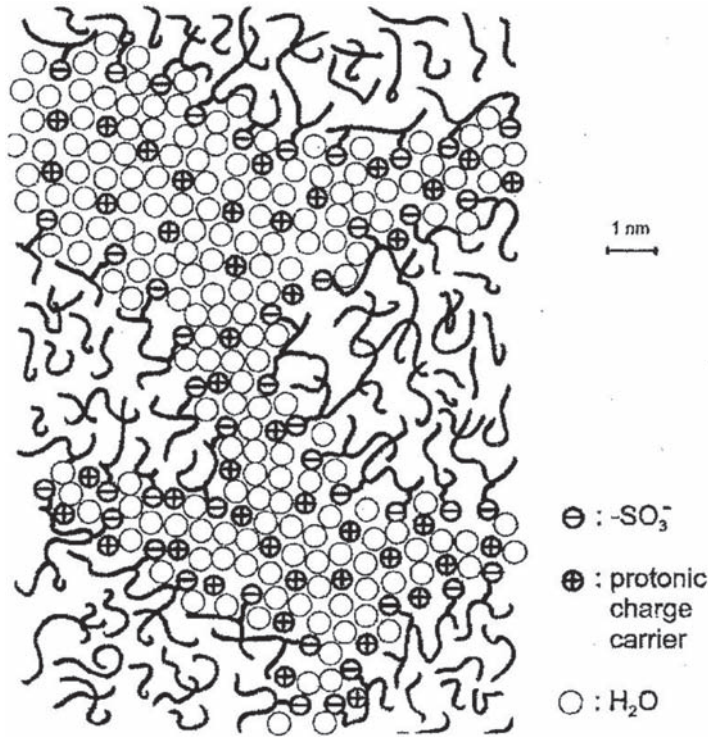
Fig. 1 Schematic representation of the microstructure of Nafion [3]

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 SiO_2, TiO_2 and 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 $SO_3^-H^+$ 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.
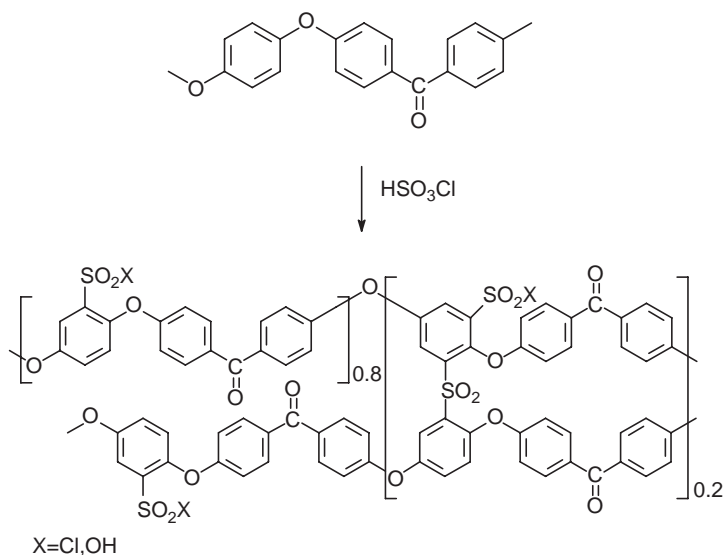
2.2   Hybrid Polymers

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 $-SO_3H$ 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 SO_2 bridges among the repeating unit of PEEK. The synthetic route takes the following steps:

- Direct sulfonation of PEEK with chlorosulfonic acid ($ClSO_3H$); 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 $-SO_3H$ functions (SOSiPEEK, Scheme 2)

Scheme 1 Synthesis of SOPEEK