European Polymer Journal 97 (2017) 14–25

Contents lists available at ScienceDirect

European Polymer Journal

journal homepage: www.elsevier.com/locate/europolj

Doping proton transport channels in poly-electrolyte membranes with high acidic site density polymers

Gert Dorenbos

T410-1118, 1107 sano, Belle Crea 502, Susono-shi, Shizuoka-ken, Japan

ABSTRACT

The phase separated pore morphology of $H_{1-x}D_x$ blends composed of host (H) and dopant (D) polymers in the presence of water is modeled by means of dissipative particle dynamics. H polymers contain a backbone of 35 connected hydrophobic A beads to which 5 branched A_5[AC][AC]) side chains are non-uniformly distributed by attaching them to the last 5 backbone beads (C beads are acidic and hydrophilic). The C bead fraction (|C|) and ion exchange capacity (IEC) of the H polymer (|C| = 0.125; IEC = 1.73 mmol/cm^3) are nearly 3 times less than of the D polymer (|C| = 0.33; IEC = 4.6 mmol/cm^3). At low dopant volume fractions (ie. small x) the D polymers are distributed near the water containing pore interface and the Bragg peak position (near ~ 11 nm) is hardly affected. With increase of x the radius of gyration of the H polymer backbone decreases and a second Bragg peak emergences near 2.5 nm. This is explained by the large difference between $<N_{\text{bond}}>_{\text{host}}$ (=11.76) and $<N_{\text{bond}}>_{\text{dopant}}$ (=1.5), which are the average number of bonds (topological distance) that A beads are separated from a nearest C bead within the host and dopant architecture, respectively. MC tracer diffusion calculations through mapped morphologies predict a decrease of water diffusion with increase of D polymer volume fraction. Since the ion exchange capacity (proportional to|C|) increases with x, optimal blending ratios may be expected that favor proton conduction. These findings can be of special importance in the optimization of poly electrolyte membranes for fuel cell applications.

1. Introduction

Micro phase separation is an important phenomenon affecting the efficiency of organic solar cells [1–4], Li-ion batteries [5] and polymer electrolyte membrane (PEM) fuel cells (PEMFC). The standard PEM is Nafion®, which is a perfluorosulfonic acid (PFSA) ionomer composed of a Teflon backbone to which (-O-CF_2-CF(CF_3)-O-CF_2-CF_2-SO_3H) side chains are attached. The SO_3H sites form ionic clusters in the dry state [6]. The ion exchange capacity (IEC) is proportional to the grafting density. When water molecules [7–14] absorbed from the environment associate with the acidic SO_3H sites a connected pore network with pores a few nm in diameter may form. For a fuel cell under working conditions protons released from the acidic sites are conducted via the pores from the anode to the cathode. The long-range transport of water and protons and the proton conductivity within PEMs increase significantly with hydration level.

Understanding of the pore networks and finding routes to enhance proton conductivity are important issues in the design of a PEMFC. In particular membranes should be cheap (the price of a Nafion membrane ~800 USD/m^2). In order to reduce CO poisoning of catalyst material, increase reaction kinetics, and to avoid a complicated water management system, efforts are devoted to the synthesis of alternative low cost polymeric membranes [15–19]. These should reveal high proton conductivities at elevated

---

E-mail address: dorenbos@ny.thn.ne.jp.

http://dx.doi.org/10.1016/j.eurpolymj.2017.09.040
Received 11 July 2017; Accepted 26 September 2017

temperature and at low a hydration level. This requires membranes for which at low λ values (number of water molecules per acidic sites) the proton channels are still sufficiently connected.

Insights from theoretical approaches can be helpful in proposing alternative architectures. For several reasons Dissipative Particle Dynamics (DPD) [20–39] is suitable for studying micro-phase separation. In DPD molecular fragments are coarse grained into beads that interact softly with each other. This allows the use of large time steps, typically of the order of 5 ps, which is O(3) times larger than in an all atom molecular dynamics (MD) simulation. Since in DPD studies (on for instance PFSA membranes [20–39]) each bead typically represents O(10) atoms, an MD simulation would require ~10 times more particles to study a system of similar size. Also unphysical bond crossings that occur during a conventional DPD simulation may result in a further speeding up towards equilibrium-like morphologies as compared to MD. As a results of these advantages morphologies close to equilibrium for large system volumes (O (10^4 nm^3)) can be obtained without sacrificing too much computational time.

The performance of PEMs is usually compared with that of Nafion1200 (Nafion1100) membranes, where 1200 (1100) is the equivalent weight (EW) which refers to the amount of grams per mole of sulfonic sites. Various modeling studies have been performed on Nafion1200. DPD simulation results on Nafion1200 confirm a water cluster size increase [20–23] with hydration level and also calculated Bragg spacings [20,21] agree with experiment [7,14]. DPD morphologies obtained for Nafion of several EW served also as input for Monte Carlo (MC) tracer diffusion calculations on a high resolution grid (64 million nodes) [21]. Using that approach the DPD pore network could be fixed in time and polymer motions were effectively frozen. Experimental water diffusion in Nafion1200 that contain 10–30 vol% water ($\varphi_w = 0.1$–0.3) could be reproduced when the water mobility within the nano-pores is assumed to be near that of water molecules in pure water [21,22].

To deepen the understanding of how pore morphology and water diffusion depend on polymeric architecture Dorenbos et al. [26–34] combined DPD with MC tracer calculations for a variety of architectures that only contain hydrophobic A and hydrophilic C beads. Most parameters were kept fixed such as the mutual interactions between A and C and W (water containing) beads and water volume fraction $\varphi_{w,}$ but the architectures were systematically varied. At fixed φ_w for architectures of the same IEC (with C bead density ($|C|$) within the range $0.1 < |C| < 0.2$) those architectures with C beads end grafted to equidistantly distributed side chains the MC derived water diffusion constant increases with side chain length [27]. This is in line with results from coarse grained (CG) molecular dynamics (MD) studies [40]. Furthermore, for fixed side chain length diffusion increases with IEC [21]. Moreover higher diffusion constants and larger pores are predicted for architectures with side chains non-uniformly distributed than for a regular distribution [22,28]. MD studies by Jang et al. [41] also revealed that for a distribution with the side chains at one end of the backbone water and proton diffusion and pore sizes within Nafion are higher than for a uniform distribution. The consistent trends observed for (CG)MD [40,41] and DPD studies support the usefulness of DPD for finding relations between morphology, water diffusion and polymeric architecture.

When interpreting DPD results it is convenient to plot structural (pore size and inter cluster distances) and dynamical (water diffusion constants and percolation thresholds for diffusion) properties vs the parameter $< N_{\text{bond}} >$ [29,30]. For a particular polymeric architecture $< N_{\text{bond}} >$, is defined as the average number of (A-A and A-C) bonds that hydrophobic A beads are separated from the *nearest* hydrophilic C bead within that architecture. It turns out that for fixed water volume fraction φ_w in general the inter pore distances, $D_{\text{Cl-Cl}}$, increase linearly with $< N_{\text{bond}} >$. Furthermore, for similar IEC membranes an increase of water diffusion and decrease of percolation threshold is expected with increase of $< N_{\text{bond}} >$. For architectures that contain branched side chains (*bsc*) $< N_{\text{bond}} >$ is high (eg. Fig. 7 in Ref. [32]) and DPD simulations indeed predict the fastest water diffusion [30,31] and lowest percolation thresholds [30] when compared to long side chain (*lsc*) and short side chain (*ssc*) architectures with smaller $< N_{\text{bond}} >$ values. The water containing pores (or channels) may also serve as the diffusive pathway for protons. Therefore for similar IEC and hydration level membranes that contain branched side chains might be good candidates in realizing high proton conductivities.

Chang et al. [42] measured the proton conductivity for a series of membranes (IEC ~2 mmol/gr) at relative humidity between 20% and 98%. The proton conductivity, σ^{H+}, was ~3 to 2 times less for *ssc* architectures that contain short $-OCF_2SO_3H$ side chains than for *lsc* architectures with the longer $-OCF_2CF_2SO_3H$ side chains [42]. Despite of slightly larger water uptake and IEC, the lowest σ^{H+} was measured for the *ssc* membrane. For their *bsc* polymers with (symmetrically) branched fluoro-alkyl sulfonate side chains σ^{H+} was much higher than for the *lsc* architectures. This increase in conductivity ($\sigma^{H+}_{ssc} < \sigma^{H+}_{lsc} < \sigma^{H+}_{bsc}$) agrees with increase in $< N_{\text{bond}} >$.

The apparent strength of DPD to predict the dependence of both pore network morphology and (water or proton) diffusion property on polymer architecture suggests that synthesizing architectures that maximize $< N_{\text{bond}} >$ may be appealing as a design route to obtain membranes with large and good connected pores and enhanced transport properties. In recent DPD studies on (hydrophobic-amphiphilic) di-block [26,32] and (hydrophobic-amphiphilic-hydrophobic) tri-block [43] copolymer architectures indeed a systematic increase of water cluster size and water diffusion with $< N_{\text{bond}} >$ was found. With respect to their application in PEMs the proton conductivity is of much more importance. Since the proton diffusion pathway within a membrane is similar to that of water, proton diffusion constants are also expected to increase with $< N_{\text{bond}} >$. But in order to realize high proton conductivities, a second requirement of a high proton concentration needs to be fulfilled. This requires a high IEC membrane. However for a pure component high IEC membrane $< N_{\text{bond}} >$ values will always be low which impairs the formation of a good connected proton diffusion pathway.

In this modeling study two recently gained insights are combined in order to try to achieve high proton conduction. This is done by proposing polymer blends in which a host polymer membrane is blended by a dopant polymer. Firstly, since the pore size and water diffusion constant increase with $< N_{\text{bond}} >$ a host polymer membrane with high $< N_{\text{bond}} >$ _value is selected. For this purpose a di-block (amphiphilic-hydrophobic) copolymer architecture for which the amphiphilic block contains branched side chains is