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Proton-Conducting Channels in Polybenzimidazole Nanocomposites

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Abstract | The interfacial interactions of hybrid organic-inorganic nanocomposite membranes, when tuned appropriately, can replicate to some extent the conduction mechanism of Nafion where hydrophilic and hydrophobic regions are dispersed randomly and the proton conduction takes place via the conducting channels. A wide variety of functionalizing molecules can be used for tuning the interface. The dynamic physical interactions between the particles and the polymer chains, and the hydrogen-bonding interactions among the functionalized silica nanoparticles in polybenzimidazole (PBI) matrix manifest as self-assembled inorganic networks or domains of different sizes depending on the filler content. These domains can trap phosphoric acid via strong hydrogen bonding and can act as reservoirs of phosphoric acid thus creating an acid gradient in the matrix. This gradient morphology gives rise to directed and faster proton conduction process in the PBI matrix. Thus, these inorganic-organic hybrid materials can be tuned for controlled conductivity as well as mechanical and thermal stability of proton exchange membrane for the fuel-cell applications.

1 Introduction

Electrochemical conversion efficiency of devices like proton-exchange membrane fuel cell, which is essentially green power technology, depends on the ion-conducting property of polymer membranes, which is sandwiched between two electrodes.[1–3] Although different kinds of ion-conducting membranes, proton-conducting polymers, or proton-exchange membranes (PEMs), as they are popularly called, have been at the crux of fuel-cell research owing to their use in proton-exchange membrane fuel cells (PEMFCs),[4,5] direct methanol fuel cells (DMFCs)[6,7] and the recently emerging microbial fuel cells (MFCs),[8,9] all of which have the potential to power automotives and even stationary power stations, provided energy-dense fuel sources like the hydrogen gas and methanol for PEMFCs and DMFCs, respectively, and of wastewater for MFCs are properly handled. While DMFCs and MFCs are yet in their nascent stages of research and development, PEMFC technologies have made significant advances in terms of materials and system performance, and have already hit the commercial market with major automobile manufacturers like Honda, Toyota, Hyundai, Daimler setting the time for full-fledged commercial production of fuel-cell vehicles (FCVs) before 2017.[10] In a PEMFC system, the membrane electrode assembly (MEA) constitutes the core component which in itself has a PEM membrane as its core material, mainly serving as a separator between the anode and the cathode, with anode facilitating the oxidation of hydrogen gas fuel thereby splitting it into protons and electrons. While the electrons pass through an external closed circuit to generate power, the protons get carried towards the cathode with the help of PEM membrane. The cathode, using the electrons and protons, then promotes oxygen reduction reaction to complete the reaction.[11–13] Hence, to fulfil its role as a separator, a proton exchanger, an electrolyte, a PEM membrane must satisfy a set of crucial properties. Firstly,

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the membrane and its constituents should be electrically insulating material so that they conduct only protons and not electrons, which may result in short-circuit. The membrane must sufficiently be impermeable to hydrogen or oxygen crossover to the other side to provide efficient fuel cell performance. For use at high temperature operations at about 120–150°C in its sandwiched position, the membrane must possess high thermal, mechanical and dimensional stability to ensure its durability during long operation time. Any significant changes in the membrane's dimension or stability during operation may lead to huge drop in fuel cell performance.[14,15] But the most important property is the proton-conducting efficiency. The proton conductivity of the PEM membrane must be as high as >0.1 S/cm, to expedite which, the polymer chemical structure and the membrane microstructure ought to provide special functional groups or morphological features so as to enable smooth and faster proton conduction. In other words, the membrane must have proton-conducting channels or pathways for feasible hydrogen ion transport from one site to another.[16–19]

2 Proton Conduction

A PEM membrane can be thought of as a two-part system, one being the base polymer membrane material that may contain another blend polymer or a nanofiller to enhance membrane stability and the other part the dopant or the protonic charge carrier. In most cases the base polymer membrane alone may not be an ion-conducting system and hence must be doped with an appropriate charge-carrying medium. There are only a few species available that can act as protonic charge carriers, the most important ones being water (for example, in water-doped sulfonated polymers the water medium helps transport the proton dissociated from the sulfonic acid moiety), oxo-acids like phosphoric acid (e.g., basic polymer adducts with the oxo-acid where phosphate anion acts as the charge-carrying species), heterocycles containing imidazole moiety (examples include most of imidazolium ionic liquids), and oxide ions on a lattice that enable hydroxide bond formation. All these protogenic species share one common characteristic property—their ability to be involved in hydrogen bonding interactions—which is one of the most important phenomena for long-range proton transport in weakly bonded molecular structures. The characteristic nature and dynamics of rapid bond-breaking and bond-forming process of hydrogen-bonding interactions brings about the "hopping" of protons from one active site to another, i.e., proton gets transferred along a chain or domains of hydrogen bonds or protonic defects. Of the several mechanisms that have been proposed for proton transport, two important mechanisms, namely, the "Vehicle mechanism" and "Grotthus mechanism" hold good for proton transport in PEM membranes. While in the vehicle mechanism, the proton just diffuses through the membrane with the aid of a "vehicle" or proton carriers like H_3O^+, NH_4^+ etc. In the case of Grothuss or the structure diffusion mechanism, the proton transfer takes place via the intermolecular hydrogen bond-breaking and forming processes.[21–25] Hence, it becomes important to establish a network of proton-conducting units (hydrogen-bonding systems) in the membrane matrix to achieve proton conductivity of values higher than 0.1 S/cm. In an effort to realise this goal, many research groups have focussed on improving the ion exchange capacity (IEC) of the membrane by attaching acidic functional groups like carboxylic, phosphonic and sulfonic acid since higher IEC (or ion-conducting groups) could lead to the formation of proper proton-conducting channels in the matrix.[26,27] Considering Nafion as the yardstick which has an IEC of around 0.9 $mmolg^{-1}$ and proton conductivity of 0.07–0.09 Scm^{-1} (at 15–20 water molecules per sulfonic acid groups), many attempts have been made with several potential polymers containing sulfonate groups and other ionic groups to increase the IEC of PEM membranes by a few times compared to that of Nafion with an aim to improve proton conductivity higher than that of Nafion.[28] Miyatake's research group synthesized several sulfonated membranes based on polyarylene ether and its derivatives with an IEC of about 1.3 $mmolg^{-1}$ and proton conductivity similar to that of Nafion.[29] Nevertheless, it has been noticed that often high ion concentration compromises with membrane stability and integrity by way of high water uptake and the consequent swelling and plasticization effects. The effect worsens when used for high-temperature applications. Understandably, the IEC of a membrane cannot solely account for high proton conduction.

As a consequence, the focus of research has been shifted, in recent times, towards tuning the morphology of PEM membranes-that single fundamental feature which could alter the polymer properties drastically. Designing nanopahase structures in the polymer matrix can create ion-conducting nanochannels which in turn can help in improving the ionic conductivity.[30–33] Inspiration

Nanochannels: Continuous network of ionic sites formed due to the interaction between particle and the polymer.

behind the idea that nanosized conductive channels with interconnected networks could improve the proton conductivity manifold comes from the widely accepted and referenced "cluster network" morphology model of Nafion proposed by Gierke and co-workers with the help of small-angle X-ray scattering (SAXS) studies (Figure 1A).[34,35]

The model suggests the formation of spherical ionic clusters in the water-swollen Nafion membrane owing to the existence of sufficient hydrophobicity difference between the perfluorocarbon backbone and the ionic groups. The ionic clusters formed by the sulfonic acid groups attached to the backbone structure are actually hydrated ionic aggregates. These were further proposed to be interconnected through narrow ion channels formed as a result of percolation effects. This channel structure is believed to be the primary reason for the high proton conductivity in water-doped Nafion. SAXS simulation studies of this model were performed later by Scmidt-Rohr et al., which suggest the presence of long parallel cylindrical channels containing sulfonic acid groups in the interior and the partially hydrophilic groups on the outside, thus forming an inverted-micelle cylinder (Figure 1B). This model, called parallel water channel model,[36] also explains the fast diffusion of protons and its persistence in Nafion at room temperature. Although these proposed models (and other models proposed earlier) are still under scrutiny, they unanimously emphasize the inevitability of interconnected ionic networks/clusters for feasible proton conduction in a polyelectrolyte membrane. Proton conduction mechanism in the nano-channels strongly depends on dielectric constant of water as revealed by several dielectric spectroscopy studies. The three different water regions, i.e., bulk water, loosely bound water and strongly bound water through hydrogen bonding, each display different dielectric responses. Tightly bound water molecules to the sulfonate groups have a lower dielectric permittivity, which prevents the structural diffusion of protons and in turn affects the conduction mechanism.[21]

In terms of proton conductivity and mechanical stability, Nafion has remained the wonder material and is the most sought-after membrane for PEMFC applications even today. Like Nafion® (Dupont) there have been other commercial membranes developed containing perfluorinated backbone with sulfonic acid groups for use as

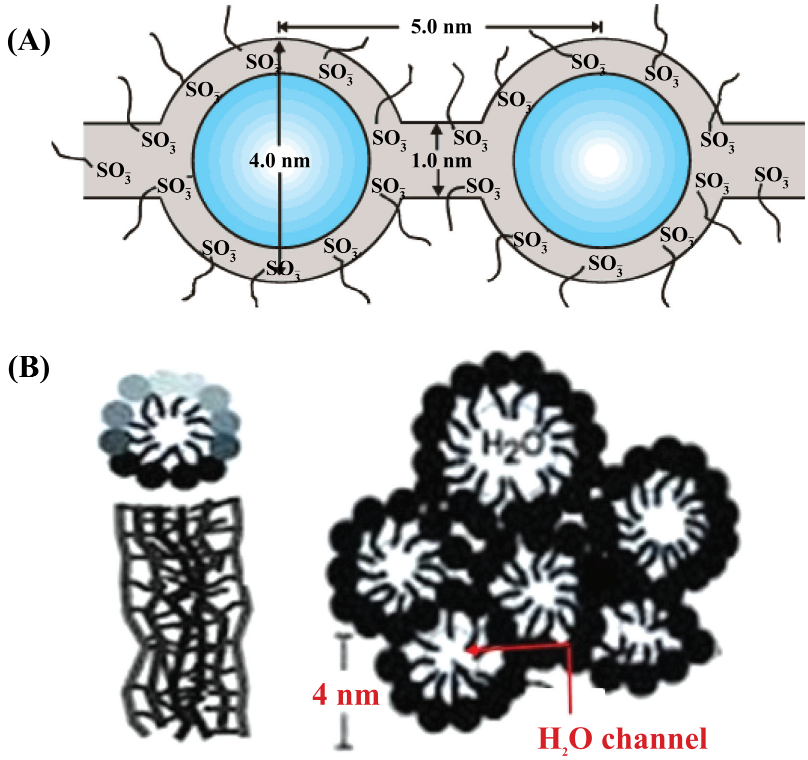


Figure 1: (A) Cluster-network morphology model of hydrated Nafion (adapted from references 34 and 35), (B) Parallel water channel of Nafion; Adapted by permission from Macmillan Publishers Ltd: [Nat. Mater.] (Reference 36), copyright (2008).

PEM material.[37,38] But major research advances have been on high temperature and low humidity fuel cell operations because of the many advantages at high temperature conditions like faster electrode kinetics, higher-carbon monoxide tolerance, freedom from water management, flexibility to use alternative low-cost catalysts. In this regard, Giner Electrochemical Systems, USA, (www.ginerinc.com) had developed perfluorosulfonic acid-based membranes with proton conductivity of about 0.1 Scm^{-1} at 120°C and 50% relative humidity.[39] However, these materials have serious drawbacks for high-temperature applications like membrane degradation and fluorine gas emission, succumb to fuel permeation, huge drop in proton-conducting efficiency due to changes in microstructure.[40,41]

Consequently, the primary objective of fuel-cell research has switched to developing alternative membranes to Nafion that can display high proton conductivity in anhydrous state, high temperature stability (120–200°C) and affordable cost. In this aim, cost-effective aromatic hydrocarbon-based polymers have gained immense attention due to the fact that aromatic C-H bonds being stronger than aliphatic bonds impart rigidity and mechanical stability as demanded by high-temperature conditions. A great deal of effort was devoted to develop sulfonated aromatic polymers like polyarylether sulfone, sulfonated polyether ether ketone, etc. which had high IEC (0.8–2.2 mmol/g) and proton conductivity (0.1 Scm^{-1}) values compared to Nafion. Still, these materials reportedly have poor durability due to their susceptibility to oxidative degradation and do not meet the stringent requirements of fuel-cell operating conditions. Moreover, the presence of sulfonate groups accelerates swelling and degradation of the membrane at high temperatures.[40–45] Therefore, there is still room for developing completely new polymeric structure which may be the most appropriate alternative to Nafion.

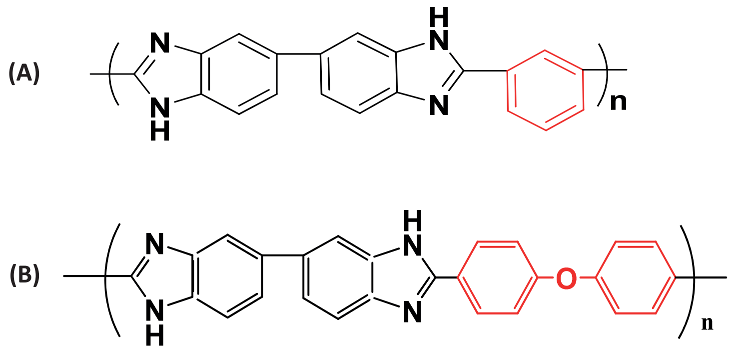
3 Acid-base Polymers—A Case Study with Polybenzimidazole

A special class of widely investigated polyelectrolyte membranes for high-operation temperatures is the acid-base polymer complexes which comprise typically a basic polymer doped with a nonvolatile inorganic acid.[46,47] These systems enable anhydrous proton conduction and hence are under active development for high-temperature PEMFC application. Usually polymers having basic functional groups like imine, imide, amide, ether form ion pairs with strong acids via acid-base reactions. But for use at elevated temperatures (100–200°C) only amphoteric acids like phosphoric acid or phosphonic acid are suitable because of their high thermal stability and low vapour pressure at high temperature as explained by Kreuer and co-workers. Also, the structure of these acids consists of both proton donor and acceptor sites which ensure high proton conductivity by rapid reorientation of the dynamic hydrogen bonds through Grotthuss mechanism. One of the very few PEM which is stable and displays good performance at above 100°C is the acid-base adduct of polybenzimidazole (PBI) and phosphoric acid (PA). The acronym PBI refers to the family of heterocyclic aromatic polymers bearing benzimidazole moiety in the repeat unit of the polymer chains. However, Celanese Corporation in 1983 used the 'PBI' abbreviation for poly(2,2′-(m-phenylene)-5,5′-bibenzimidazole) polymer to commercialize it under the trade name 'Celazole'® (Scheme 1A).[48,49]

Grotthuss mechanism: Proton hopping mechanism where a proton tunnels from one water molecule to the next via an infinite network of hydrogen bonds.

By varying the combination of tetramine and diacid monomers, hundreds of modified PBI structures have been developed for fuel-cell use with an aim to improve solubility and processability, tune molecular weight and tailor the basicity. Physical characteristics like colour, mechanical strength and stiffness also vary depending on the chemical structure of the repeat unit. One important derivative is the diarylether derivative called oxy-PBI (OPBI) (Scheme 1B) which is a recently developed PEM material but has gained immense popularity due to its attractive properties.[50] Solubility of PBI polymers is a tricky issue and hinders membrane-forming capacity of the material. Incorporation of an ether linkage in the main backbone makes the structure flexible by lowering the glass transition temperature, decreases crystallinity and hence improves solubility in solvents like DMAc and formic acid, unlike the meta-phenylene unit in m-PBI that confers rigidity to the structure and gives rise to solubility hurdles.

The aromatic benzene groups bestow the polymer with incredible thermal, mechanical and dimensional stability and hence were used initially in making aeronaut suits and military equipment. It has a high glass transition temperature, T_g (300–400°C), high tensile strength (>150 MPa), and good chemical resistivity from most acids and bases. All these properties make PBI a promising candidate for HT-PEMFC use.[51] But its most important attribute is proton conduction. By its very nature PBI is not a proton-conducting polymer and hence cannot function as a polyelectrolyte membrane. The proton conductivity of dry PBI membrane was found to be 10^{-7} S/cm by Bouchet



Scheme 1: Chemical structures of (A) poly[2,2′-(m-phenylene)-5,5′ bibenzimidazole](m-PBI), (B) poly(4,4′-diphenylether-5,5′-bibenzimidazole) (OPBI).

and Siebert.[52] So, in the undoped state strong inter-chain hydrogen bonding interactions exist which results in high mechanical stability of PBI. But being a basic polymer it can be readily doped with strong acids like phosphoric acid (H_3PO_4). Upon doping, the cohesive forces between the chains decrease and acid-base interactions between imidazolium moiety of PBI and the acid molecule is established via hydrogen-bonding interactions. This interaction is the fundamental factor for proton conduction in a PBI matrix.[53] The order of rate of proton transport among different protogenic species as proposed by Ma et al is H_3PO_4 to $H_2O > H_3PO_4$ to $H_2PO_4^- >$ N–H$^+$ to $H_2PO_4^- >$ N–H$^+$ to $H_2O >$N–H$^+$ to N–H.[54] The acid doping level usually expressed in moles of acid per repeat unit of polymer can range from 5 to 20 at ambient temperature. Given the structure of PBI, at the most only 4 molecules of PA can protonate the repeat unit and the rest of the acid remains in undissociated form as disclosed by spectroscopic investigations. The excess acid forms hydrogen bonded network and gives rise to proton conductivity of the PEM membrane. Studies have also revealed that high proton conductivity (> 0.1 S/cm) can be achieved with higher quantum of free acid in the membrane matrix.[53]

Membrane morphology influences the proton transport process greatly as elucidated in the case of Nafion. An NMR study of PBI membranes cast from polyphosphoric acid (PPA) and DMAc showed different proton diffusivity rates, with the PPA cast membranes showing higher conductivity. An apparent reason is the additional proton transport sites involving rapid exchange interactions between phosphoric acid and pyrophosphoric acid species. Although conductivity could be improved by membrane casting in different solvents, the strategy is offset by poor mechanical stability of the resultant membranes.[55,56] Recent approaches to improve conductivity by modification of morphology include N-substitution of the polymer backbone chain, synthesis of block copolymers, acid functionalization. These methods were successful to some extent in improving the conduction.

4 Organic-Inorganic Hybrid Nanocomposite Membrane

The most effective and simple way to tune the morphological features for generating ion-conducting channels is through the design and development of organic-inorganic hybrid nanocomposite membranes, an approach which offers a wide range of inorganic nanomaterials to choose from, which, when combined with an organic polymer backbone can yield membranes with the desired morphology and properties. A judicious choice of the nanofillers can also confer the PEM membranes with good adaptivity to fuel-cell environment without any tradeoffs. Different categories of inorganic fillers are available nowadays like metals (Al, Ag, Au), metal oxides (SiO_2, TiO_2, SnO_2), carbon-based materials like graphene oxide, graphene, nanotubes, nanoclays (montmorillonite, laponite). Incorporation of the right choice of nano-sized fillers at an appropriate concentration in the organic polymer matrix can help in improving several key properties of PEM membranes such as proton conductivity, mechanical and thermal stability, swelling behaviour, retention of the conducting medium at high temperatures. The resultant property of the material would be due to the strong synergetic interactions over extended interface created by the organic and inorganic components and not due to sum of the properties of individual constituents.[57–59] Of the various kinds of nanofillers mentioned above, silicate-based nanofillers, namely, silica nanoparticles and montmorillonite nanoclays have found great success as potential fillers for PBI-based PEM.

A brief account of the structure and characteristics of silica nanoparticles and nanoclay is given below to appreciate their role in proton transport.

Interface: The boundary region between nanoparticle surface and bulk polymer where polymer properties are different compared to those of the bulk polymer.

4.1 *Silica nanoparticles*

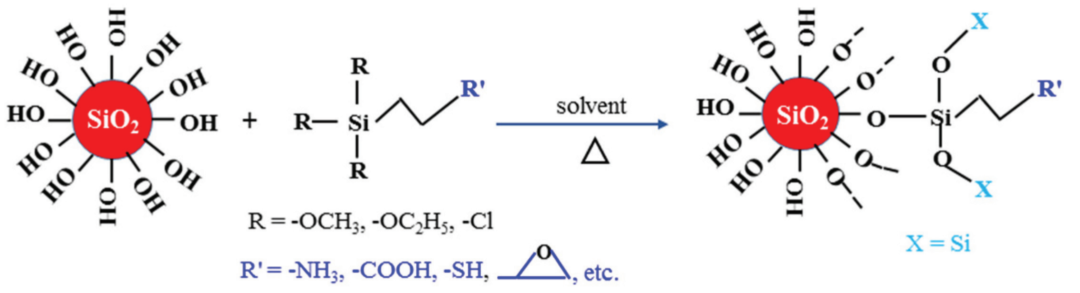
Spherical silica nanoparticles are amorphous in nature and the structure consists of silicon and oxygen atoms forming a three-dimensional network of Si-O-Si bonds with siloxane and silanol (Si-OH) groups on the particles surface. They do not have the long-range ordered arrangement of atoms and hence contain void spaces in the structure that makes them highly porous materials. The hydroxyl groups on the surface give them their hydrophilic property. But they can be made to react with suitable organic molecules to render them fluorophilic or amphiphilic or hydrophobic according to requirement. Unlike other nanoparticles, ease of surface modification is a big advantage with silica nanoparticles. The particles have their own unique characteristics because of which they are the most coveted of all the nanofillers available for both academic as well as industrial research. Firstly they are easy to synthesize using the popular Stöber's process, which yields monodisperse spherical particles and offers control over particle size. Though there are other routes to synthesize SiO_2 particles, Stöber's method is widely preferred because of the use of mild reaction conditions and simple processability. They have high specific area, large porous volume, high chemical, mechanical and thermal stability owing to the strong Si-O bonds, low coefficient of thermal expansion coefficient, non-toxic nature. These are essentially the characteristics required for PEM membrane for fuel-cell applications as described earlier. Clearly, SiO_2 nanoparticle-incorporated in PEM would result in improved properties especially proton conductivity while retaining the mechanical integrity of the membrane.[60–62]

But the key to successful incorporation of the nanoparticles and objectify superior proton transport processes lies in creating a strong interfacial region between the nanoparticles and polymer. Interface is the region where polymer chains are bound tightly to nanoparticle surface via chemical interactions and may extend up to few tens on nanometers. The interactions can either be weak like van der Waals, ionic bonding, hydrogen bonding or strong that include covalent or ionic-covalent bonding. Therefore, to generate such useful interactions at the interfacial region one has to introduce suitable functional groups such as $-NH_2$, -SH, -COOH, imidazole by surface functionalization strategies.[63,64] These polar groups around the nanoparticles in the matrix actually help in forming a bound layer of the charge-carrying medium like water or acid that could facilitate proton hopping via hydrogen bonding interactions. Hence, proton conductivity can hugely benefit from such organic-inorganic hetero-component interactions as it may lead to the formation of interconnected conductive channels or directed pathways for proton transport. A wide variety of silane coupling agents is used as potential surface modifying molecules (Scheme 2).

Recently, living polymerization techniques like atom transfer radical polymerization (ATRP), reversible addition-fragmentation chain-transfer (RAFT) have also been used to create polymer brushes on particle surfaces as part of nanoparticle functionalization procedures. Nevertheless, designing polymer brushes on particle surfaces involves a complicated process and the technique is yet in budding stage.[65]

4.2 *Montmorillonite nanoclays*

Montmorillonite is a naturally occurring clay mineral that is found in sedimentary rocks and volcanic ash and has been widely used as reinforcing filler material since the inception of human civilization. It has a two-dimensional layered sheet-like structure whose lateral dimension may extend to several microns in length depending on



Scheme 2: Surface modification of silica nanoparticles by silane coupling agents.

the source of clay and its formation process. The sheets are arranged in a stacked fashion one on top of the other with a regular van der Waals spacing of ~1 nm between them, which is called the inter-gallery distance. Each sheet or clay platelet is made up of octahedral layer of alumina as a middle layer enveloped on its both sides by tetrahedral silicate layer. Thus the three layers fused together by shared oxygen atoms constitute a unit layer (2:1 layered silicate). Isomorphous substitution of Al^{3+} ions by Mg^{2+} ions in the middle octahedral layer make them negatively charged which is balanced by the presence of positively charged cations like Na^+, Ca^{2+} in the inter-gallery. These inorganic cations can be replaced with organic surfactants or polymers to render them hydrophobic. This type of ion exchange reaction lowers the interfacial tension between the particle and polymer and enables thorough mixing and strong chemical interaction among the functional groups of the heterogeneous components. There can also be physical interfacial interactions like adsorption. Polymer chains in the vicinity of the clay layers get adsorbed to the surface of clay layers. These physical and chemical interactions together contribute to a stronger interface and improve the thermal and mechanical stability and glass transition temperature of the polymer.[66,67]

But the most important advantage with the nanoclays for proton transport process is the two-dimensional structure. The stacked lamellar clay layers act as 2D nanochannels for directed proton transport when incorporated in a proton-conducting polymer matrix. The polymer chains intercalated into the inter-gallery spacing along with the oxide groups of the silicate layers, which are negatively charged, help adsorb sufficiently large amount of the positively charged proton from the conducting medium which fills the inter-gallery layers. As a consequence of this continuous network of proton-conducting medium, hopping of protons becomes more coordinated and uninterrupted by effortless hydrogen bond breaking and forming inside the 2D nanochannels of the clay particles. These can be referred to as “bulk nanostructured materials”, i.e., the size of the stacked silicate layers (or a tactoid) may extend up to several micrometers but the structural unit responsible for transport function is in the nanometer scale.[68] Another favourable aspect of the clays particles is that the layers prevent the leaching out of the conducting medium, a common phenomenon observed at high temperatures, from the polymer matrix. The entrapped water/acid molecules remain confined inside the 2D inter-gallery and contribute to proton conduction at high temperatures even after the loss of significant amount of acid from the membrane matrix.[69]

5 Proton Conduction in PBI Nanostructures

Clearly, a well-connected ionic nanochannel is one of the defining factors for improving proton conduction in a polymer matrix. This is schematically presented in Figure 2. In Figure 2A the morphology is characterized as tortuous conduction pathway whereas Figure 2B suggests more effective proton mobility because of the linear conduction pathway.[70]

If we consider Nafion to be a nanocomposite system with nanosized hydrophilic clusters dispersed in a hydrophobic perfluorocarbon matrix, then we can deduce that careful tuning

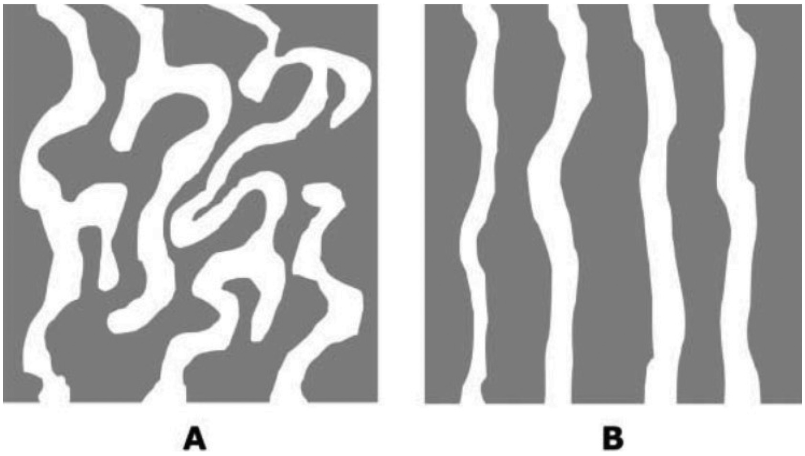


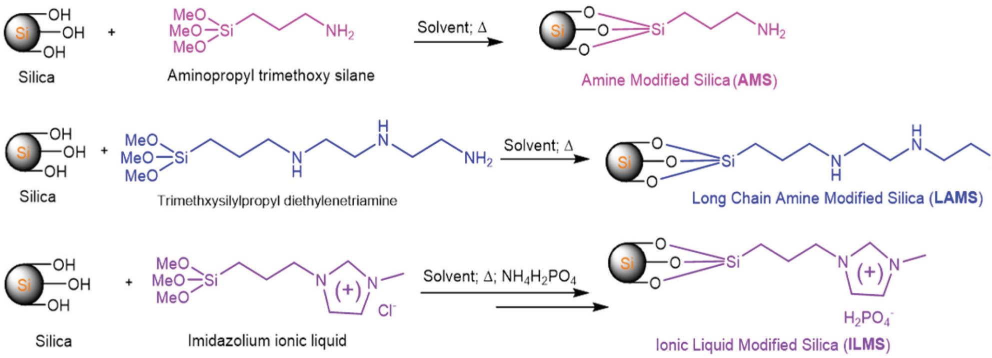
Figure 2: Connectivity of aqueous domains in PEMs (reproduced from reference 70 with permission from the Royal Society of Chemistry).

of the interface in organic-inorganic hybrid nanocomposites could reproduce to some extent the environment in Nafion where the inorganic nanoparticles or their clusters help to form interconnections for proton conduction between the hetero-components like PBI matrix and phosphoric acid.[28] There is a large body of literature on PBI nanocomposites for fuel cells with different kinds of fillers like titania, carbon nanotubes, graphene, heteropolyacids, zeolites, fullerenes focussing on improving the mechanical stability and proton conductivity. But only a handful of reports exist on silicate-based (silica nanoparticles and nanoclays) PBI nanocomposites. An early report on fluorine-containing PBI/silica nanocomposites prepared by sol-gel process by Chuang et al. mainly discusses the effect of silica on mechanical properties and methanol permeability.[71] Following this, many similar articles emerged with either modified PBI structures or modified silica nanoparticles like sulfonated silica,[72] zwitterion coated silica,[73] mesoporous silica and other functionalized silica nanoparticles. Similarly, nanocomposites of PBI with different nanoclays like montmorillonite, kaolinite with different surface modifications were evaluated by different groups and their effect on thermal and mechanical property, and proton conductivity were studied. Although some of these reports show improved properties and proton conduction but there is a lack of morphology-property correlation study in the available literature, probably owing to the number of trial-and-error experiments that needs to be done especially with respect to proton conductivity. The functional groups provided by the surface of the silicate nanoparticles can be tapped usefully for the formation of proton conduction networks in the polymer matrix as illustrated in the case of heterogenous doping of weak electrolytes, i.e., the incorporation of oxide particles helps in trapping the conducting ions via interactions which leads to the accumulation of the compensating ions in the space charge region.[74] A systematic and step-by-step approach towards understanding the interactions between PBI and nanoparticles can be a major step forward towards interpreting proton conduction processes related to morphological features. We, in our group, attempted to study the extent of interfacial interactions between silica nanoparticles and PBI, and its influence on proton conductivity. By judiciously selecting the organic modifier molecule we could observe a definite morphology-dependent conduction behaviour. Silica nanoparticles were surface-modified (Scheme 3) with aminopropyl trimethoxy silane,[75] trimethoxysilylpropyl diethylenetriamine[76] and imidazolium ionic liquid[77] to produce aminemodified silica (AMS), long-chain amine-modified silica (LAMS) and ionic liquid-modified silica (ILMS), respectively, and their nanocomposites were prepared with OPBI polymer.

With change in the number and type of interacting groups on the surface of the silica particles significant changes in the polymer (OPBI) nanocomposite morphology was observed in terms of formation of self-assembled nanostructures by the particles, which altered the proton conductivity. The ordered self-assembly of the nanoparticles in OPBI matrix is shown in Figure 3.

Self-assembly: A phenomenon where nanoparticles assemble spontaneously due to physical or chemical interactions to form larger ordered structures.

Each of the surface-modified nanoparticles experience two types of forces: (a) van der Waals attractive forces among themselves owing to their small size, and (b) tendency of the particles to interact with the polymer functional groups. In the process of balancing these forces the particles form sheet-like self-assembly in the matrix. But the pattern of assembly is different in all the cases. The AMS-modified silica particles have only one primary amine group whereas the LAMS particles



Scheme 3: Surface modification of silica nanoparticles by various functional groups.

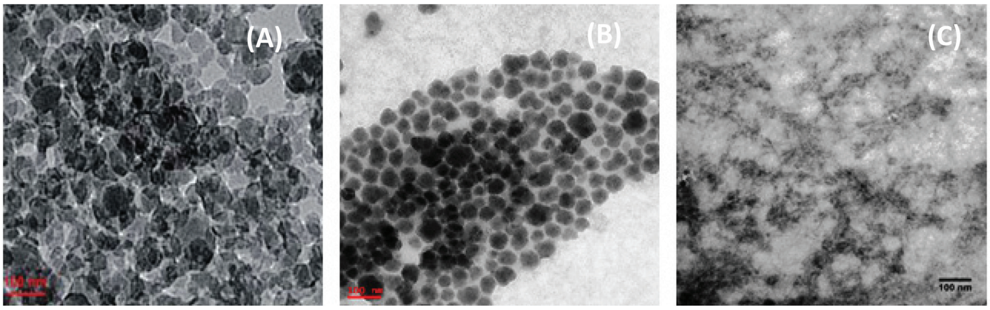


Figure 3: TEM micrographs showing the self-assembly of nanoparticles, (A) OPBI/AMS-15%, (B) OPBI/LAMS-15%, and (C) OPBI/ILMS-15%. The scale bar for all the images is 100 nm and these images are reproduced from references 75–77 with permission from the publishers.

have one primary and two secondary amine groups to interact with the imidazole moiety of OPBI. Owing to the multiple interaction points in LAMS compared to that of AMS, the former particles steer themselves to form monolayered domains of self-assembled nanostructures through hydrogen-bonded networks. These structures are similar to those observed by Akcora et al. in polystyrene grafted silica nanoparticles in a polystyrene matrix where temporal evolution of anisotropic superstructures of nanoparticles was observed.[78] And the ILMS particles form a mesh-like assembly owing to the ionic interactions between the imidazolium groups of both the IL and OPBI. The differently assembled morphology actually plays a role in proton conduction in the OPBI matrix. The Nyquist plot of the membranes and the corresponding proton conductivity at 160°C of all the nanocomposite membranes is compared with that of the pristine OPBI in Figure 4.

The conductivity of the membranes follows the order OPBI (0.04 S/cm) < OPBI/AMS-15% (0.1 S/cm) < OPBI/LAMS-15% (0.18 S/cm) < OPBI/ILMS-15% (0.24 S/cm). The excessive hydrogen-bonding network formed due to interactions between the particle and polymer provides facile pathways for proton conduction in the case of nanocomposites as a result of which the hopping kinetics, i.e., the mobility of the protons increases and hence the conductivity. In other words, the nanoparticle domains in the matrix act as reservoirs of phosphoric acid where more number of acid molecules is trapped via interactions compared to the bulk polymer. This gives rise to a concentration gradient of PA in the matrix and this gradient actually guides the proton transfer in the nanostructures in the nanocomposite membranes unlike the gradient-less morphology in pristine OPBI where proton hopping occurs in a random fashion. The ILMS molecules contain imidazolium cations and phosphate anion and both together contribute to increased acid uptake levels in the membranes. Clearly, the surface modifier molecule plays a crucial role in proton transport process.

Similarly, the nanoclays were modified with three different surfactants, namely, cetyl trimethylammonium bromide (CTAB), cetyl pyridinium bromide (CPyB) and cetyl imidazolium bromide (CImiB), and their effect on proton conduction of OPBI was studied. Chemical structures of these surfactants are shown in Scheme 4 for ease of understanding. The nanoclay used here was the Cloisite nanoclay and after organic modification with surfactants CTAB, CPyB and CImiB, they are denoted as C-CTAB, C-CPyB and C-CImiB, respectively. These surfactants differ only in their cationic head group and the hydrocarbon chain length was maintained constant.[69] The proton conductivity of the nanocomposite membranes obtained by using these organically modified Cloisite clay at 180°C is shown in Figure 5.

In general, the two-dimensional clay layers form a bound layer of acid molecules in the matrix and improve the conductivity. But the data show that conductivity can be tuned by the choice of the organic modifier molecules too. Each of the different surfactants has different basicity because of which their degree of interaction with OPBI as well as the doped PA is different. This again creates a concentration gradient in the OPBI matrix which causes a push for faster proton hopping in the matrix.

Contrary to the common belief that a well dispersed and exfoliated particle morphology only can yield improved properties, the work described in this article proves that controlled particle assembly could lead to unexpected and fascinating properties in terms of conductivity and mechanical stability. A variety of functional groups can be chosen for controlling the interparticle as well as

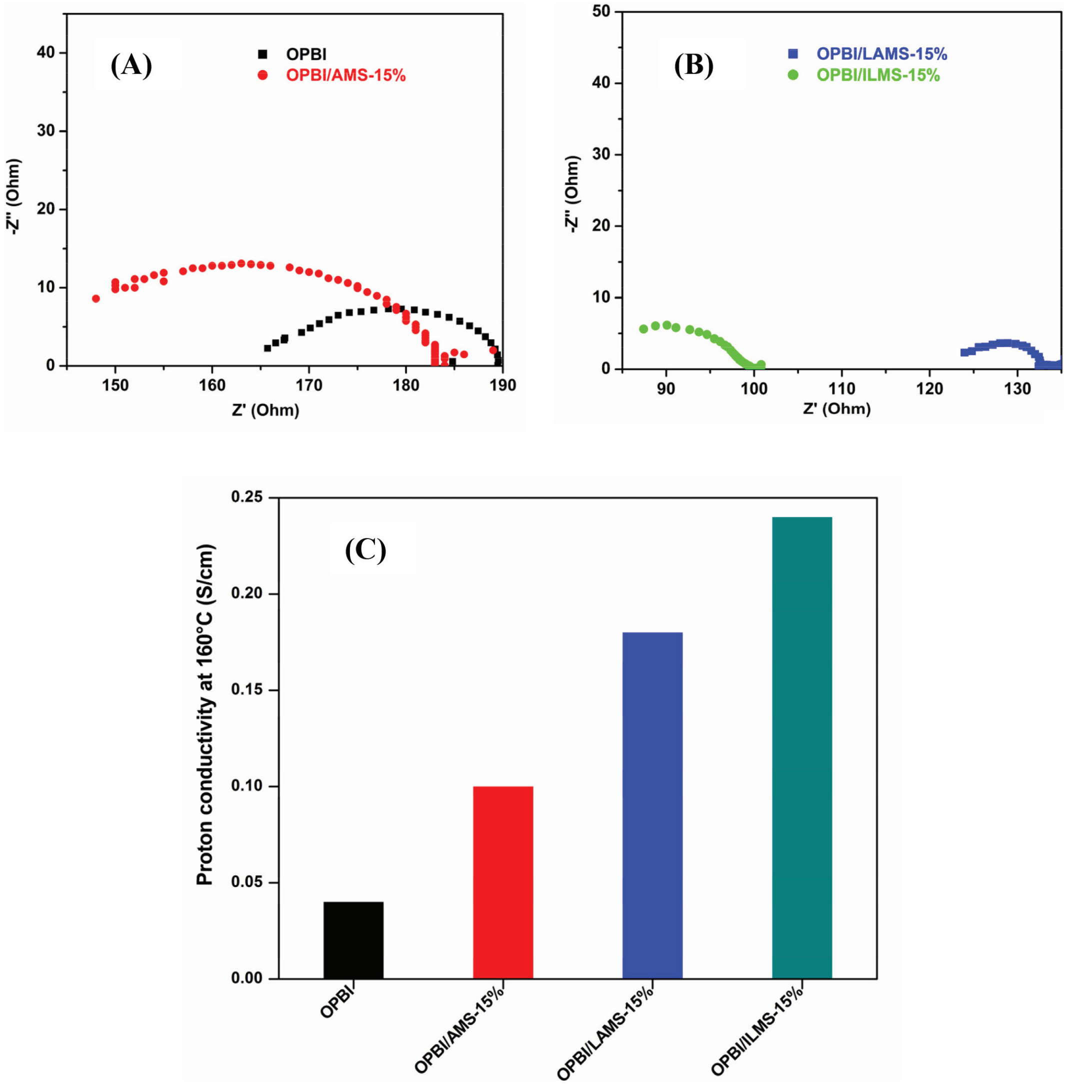
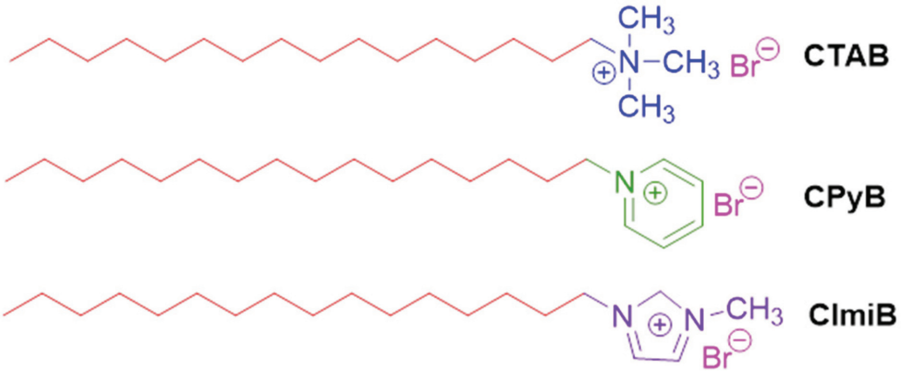


Figure 4: Nyquist plots (A and B) and proton conductivity (C) of OPBI and its nanocomposite membrane. Data shown in the figure are obtained from references 74–76.



Scheme 4: Chemical structures of surfactants cetyl trimethylammonium bromide (CTAB), cetyl pyridinium bromide (CPyB) and cetyl imidazolium bromide (CImiB) which were used to organically modify the Cloisite clay.

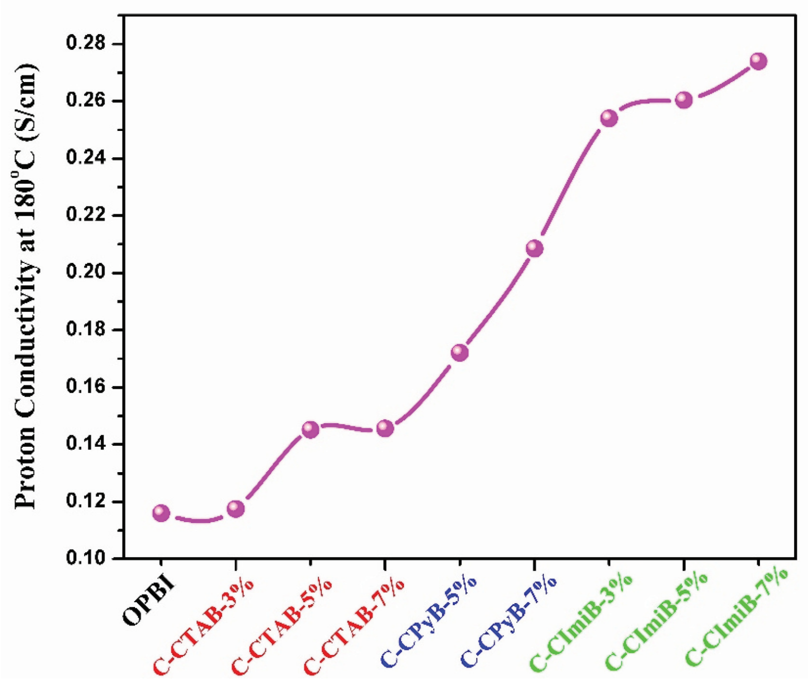


Figure 5: Proton conductivity of OPBI nanocomposite membranes at 180°C. These OPBI nanocomposites were prepared using varieties of organically modified Cloisite clay as nanofillers. Data plotted in this figure are obtained from reference 69.

polymer-particle interaction which provides us the ability to tune the transport properties of the polymer. Use of nanocomposites for morphology control is simpler compared to other existing strategies like synthesizing block copolymers for the same purpose. In fact, this technique also suggests that even complex morphological features can be obtained by varying the chain length of the molecule used or by using polymer brushes which can help in faster proton dissociation and transfer.

6 Conclusion

This article highlights the importance of surface functionalization of nanoparticles and their role in forming discrete morphological patterns in the polymer matrix. Ordered nanostructures of the differently functionalized silica nanoparticles were observed in the matrix which was found to influence the proton conductivity. It is demonstrated that the type and number of interacting groups are important in creating an interfacial region and the degree of hydrogen bonded network. Attention was mainly focused on molecules containing amine groups starting from one to three amine moieties and it was observed that more number of interacting points essentially promote stronger interaction and a better self-assembly pattern of the particles in the matrix. Use of different cationic groups in the nanoclay layers was found to be influencing the proton conduction process by virtue of their different basicity. Hence, proton conductivity can be tuned by appropriately designing the composite morphology and nanostructures.

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