Chapter 35

Inorganic/organic composite membranes

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1 INTRODUCTION

Inorganic/organic composite membranes are characterized by the incorporation of a variable amount of an inorganic solid into an organic polymer that serves as the matrix component. The inorganic solid might, but not necessarily, present intrinsic proton-conduction properties, in which case the solid is generally acidic. In other cases, for example, with silica, titania or zirconia, the inorganic component is not inherently proton-conducting. Whereas the term "composite" is used here to describe all membranes associating an inorganic and an organic component, the designation "hybrid" is reserved for membranes characterized by nanoscale mixing, generated frequently by in situ formation of the inorganic component in the polymer membrane or solution, and driven by the formation either of strong (covalent, ionic) or weak or physical interactions, hydrogen bonding.[1–5] Hybrid membranes embrace all stages of interconnectivity, extending from discrete nanometric inorganic particles embedded in the polymer matrix to co-continuous and interpenetrating inorganic and organic networks.

There are several reasons justifying the increased effort seen in recent years in developing composite inorganic/organic proton electrolyte membranes for fuel cell applications. First, a homogeneously dispersed hydrophilic inorganic solid assists in improving membrane water management, both by improving self-humidification of the membrane at the anode side by enhancing the back-diffusion of water produced at the cathode[6] and/or by reducing electroosmotic drag. These are key factors for fuel cell functioning with no or low humidification of reactant gases. Decreased electroosmotic drag reduces drying-out of the membrane at the anode side, and could also participate in suppression of fuel crossover in direct methanol fuel cells (DMFCs). The presence of finely divided inorganic particles also contributes to inhibiting direct permeation of reaction gases by increasing transport pathway tortuosity, by the possible interaction of diffusing species with the surface of the inorganic phase, and by a molecular size exclusion effect in a porous arrangement.[7]

Considerable efforts have been made in recent years to develop alternative, nonperfluorosulfonated low-cost proton-exchange membranes, based on sulfonated polyaromatic and polyheterocyclic polymers, as well as attempts to increase the operation temperature to above 90 °C.[8–13] In this context, the use of less sulfonated polymers is especially advantageous, since their degradation mechanism seems to be associated with a high degree of sulfonation. This aspect is also important with regard to the high swelling that is generally associated with such highly sulfonated hydrocarbon-based polymers. Inclusion of a proton-conducting inorganic material allows the use of a less conducting organic matrix which, since it is less highly sulfonated, is less susceptible to swelling. Beyond the reinforcement or enhancement of proton-conduction properties compared with the organic polymer-only system, the presence of inorganic particles may also

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impede the diffusion of radical species that could contribute to oxidative degradation in nonfluorinated membranes.[14] Improvements in mechanical properties are also to be expected when a specific interaction is favored between the inorganic and organic components.

It is desirable that the inorganic solid be highly and homogeneously dispersed so as to increase the interface between inorganic and organic components and so increase the possibility of materials synergism. In general, the simple dispersion of an inorganic solid in a polymer solution is inclined to lead to nonhomogeneous composite membranes with rather large agglomerations of inorganic material, so restricting the lower limit of membrane thickness. In addition, since the proton-conduction pathway for many inorganic materials is across the surface rather than through the bulk, proton-conductivity tends to increase as the particle size is reduced. This is most readily achievable using in situ methods of inorganic particle formation making using of sol/gel or ion-exchange techniques which allow the growth of inorganic material at low temperatures in the presence of water, without recourse to high-temperature treatment. In situ formation of the inorganic component also opens up the possibility of modifying the polymer microstructure and influencing hydrophobic/hydrophilic characteristics, conductivity and swelling. In particular, polymer solution generation of an inorganic network in sufficient proportion relative to the organic "matrix" extends the boundary from polymer-confined inorganic component membranes to those in which inorganic network confines an ionomer.

In addition to comprehensive electrochemical characterization of the composite membranes, detailed investigation of the membrane microstructure and inorganic particle size, and also the nature of the interaction between inorganic and organic components, are all required in order to relate these effectively to the observed physical properties.

2 PREPARATION OF COMPOSITE MEMBRANES BY BULK MIXING OF INORGANIC AND ORGANIC COMPONENTS

This method makes use of the mixing of pre-formed inorganic proton-conductors or ceramic oxides with a polymer solution, followed by film casting and drying. Both proton-conducting ionomers and nonfunctionalized polymers have been used as organic matrices. In the former case, the studies performed have the principal objective of improving water management and reducing gas crossover, since the conductivity is generally adequately high, and thus the addition both of proton-conducting materials and nonconducting silica or titania (generally ca. 5 wt%) is encountered. On the other hand, addition of an inorganic component to a nonsulfonated polymer should also provide proton-conduction properties, and the relatively high proportions required (e.g., 30–70 wt%) can be detrimental to the mechanical properties of the composite membrane.

2.1 Dispersion of powdered form inorganic solids in a polymer solution

Recently, composite membranes have been described based on diverse nonsulfonated and sulfonated polymer systems, including polybenzimidazole (PBI)[15] and styrene/ethene/butene/styrene copolymer[16] incorporating tungstophosphoric acid, poly(vinylidene fluoride) (PVDF) with silica and alumina,[17] sulfonated poly(ether etherketone) (sPEEK) with zirconium sulfophenylphosphonate,[18] tungstophosphoric, tungstomolybdic acids[19] and boron phosphate,[20] sulfonated polystyrene incorporating antimonic acid,[21] sulfonated polysulfone incorporating phosphatoantimonic acid,[22] and Nafion® incorporating silica,[23, 24] titania[6] or tungstosilicic acid,[25] for example, in weight proportion up to 70%.

The methodology for the preparation of the membranes remains a straightforward mixing of the powder-form inorganic component, which could lead to heterogeneity both of the size of the particle agglomerates and of their dispersion through the organic matrix. This aspect is often not studied although, for example, in two types of composite membrane based on sPEEK, scanning electron microscopy showed well dispersed heteropolyacids[19] and boron phosphate[20] of particle size 0.05–0.15 and 0.1–0.3 μm, respectively. The second of these studies also revealed a largely increased membrane porosity (pore diameters 3–10 μm) accompanying composite membrane formation.

A number of the composite membranes have higher proton conductivity than the polymer-only system measured under the same conditions, and some potentially beneficial associated procedures have been developed. For example, in a study leading to electrically insulating composite membranes of PVDF and silica, acid doping led to membranes of conductivity $>0.2\,\mathrm{S\,cm^{-1}}$ (25 °C),[17] which have been tested in DMFCs.[26] Significant improvements in conductivity are also seen in membranes of nonsulfonated PBI loaded with 60 wt% of 30 wt% silica-supported tungstophosphoric acid, which reaches $1.4 \times 10^{-3}\,\mathrm{S\,cm^{-1}}$ at 150 °C (100% relative humidity (RH)).[15] This is still a factor ca. 100 lower than the conductivity of Nafion® measured at 100% RH and 100 °C,[27] but is nevertheless a large increase on the conductivity of

$<10^{-6}$ S cm^{-1} given by the corresponding noncomposite PBI membrane.[11]

Amongst composite membranes reported based on ionomers, the addition of 3% SiO_2 to Nafion® solution has been reported to improve water retention properties, by maintaining the water balance of the membranes produced by both the back-diffusion of water from the cathode where it was produced, and reducing the water migration under the influence of the generated current density by adsorption on the SiO_2 surface. The water content was shown to increase from 17% for an unmodified Nafion® membrane to 43% for a membrane containing 3 wt% of silica (weight gain measured by humidification at 60 °C of membranes previously dried at 80 °C), and was such that humidification of reactant gases in an H_2/O_2 fuel cell operating at 80 °C could be eliminated (Figure 1).[23] Building on this approach, subsequent thermal treatment (130–150 °C) of Nafion®-SiO_2 membranes was reported to avoid adventitious amorphous to crystalline phase transition on fuel cell operation above 130 °C,[24] so extending the temperature at which Nafion® membranes may be operated. In addition, the diffusion coefficient of methanol across Nafion®/SiO_2 under working DMFC conditions was a factor of 10^3 lower than that in unmodified Nafion® whereas its proton conductivity was similar to that of unmodified Nafion®. Reduction in methanol crossover might be accompanied by a lowering of the proton conductivity; that this is not the case here implies real progress. Using Nafion®-SiO_2 membranes, peak power densities of 150 and 240 mW cm^{-2} and open-circuit voltages of 0.82 and 0.95 V were recorded with air and oxygen, respectively, at a cell temperature of 145 °C, and feeding reactant methanol and oxidant humidified at 85 °C (Figure 2).[24] In the Nafion®/tungstosilicic acid system, water uptake was observed to be twice that of Nafion® 117 (same membrane thickness). Figure 3 compares the cell performance of this and of a three-component Nafion®/tungstosilicic acid/thiophene membrane.[25] There is a significant change in the electrode kinetics in the composite membranes and, for example, the current density at 900 mV is increased, owing to improved interaction between the membrane and the electrocatalyst in the membrane/electrode assembly.

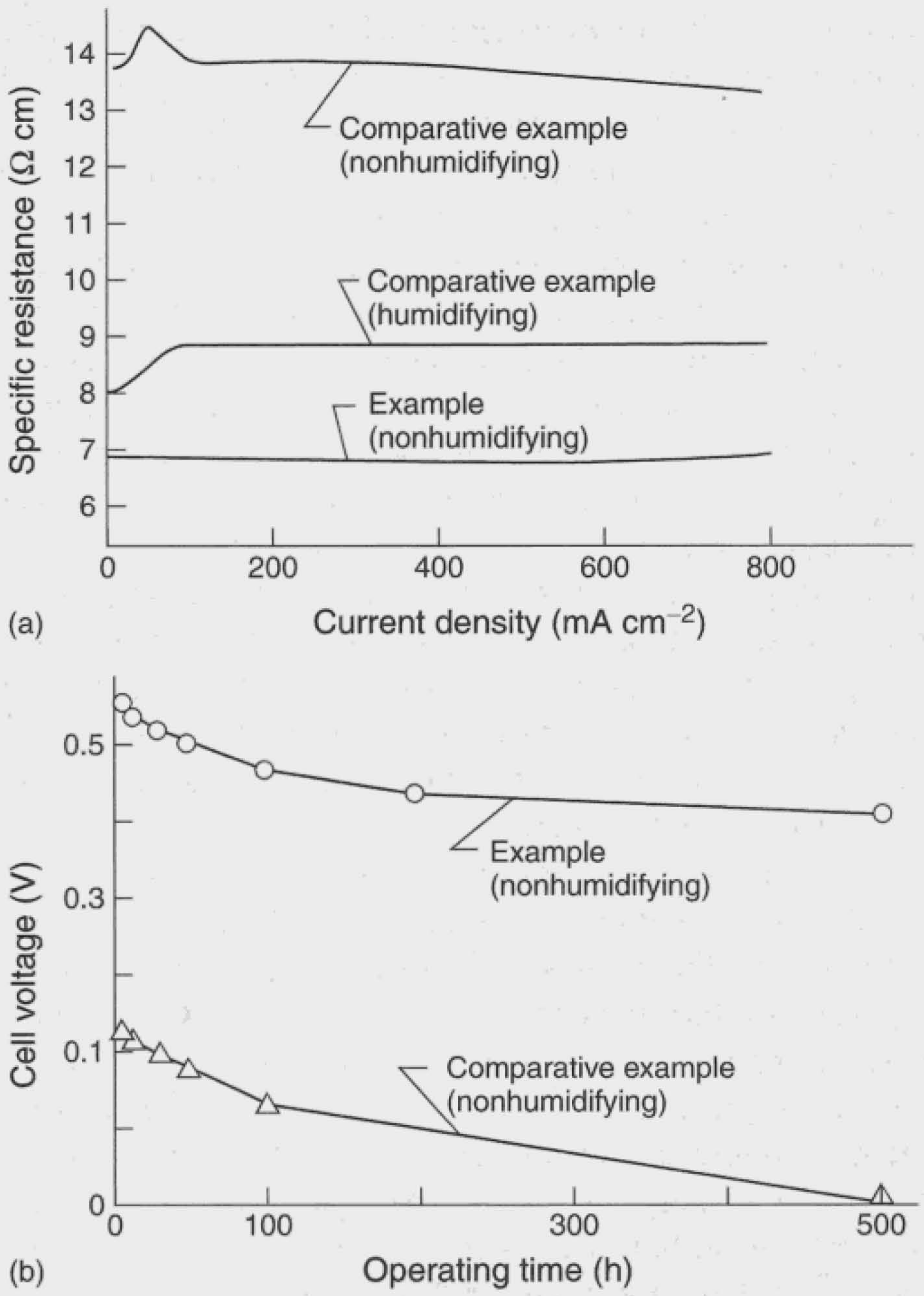

Figure 1. (a) Comparison of specific resistance of Nafion®/SiO_2 fuel cell (nonhumidifying conditions) with Nafion® fuel cell (humidifying and nonhumidifying conditions). Membrane prepared by dispersion of 5 wt% silica of particle size 0.007 μm in Nafion® (5 wt%) solution. Cell temperature, 80 °C, humidifying temperature, 80 °C; cell pressure, atmospheric; reaction gases, H_2, O_2. (b) Cell lifetime expressed by cell voltage of Nafion®/SiO_2 fuel cell and Nafion® fuel cell (nonhumidifying conditions). Current density, 350 mA cm^{-2}. Other conditions as in (a).[23]

Composite organic/inorganic membranes based on nonperfluorinated polymers can show similar improvements in water retention and conduction properties. For example, inclusion by bulk mixing of precipitated silica (10 wt%) in sulfonated PEEK gave membranes of higher conductivity at 100 °C and in the relative humidity range 75–100% than that of sPEEK only, reaching 9×10^{-2} S cm^{-1}.[18] Similarly, both the water uptake and the conductivity of sPEEK-based heteropolyacid composites are higher than those of the pristine sPEEK used.[19, 20] Heteropolyacid hydrates are attractive inorganic components from the point of view of their conductivity, but are water soluble, and their possible progressive elution in a working fuel cell must be evaluated, in particular in a polymer environment where there exists no particular stabilizing interaction between the organic and inorganic components. Indeed, only weak hydrogen bonding interactions exist in any of the above compositions involving sulfonated polymer/acidic proton-conducting or ceramic components.

2.2 Dispersion of colloidal inorganic oxides or proton conductors in a polymer solution

A number of layer-structured solids can be broken down into building blocks of reduced dimensions by delamination

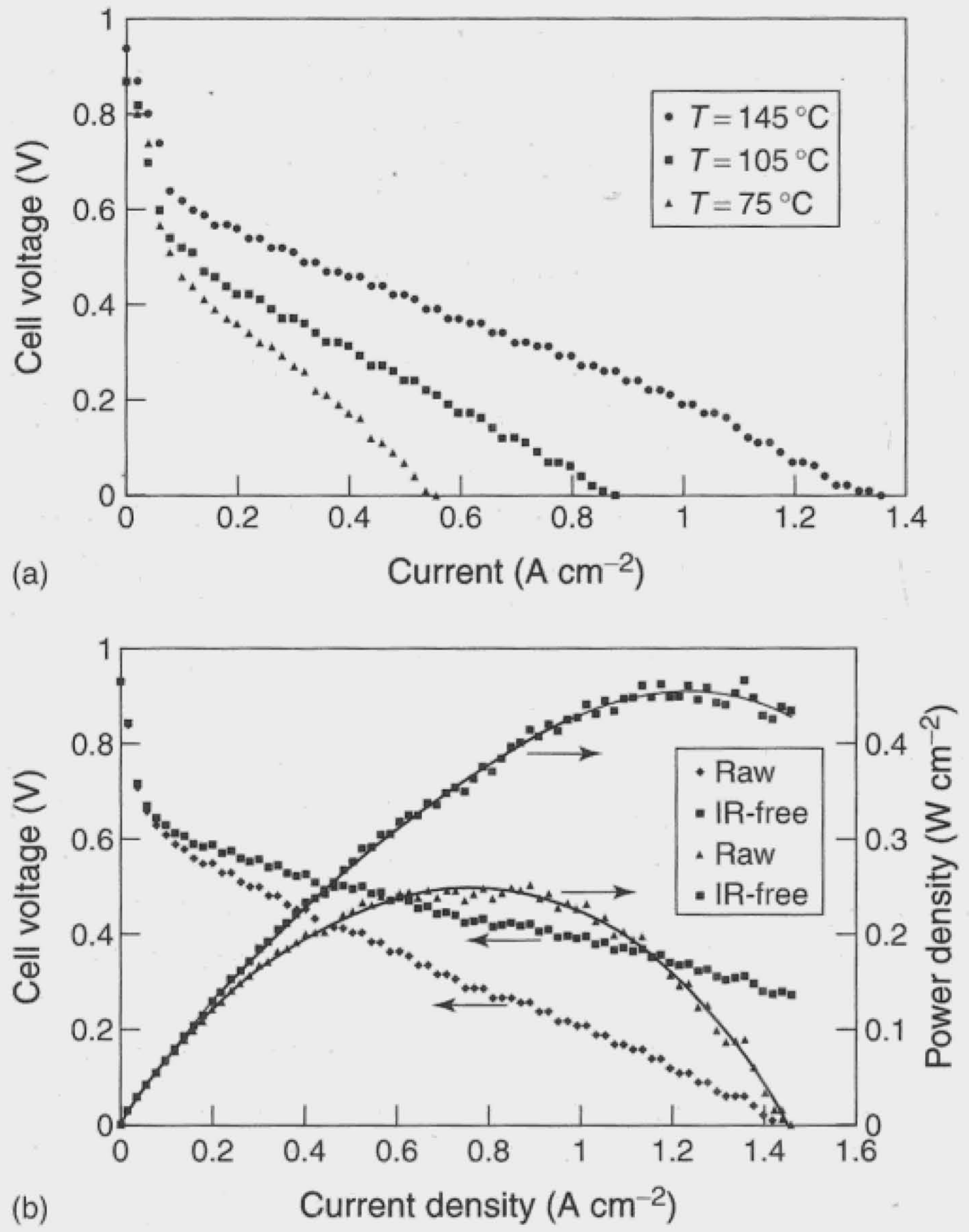

Figure 2. DMFC operation (air feed) with Nafion®/SiO_2 membrane.[24] Membrane prepared by dispersion of 3 wt% silica (Aerosil 200) in Nafion® (5 wt%) solution. (a) Influence of the operating temperature on the polarization behavior; (b) raw and IR-free polarization and power density curves at 145 °C (2 M CH_3OH, 4.5 atm CH_3OH; 5.5 atm air). Cell size, 5 cm^2. (Reproduced from Antonucci *et al.*[24] with permission from Elsevier Science.)

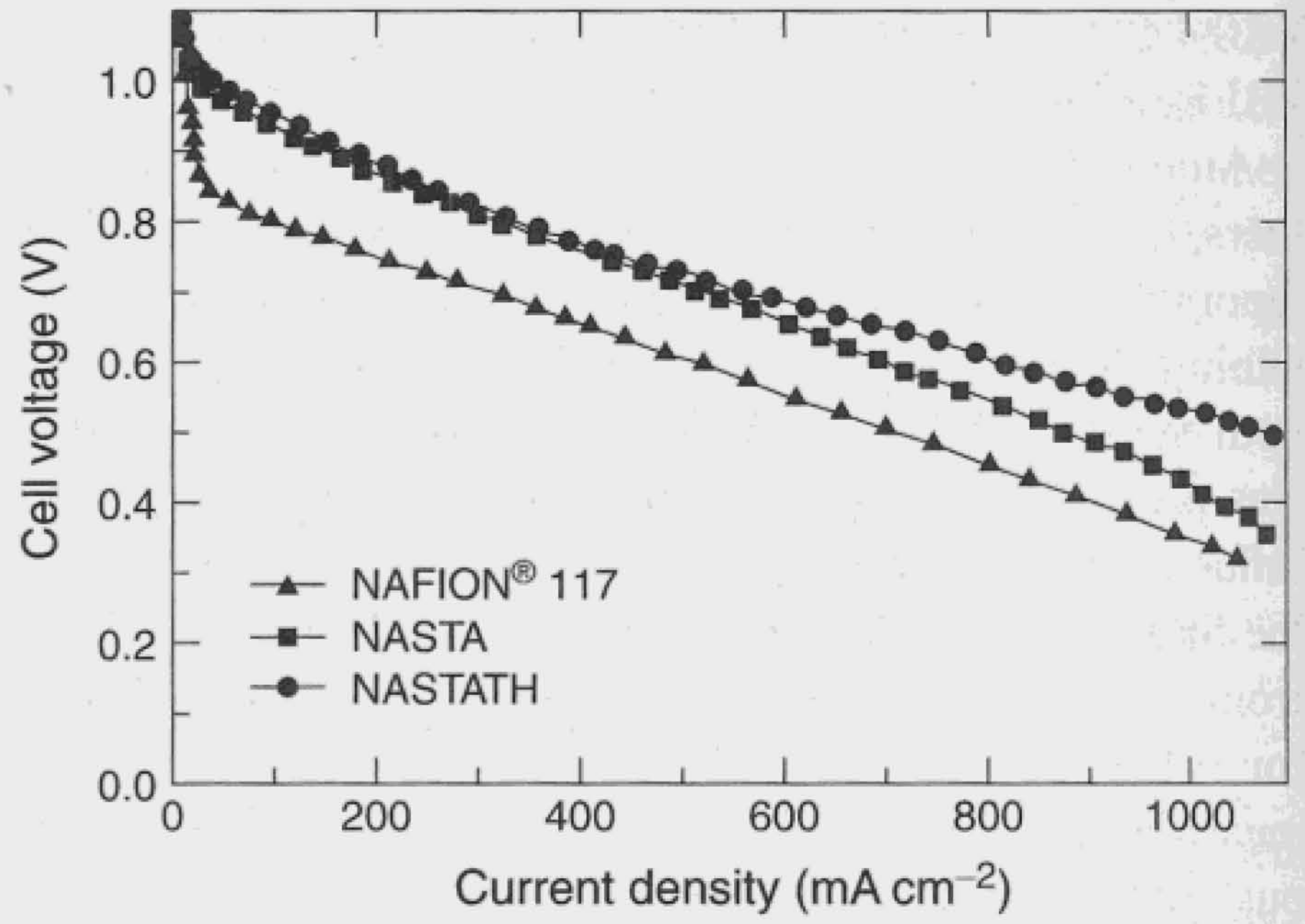

Figure 3. Potential/current polarization curves at 80 °C of H_2/O_2 fuel cells using Nafion® 117 (thickness 180 μm) and water uptake of 30%), composite Nafion®/silicotungstic acid membrane (NASTA, thickness 175 μm and water uptake of 60%) and composite Nafion®/silicotungstic acid/thiophene membrane (NASTATH, thickness 170 μm, water uptake 60%). Anode and cathode based on 0.35 mg Pt cm^{-2} from 20% Pt/C catalyst. H_2/O_2 pressure ratio = 3/5 atm; gas flow rates, $O_2 = 0.81\ \mathrm{min}^{-1}$; $H_2 = 1.21\ \mathrm{min}^{-1}$. (Reproduced from Tazi and Savadogo[25] with permission from Elsevier Science.)

(exfoliation) in a solvent of appropriate dielectric constant. This property is best known for clays, but under particular conditions proton-conducting zirconium phosphates and zirconium phosphate sulfophenylphosphonate will also form colloidal suspensions in which only a small number of layers are associated, and which can be used in alliance with a sulfonated polymer solution to produce hybrid membranes.[18, 28] This method represents a powerful means for high intimacy of contact between components, as long as flocculation on transfer of the inorganic phase to the polymer solution can be prevented and the sub-micrometric inorganic platelets of the exfoliated phase maintained. Composite Nafion®/titanium phosphate/sulfophenylphosphonate membranes prepared by bulk mixing have been reported to give conductivities lower than either of the components separately.[29] However, for hybrid membranes based on sPEEK in which 40 wt% of exfoliated $Zr(HPO_4)_{2-x}(O_3PC_6H_4SO_3H)_x$ ($x = 1, 1.5$) was dispersed, conductivities lie between those of the two components, being $>10^{-2}$ S cm^{-1} at 100 °C and 90% RH and 0.040 S cm^{-1} at 150 °C and 100% RH.[18] These membranes show stable H_2/O_2 fuel cell performance up to 95 °C. Combining the organic and inorganic phases without drastic reprecipitation of the latter can be achieved when the polymer solvent and the dispersion medium for the inorganic phase are similar or identical. In an alternative approach, the transfer of nanometric-sized silica particles from commercial aqueous silica suspensions to higher boiling point solvents for sPEEK such as *N*-methylpyrrolidone (NMP), dimethylacetamide (DMAc) or dimethylsulfoxide (DMSO) has been proposed.[30] Transmission electron microscopic analysis of the hybrid membranes prepared showed regions of agglomerated silica, which could be completely avoided by partial surface modification with amine functions during the solvent transfer reaction. Thus, even when the colloidal suspension is composed of well-defined primary particles of nanometer dimensions, amassing will tend to occur on transfer into the polymer medium in the absence of a built-in interparticle repulsion (see Section 3.2).

3 IN SITU FORMATION OF INORGANIC COMPONENT

In situ preparation within the organic phase by precipitation, or hydrolysis and condensation of organometallic precursors in an acid- or base-catalyzed sol/gel process, favor intimate combination of the polymer with inorganic precursor monomers and represent an effective alternative to the direct incorporation of a powder-form inorganic material. Two means of polymer in situ chemistry have been developed, and the preferred use of one or the other is a function of the nature of the precursor and the properties of the polymer. In the first route, the inorganic sub-lattice is formed locally in a pre-formed sulfonated polymer membrane, and it requires the incorporation by ion exchange or impregnation/permeation of an appropriate precursor, followed by hydrolysis or precipitation, aging and drying steps. In the second route, an inorganic alkoxide monomer is added to a solution of the polymer, and hydrolysis and condensation are induced by the addition of water and catalyst. The ultimate morphology of the inorganic phase formed will differ depending on which of the above schemes is adopted, since on the one hand use is made of a pre-existing phase separation, when nascent inorganic particles develop largely preferentially in the hydrophilic regions of the polymer membrane, whereas on the other hand inorganic particles precipitated in the polymer solution medium will evolve and ripen on solvent removal and film formation, and could influence the polymer microstructure.

3.1 In situ local growth of inorganic materials in a pre-formed polymer membrane

The preparation of hybrid membranes by intramembrane growth within a proton exchange membrane was first described by Mauritz and co-workers.[7, 31, 32] In a significant step forward, this group made use of the quasi-ordered nanophase-separated morphology of Nafion® to act as a polymerization template to direct the growth of the inorganic phase within the nanoreactors of the ionic clusters. Furthermore, tailoring of compositional gradients was achieved at the nanoscale, by shell-like construction of ceramic particles and of organically coated nanoparticles, and by the creation of compositional profiles across the membrane thickness by permeating the precursor silicon, zirconium, titanium or aluminum alkoxides from one side only of the Nafion® membrane (Figure 4). Small-angle X-ray scattering (SAXS) analysis of the Nafion®/silica membranes prepared by permeation of tetraethoxysilane (TEOS) show a scattering maximum ("ionomer peak") at $q_{\max} \sim 2.0\,\mathrm{nm}^{-1}$, which defines a correlation distance associated with intercluster spacings of the order of 5 nm.[33] These results establish that the original phase-separated morphology of Nafion® persists into the hybrid system. Such nanophase separation exists also when incorporated silica is post-reacted with a monofunctional ethoxytrimethylsilane, but post-reaction with difunctional diethoxydimethylsilane generates a co-continuous phase, no longer characterized by an ionomer peak in SAXS owing to lowered electron density contrast (Figure 5). Fourier transform infrared (FTIR) spectroscopy of difference spectra (spectrum of a pristine membrane subtracted from those of hybrid membranes) depicted an inorganic network that grows to be increasingly less branched with increasing silicon oxide content, with fewer cyclic molecular sub-structures, more linearity and inter-linking between adjacent clusters.[31] Gas permeation

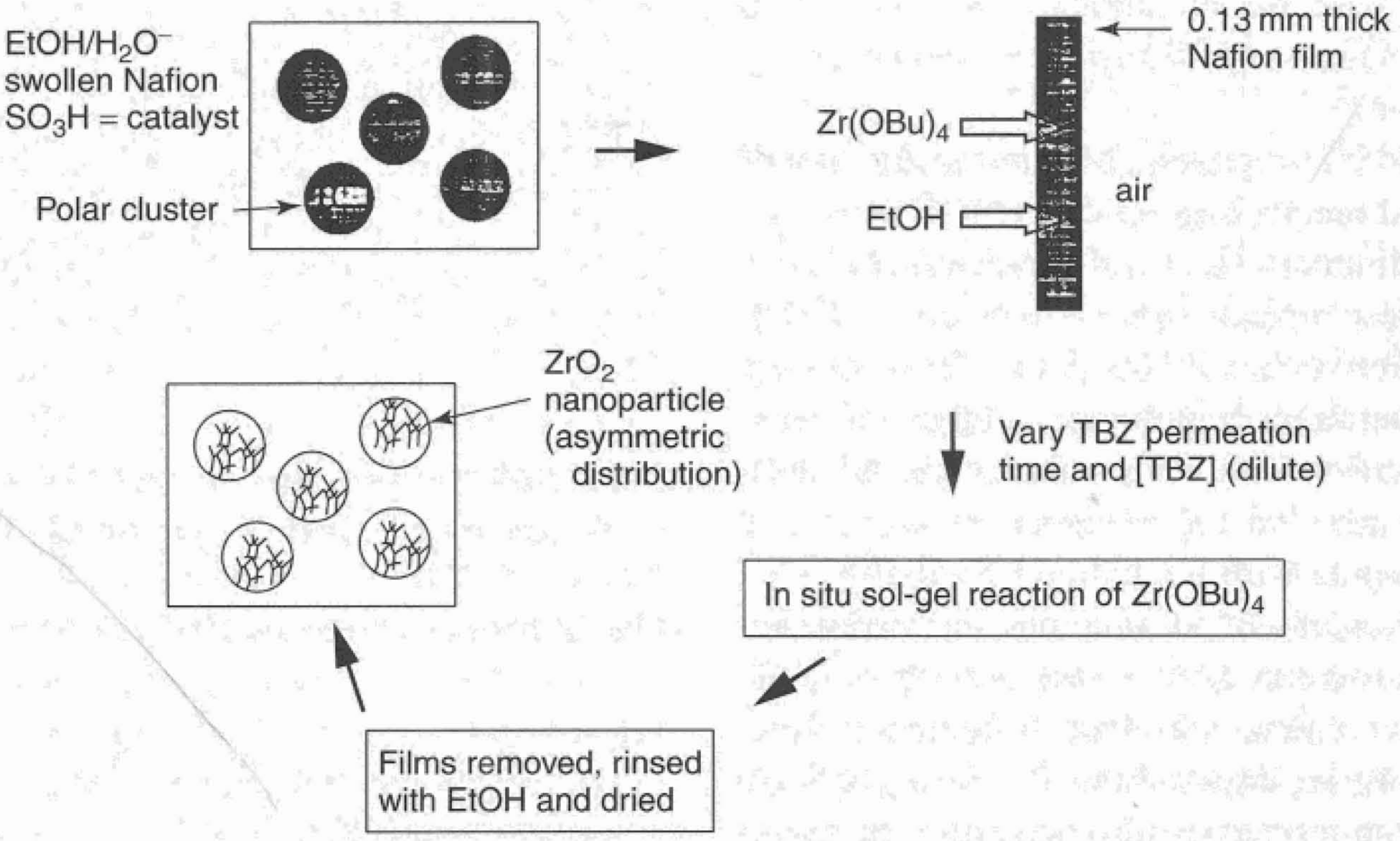

Figure 4. Schematic depiction of hybrid, Nafion®/ZrO_2 membrane formulation via in situ sol/gel reaction in a pre-formed membrane and initiated in sulfonic acid cluster regions. Concentration profile of ZrO_2 created by one-sided permeation of tetrabutylzirconate (TBZ).[7, 32] (Reproduced from Mauritz[7] with permission from Elsevier Science.)

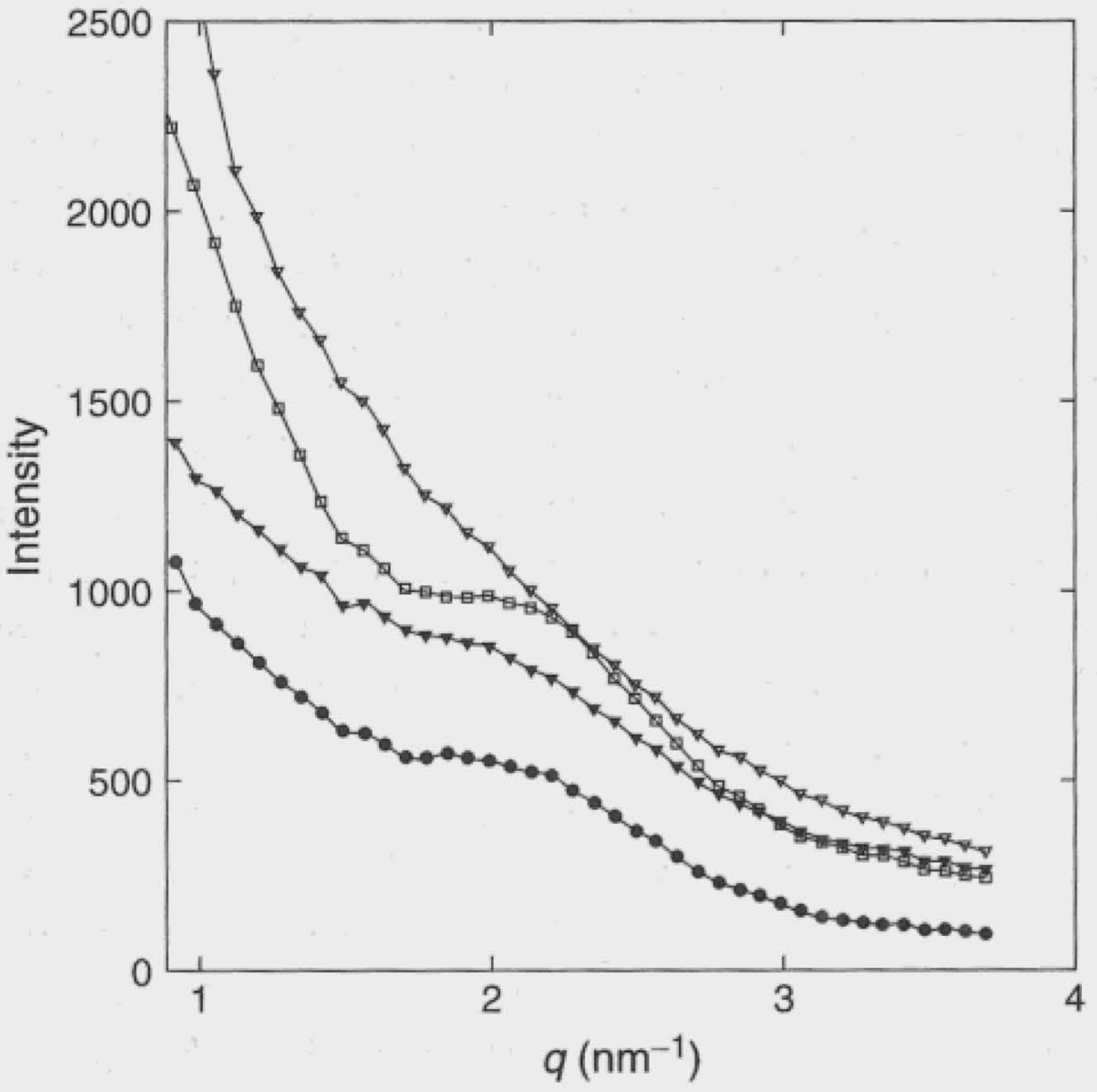

Figure 5. SAXS intensity profiles for unfilled, dry Nafion®/H (□), Nafion®/silicon dioxide (●), Nafion®/silicon dioxide post-reacted with diethoxydimethylsilane (▽) and Nafion®/silicon dioxide post-reacted with ethoxytrimethylsilane (▼). (Reproduced from Deng *et al.*[33] with permission from John Wiley & Sons, Inc.)

of helium and carbon dioxide through these asymmetric Nafion®/silica and -zirconia hybrid membranes, respectively, provides opposing trends of the evolution of the gas permeability with upstream pressure. The results indicate a dual mode of sorption in the Nafion®/silica membrane: dissolution in the polymer matrix and adsorption on to porous silica and interaction of gas molecules with SiOH groups, whereas for Nafion®/zirconia membranes, the dissolution term predominates, suggesting diffusion accompanied by complex plasticization.[7, 31, 32]

Despite the detailed interrogation of the microstructure of hybrid Nafion®-based membranes on different dimensional scales, only very preliminary electrical characterization has been performed. These results suggest that at 80 °C the conductivity of Nafion®/silica (0.099 S cm^{-1}) is slightly higher than that measured for Nafion® alone under the same conditions of equilibration with water vapor, close to 100% RH (0.074 S cm^{-1}), and that the methanol crossover rate was unchanged compared with unmodified Nafion®.[34]

The hydrophilic domains of an ionomer membrane are thus favored local structural regions for growth of inorganic particles. In a scheme different from that above, further advantage may be drawn from the ionic sites by using the ion-exchange properties to introduce a metal ion that can act as a center for particle growth either in a subsequent sol/gel process, or by conditioning the metal ion-exchanged membrane in an appropriate solution of a counter-ion. This method has been used for the preparation of hybrid membranes based on sPEEK[11, 18, 35] and Nafion®[36, 37] incorporating the layered metal(IV) hydrogenphosphates $M(IV)(HPO_4)_2 \cdot nH_2O$, with M = Zr, Ti, Sn. Process variables include the concentrations of metal salts and phosphoric acid used for the ion-exchange reaction and for precipitation of the corresponding layered phosphate, respectively, as well as the temperature and the duration of the reactions. These parameters allow both modulation of the use of the ion-exchange capacity (IEC) of the ionomer membrane (i.e., the ultimate inorganic component content), and a certain degree of control over the extent of crystallinity of the inorganic phase formed. Transmission electron micrographs of sPEEK membranes containing zirconium phosphate (ZrP) and tin phosphate (SnP) showed the presence in the former of particles of elongated, rectangular morphology of dimensions ca. 15–30 nm in length and 5–10 nm in width.[11] The particle size was smaller in sPEEK/SnP membranes, ca. 5 nm. This marked difference in particle size under similar conditions of preparation is also found in the corresponding bulk phases. The composition of these hybrid membranes permits the use of probe techniques, and X-ray absorption spectroscopy (extended X-ray absorption fine structure and X-ray absorption near-edge structure) at the metal edges was used to follow the precipitation reaction and compare the local structure with that of known bulk materials prepared under various conditions.[35] The conductivity of sPEEK/metal phosphate hybrids containing 25 wt% of inorganic component is only weakly temperature dependent, being up to 8×10^{-2} S cm^{-1} at 100 °C/100% RH.[18] Proof in favor of the advantage of hybrid inorganic/organic membranes compared with the corresponding polymer-only counterpart is provided by Figure 6, which shows that for all values of relative humidity at 100 °C, the conductivity of sPEEK/zirconium phosphate membrane is higher than that of unmodified sPEEK. Such membranes have been operated at up to 130 °C in a hydrogen/air fuel cell, and have provided 700 mV at 0.5 A cm^{-2} on oxygen at 90 °C under a pressure of 3.6 bar.[18]

3.2 Polymer in situ sol/gel reactions of inorganic alkoxides and alkyl- or arylalkoxysilanes

One of the constraints on the use of a pre-formed membrane as template for inorganic particle growth is the content of the inorganic material that can be incorporated. For ion exchange/precipitation, the limit is given by the IEC of the membrane (e.g., 30 wt% ZrP can be grown inside sPEEK of IEC 1.3 meq g^{-1}) and for permeation the limit is around 40 wt%. This restriction is lifted when the inorganic component is grown in a polymer solution, and in principle

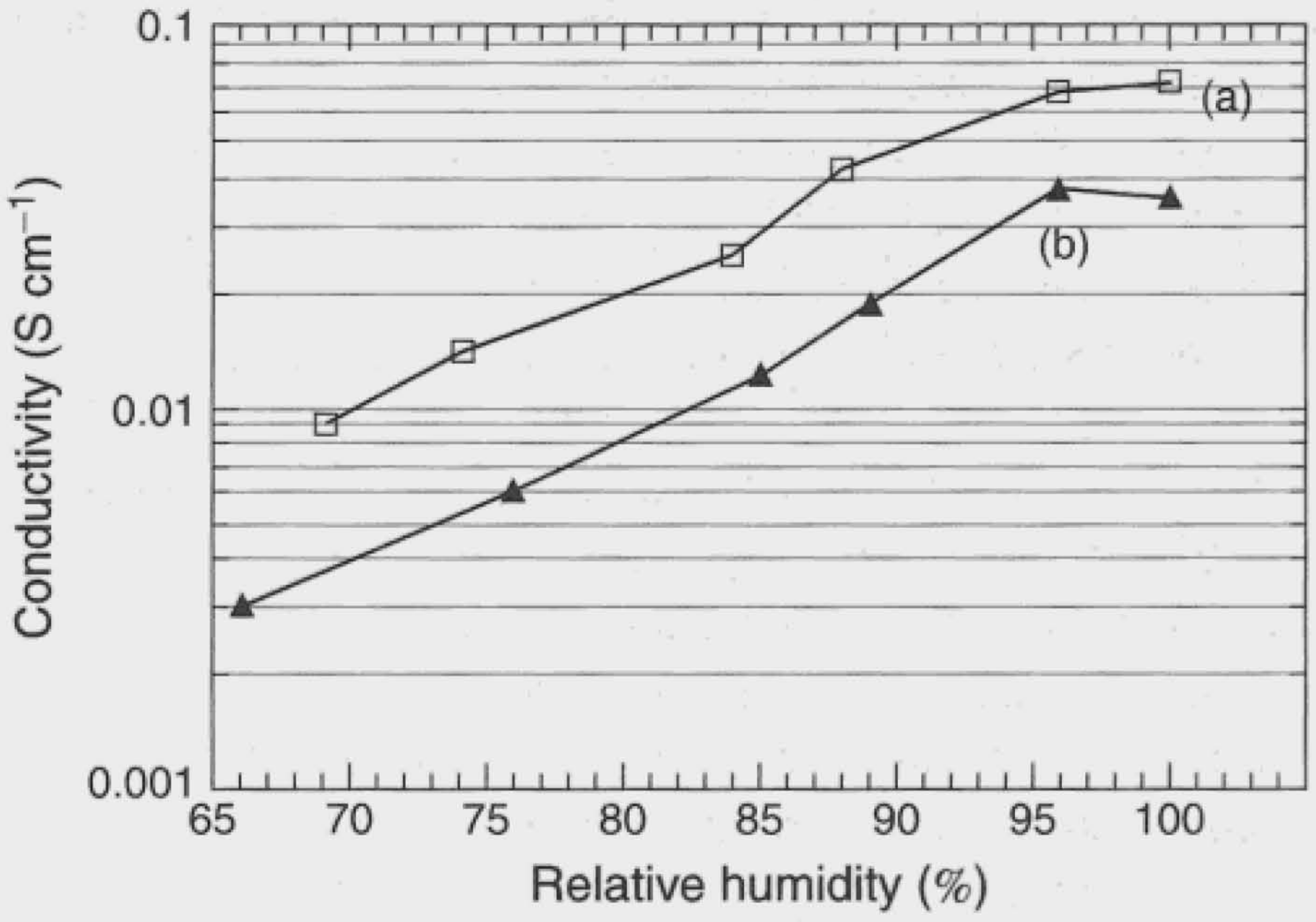

Figure 6. (a) Conductivity of sPEEK/ZrP containing 20 wt% zirconium phosphate as a function of relative humidity and (b) comparison with conductivity of unmodified sPEEK. All membranes were pre-treated in 85% H_3PO_4 for 5 days at 80 °C, then washed in boiling water for 4 h prior to measurement.[18]

continuously increasing amounts of inorganic phase can be grown, to give membranes ranging from pure organic to pure inorganic. In recent years, a number of polymers have been used as host matrix for in situ polymerization of metal alkoxides, and in the majority of cases the materials prepared are polymer/silica hybrids. These include the use of polydimethylsiloxane,[38] poly(tetramethylene oxide),[39] poly(methylmethacrylate),[40] epoxy resins[41] and polyimides,[42] for which the inclusion of metal oxide particles led to hybrid membranes with mechanical properties superior to those of the pure organic matrix.

Nafion®/silica membranes containing between 6 and 54 wt% of silica have been prepared by adding TEOS [and, in some cases, to introduce more flexible segments, 1,1,3,3-tetramethyl-1,3-diethoxydisiloxane (TMDES)] to Nafion® solution in propanol/water and catalyzing the sol/gel reaction by addition of HCl.[43, 44] The Nafion® microstructure reforms at the same time as the inorganic polymerization reaction and the membranes obtained show diverse morphologies. For example, in a hybrid of 6.5 wt% SiO_2, bands of silica of width 1.2 μm, aligned in the direction of the solvent evaporation path, were differentiated by transmission electron microscopy (TEM). At >10% substitution of TEOS by more hydrophobic TDMES phase segregation occurred, although a laminar organization of inorganic domains was also observed.[43] Electron energy loss spectral analysis indicated the complete absence of silica in the polymer-rich regions of the hybrid. Nafion®/SiO_2 membranes containing 22 wt% silica were rigid and brittle. The flexibility and elasticity of 15–20% substituted TDMES membranes were higher, with values of the storage and dissipative moduli close to those of Nafion®.[43] The conductivity of such hybrid membranes has only been reported under conditions of dry argon up to 100 °C, when the range of conductivity is 10^{-7}–10^{-5} S cm^{-1} depending on composition and temperature.[44] It is noted that neither Nafion®/silica hybrids prepared using a pre-formed membrane nor those prepared by precipitation in the polymer solution have yet been satisfactorily characterized for their electrochemical properties, in contrast to the more extensive investigations carried out on composite recast Nafion®/silica membranes prepared by bulk dispersion.

Hybrid membranes based on polymer in situ growth of silica in sPEEK have been prepared in recent work, but in this approach a growing silica network derived from TEOS is surface functionalized by reaction with aminophenyltrimethoxysilane (APTMOS).[30] Proton transfer from the sulfonic acid groups of sPEEK to aminophenyl end-capped silica causes ionic charging of the particles, which has the two-fold effect of preventing auto-aggregation and favoring ionic crosslinking with sulfonate groups. The expectation that the ionic interaction $-NH_3^+\text{- - }^-O_3S-$ would improve mechanical properties compared with non-functionalized sPEEK/SiO_2 hybrids was borne out by experiment. For the latter, the maximum strength drops from 39 to 6 MPa on introduction of 20% SiO_2, but recovers to 37 MPa on partial substitution of TEOS with APTMOS. The membranes are also characterized by decreased elongation at break and, for optimized compositions, a higher mechanical modulus than for unmodified sPEEK. The presence of APTMOS strongly influences the degree of dispersion of silica throughout the membrane (Figure 7a). The conductivity of sPEEK/aminophenyl-functionalized silica containing 10–20 wt% SiO_2 is 3–4×10^{-2} S cm^{-1} at 100 °C/100% RH. These values are only slightly lower than for unmodified sPEEK, despite the fact that the effective IEC of the hybrid system is reduced by the protonation of amino groups.[30]

Above inclusion of ca 30 wt%, the ionic crosslinking $-NH_3^+\text{- - }^-O_3S-$ is insufficient to ensure complete dispersion of the inorganic phase in the absence of other favorable factors, such as the dielectric constant of the solvent. Continued increase in the amount of aminophenyl groups in any case further reduces effective IEC. High dielectric constant solvents solvate ion pairs via electrostatic interactions, allowing phase separation into inorganic- and organic-rich domains to be avoided, but at the same time not hindering the ionic interaction at the interface.[45] It has been shown that transparent hybrid membranes of sulfonated polystyrene(sPS) and aminopropyl-functionalized silica (50 wt% SiO_2) can be prepared that have increased storage modulus in the elastic state compared with non-hybrid sPS, this being attributed to an increase in ionic

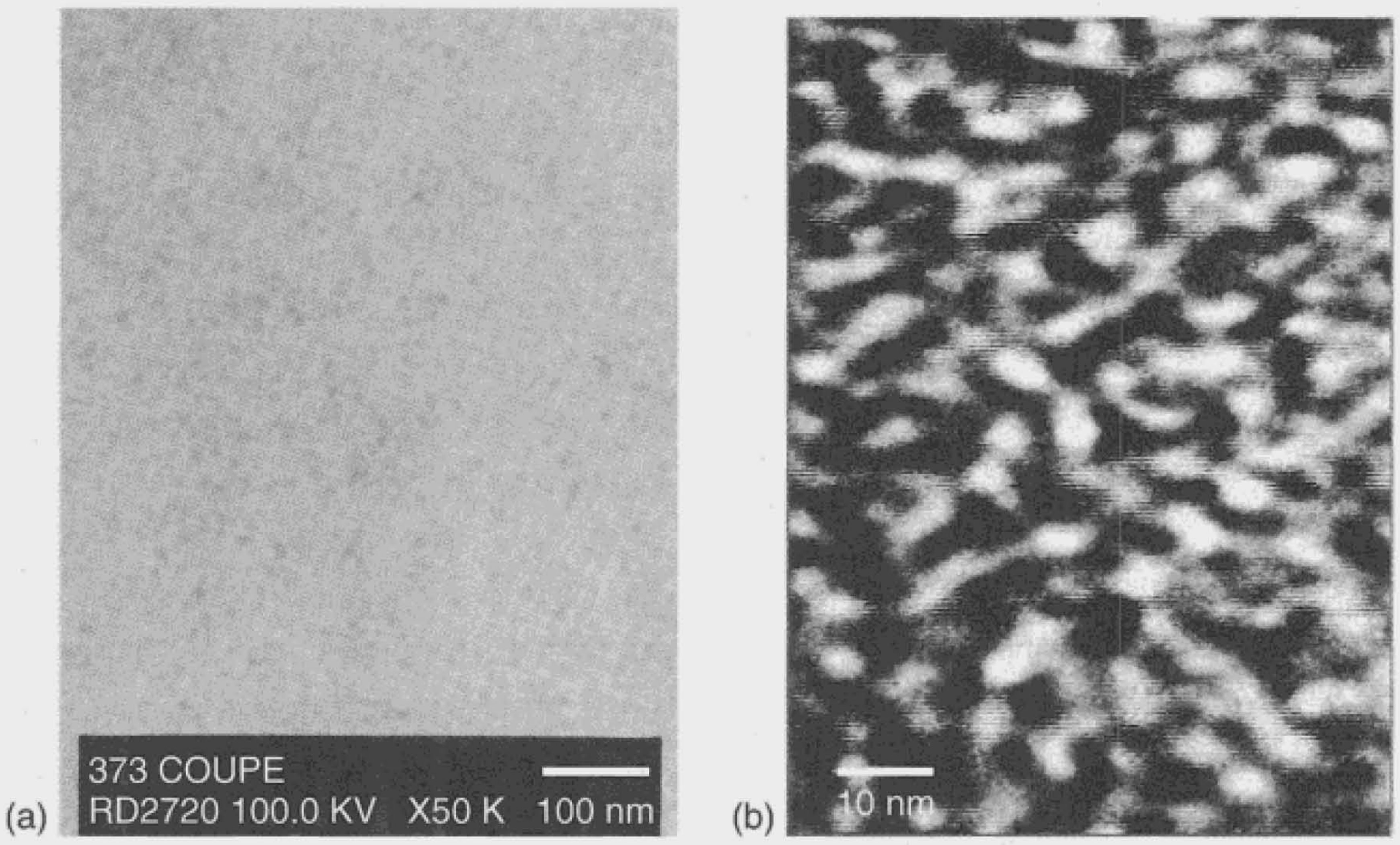

Figure 7. Transmission electron micrographs of hybrid membranes of sPEEK/aminophenyl-functionalized silica prepared by in situ sol/gel reaction in sPEEK solution containing (a) 10 wt% SiO_2 showing discrete and well dispersed particles (dark regions) of size ca. 10 nm and (b) 50 wt% SiO_2 showing nanometer-level separation of inorganic (bright regions) and organic (dark regions) components with co-continuous domains of equal size, ca. 4–5 nm.[30]

interactions between sPS chains and a consequent reduction in their mobility.

Nanophase-separated, flexible hybrid membranes with up to 50 wt% silica have been obtained with sPEEK using DMSO, although turbid or translucent and more brittle systems resulted with solvents of lower dielectric constant such as dimethylformamide, DMAc or NMP. Importantly, the conductivity of sPEEK/aminophenyl-functionalized silica membranes (50 wt% SiO_2) is maintained at $>10^{-2}$ S cm^{-1} at 25 °C (100% RH), even though it could be expected that the conductivity of such membranes would be drastically lowered in the presence of a high content of a noninherently proton-conducting inorganic phase. This observation provides support for a modified membrane microstructure and extensive silica–polymer interfacial regions, improving proton transport properties. Indeed, TEM shows that the sPEEK polymer and aminophenyl-functionalized silica networks interpenetrate with similar domain size of ca 4 nm (Figure 7b), and the polymer can be considered as confined within the pores of an in situ-formed amorphous silica structure.[30]

4 CONCLUSION

Improvements in proton-conduction properties and water management, extension of the working temperature range and reduction in direct fuel crossover are among the positive properties reported for composite inorganic/organic membranes compared with their polymer-only congeners of relevance to fuel cell applications. These properties are of particular interest in the context of the use of hydrocarbon fuels or reformate gas, and of fuel cell operation in the medium-temperature range, with low humidification of reaction gases. When the inorganic component is precipitated in situ in the polymer, rather than by bulk mixing of the polymer with a powdered ceramic or proton-conducting solid acid, a more homogeneous dispersion of the inorganic phase through the organic matrix results, with associated advantages for, or even increased, proton conductivity and mechanical strength. The recent concepts of ionic crosslinking between inorganic and organic phases, interpenetration of functional inorganic and organic networks and modulation of membrane morphology provide exciting areas for the development of fuel cell membranes, while the electrochemical characterization of hybrid systems designed for other applications should also be completed.

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