

### Proton Diffusion in High Temperature Polymer/Inorganic Nano-composite Membranes

Pyoungho Choi, Tony Thampan and Ravindra Datta

Fuel Cell Center, Department of Chemical Engineering,  
Worcester Polytechnic Institute, Worcester, MA 01609, USA.

#### Introduction

Recently, extensive research efforts have been made worldwide to find new proton conducting materials for proton-exchange membrane (PEM) fuel cell applications that can overcome the limitations of conventional polymer electrolytes such as Nafion<sup>®</sup>, currently one of the main obstacles to commercialization of PEM fuel cells. They are expensive, mechanically unstable at high temperatures, and conductive only when soaked in water, which limits the fuel cell operating temperature to 80<sup>o</sup> C, which in turn results in low CO tolerance. The operation of fuel cells at higher temperature provides many advantages such as improved kinetics at the surface of electrodes, which is especially important in methanol and CO-containing reformat feeds, faster conduction of protons across PEM, more efficient cooling, and the possibility of integrating fuel cells with methanol reformer, which can result in a compact fuel cell system. Thus, the development of membranes which are mechanically and chemically stable at high temperatures while providing good conductivity under low relative humidity (RH) is an active area of research.

A route to developing “high temperature membranes” is via modification of polymer (host membrane) by the incorporation of hygroscopic oxides such as SiO<sub>2</sub> to increase water uptake, or inorganic solid acids such as heteropoly acids and zirconium phosphate to increase the water uptake as well as the concentration of acid sites to further enhance proton conductivity of the membrane.<sup>1</sup> Recent inorganic materials incorporated in PEMs are SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, ZrO<sub>2</sub>, ZrP, PTA, and zeolite, etc. These membranes can be prepared by casting a bulk or colloidal mixture of powder with a polymer solution, or alternatively *in-situ* formation within a preformed polymer membrane. The size and dispersion of solid particles are of special importance in either fabrication methods. The *in-situ* method is based on sol-gel reactions in the membrane and the formation of nanometer sized particles within the host membrane. These composite membranes prepared via the sol-gel method include Nafion<sup>®</sup>/ZrO<sub>2</sub>, Nafion<sup>®</sup>/SiO<sub>2</sub>, Nafion<sup>®</sup>/TiO<sub>2</sub>, and PEO<sup>®</sup>/SiO<sub>2</sub>, etc.

The composite membranes show a higher water uptake, reduced methanol crossover, improved mechanical properties at higher temperatures, and improved fuel cell performance, although the reasons for the performance enhancement are not clearly elucidated and the long-term stability of these membranes is still in question. In spite of their substantial increase in water uptake, the improved proton conductivity has not been yet proven and is an object of current debate.<sup>2,3</sup> Therefore, it is of interest to analyze the proton transport mechanisms in polymer and polymer/inorganic membranes, which might provide a better understanding of the strengths and weaknesses of alternate approaches for developing good proton conducting materials suitable at high temperatures.

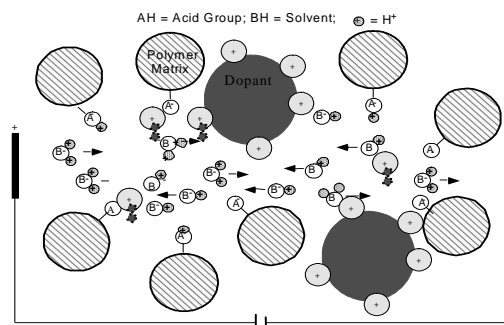
In spite of substantial efforts<sup>4-6</sup> to understand proton transport in PEMs, an accepted transport mechanism in PEMs has not advanced yet due to their complex nanostructure and inhomogeneous nature when hydrated. The objective of this chapter is to develop an understanding of the proton transport mechanisms in composite membranes, so that a framework for the design of high proton conductivity can be developed. A theoretical proton conductivity model is, thus, developed here based on the parallel pore model incorporating various proton transport mechanisms within proton exchange membranes.

#### Theory

Figure 1 shows a schematic representation of the composite membrane in which both the polymer and the inorganic particles are viewed as “dust” species, each possessing acid sites.

Figure 1. Schematic representation of the composite PEM.

The absorbed water molecules interact with the host membrane as well as solid inorganic particles depending upon their hydrophilicity and acid strength of the ionic sites. The water molecules within the composite membrane may be classified as “bulk water” away from the acid groups and “surface water” in proximity of the acid groups. Thus, it is assumed that the



protons in the composite membranes diffuse via i) surface diffusion mechanism occurring close to the acid groups, the primary mechanism under low water activity, and ii) bulk diffusion mechanism in the region away from the acid groups, the dominant mechanism under high water activity condition. In the bulk, proton diffusion is predominantly via the Grotthuss mechanism but the H<sub>3</sub>O<sup>+</sup> ion can also undergo traditional mass diffusion, *i.e.*, the so-called *en masse* diffusion.

The overall proton conductivity of composite membranes  $\sigma_{H^+}$  can, thus, be written as

$$\sigma_{H^+} = \frac{\epsilon_i}{\tau} \left[ \frac{F^2}{RT} \left( D_{H^+}^{\Sigma} C_{H^+}^{\Sigma} + D_{H^+}^G C_{H^+}^G + D_{H^+}^E C_{H^+}^E \right) \right] \quad [1]$$

where  $\epsilon_i$  is porosity of membrane,  $\tau$  is tortuosity factor,  $F$  is Faraday's constant,  $R$  is gas constant,  $T$  is temperature,  $D_{H^+}^{\Sigma}$ ,  $D_{H^+}^G$ , and  $D_{H^+}^E$  are the diffusion coefficients for surface, Grotthuss, and *en masse* mechanisms, respectively, and  $C_{H^+}^{\Sigma}$  and  $C_{H^+}^{\Sigma}$  are the concentrations of protons participating in diffusion in the bulk and surface phases, respectively.

The total proton conductivity in the membranes depends on the sorption equilibrium which affects water content and thus the porosity and tortuosity factor, diffusion coefficients, and acid concentration and distribution between surface and bulk. The fundamental analysis of proton transport in nanocomposite membranes provides very promising results in terms of higher proton conductivity along with improved mechanical stability at higher temperature and reduced methanol crossover compared with host membrane.

#### References

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