

Ab initio study of interfacial correlations in polymer electrolyte membranes for fuel cells at low hydration

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Abstract

Polymer electrolyte membranes (PEMs) are the critical components of polymer electrolyte fuel cells (PEFCs). Proper operation of current PEMs hinges on sufficient amounts of water as the medium for proton conduction. Membrane dehydration, thus, causes failure of the fuel cell. For the design of advanced PEMs it is of foremost interest, whether high-proton mobility could be attained at low hydration and elevated temperature (>100 °C). Under such conditions structural correlations and interfacial proton transport at acid-functionalized hydrated polymer aggregates are vital for membrane operation. We consider a minimally hydrated, densely packed array of proton-binding surface groups as a model of microscopic interfacial elements in PEMs. Terminating carbon atoms of these surface groups are fixed at the positions of a regular hexagonal array. We explore the role of density, chemical architecture, and conformational flexibility of surface groups on interfacial correlations and acid dissociation. The transition from highly ordered to clustered conformations occurs at the same critical density of surface groups for all systems. For longer polymeric sidechains, the formation energy at the most stable conformation decreases slightly, while the range of 2D correlations extends to markedly reduced densities of surface groups.

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1. Introduction

Due to their unrivaled thermodynamic efficiencies, high-energy densities, versatility, and ideal compatibility with hydrogen as a fuel, polymer electrolyte fuel cells (PEFCs) are widely considered as a primary solution to the global energy challenge [1,2]. They could replace internal combustion engines in vehicles and provide power to portable and stationary applications. The successful introduction of PEFC hinges, however, on the development of advanced materials and the engineering of cells and stacks that optimize power density at given cost and lifetime. Decisive progress is expected from the development of advanced functional polymer electrolyte membranes (PEMs) [3–8]. The electronically insulating, proton-conducting

PEM separates anodic and cathodic reactions in a PEFC. This spatial separation enables the direct conversion of chemical into electrical energy.

As the critical functional component in PEFCs, the proton-conducting material determines the operational range and the principal layout of the fuel cell. Over the last 30 years, NafionTM ionomer, invented by E.I. DuPont de Nemours in the mid-1960s has been the primary choice in PEFCs due to the high durability and proton conductivity. In contact with water hydrophobic and hydrophilic polymer constituents self-organize into a phase-segregated random structure that bears water-filled pathways for the transport of protons. Mobile protons result from the dissociation of hydrophilic acid groups (mainly SO₃H). Polymeric sidechains, which bind the hydrated anions (–SO₃[–]), remain fixed at the surface of hydrophobic polymer aggregates, where they form a charged, flexible interfacial layer relative to which protons and water molecules move.

Under normal operating conditions, there is no principal problem with the level of performance of current PEMs. Nafion-

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type membranes meet the requirements of fuel cell developers in terms of proton conductivities at high water content w ($\sigma_p \sim 0.01\text{--}0.1\text{ S cm}^{-1}$ at 30°C and relative humidity in the range of 30–100%), and stability. The major issue, aside from the currently high cost, is the dependence of structural and operational characteristics on water as the working liquid. This incurs the problem of water management in PEFCs in all components and at all scales. At high w , current PEMs promote excellent proton conductivities through low activation energies of proton transport (PT), high concentrations of mobile protons, and well-connected water networks [9–11]. These PEMs operate poorly at elevated temperatures ($>80^\circ\text{C}$) due to the evaporative loss of water. Moreover, at high-current densities the electro-osmotic drag effect causes membrane dehydration close to the anode side. Low humidification extinguishes the most favorable mechanism of structural diffusion of protons in bulk-like water [12,13].

Tremendous efforts at the materials science front explore the design and fabrication of anhydrous proton conductors that are completely independent of the presence of water for their performance [7,8,14–17] or membranes that retain sufficient proton conductivity under minimal hydration [18,19]. Such materials would help expanding the operational range flexibility of fuel cells with proton-conducting electrolytes, enabling sustained operation at $T > 100^\circ\text{C}$.

There is thus a great interest in the theoretical understanding of conditions, for which aqueous-based PEMs could attain high rates of proton transport with a minimal amount of water that is tightly bound to a stable host polymer. Under these conditions, proton transport is largely controlled by the complex interfaces between polymeric aggregates and water in nanochannels. In the limit of low hydration, the interfacial regions between polymer aggregates and water play a vital role for structure and performance of PEMs.

Our studies focus on understanding the structural correlations and molecular mechanisms of proton transport at such interfaces. We strive to rationalize dependences of lateral proton migration on packing density of proton-binding surface groups (SGs), tethered to the interface, length and chemical structure of the polymeric sidechains, and their flexibility. Further incentive for these efforts stems from a number of experimental studies, which suggest that proton mobility along cellular membranes and lipid monolayers could be rather high at a critical packing density of protogenic SGs—approaching 1/2 of the value of the proton mobility in bulk water [20–23].

In spite of their obvious ubiquitous importance for biophysical processes and proton-conducting materials, molecular mechanisms of PT at dense interfacial arrays of surface groups are rather unexplored. In principle, studies on structural correlations and surface-mediated mechanisms of proton transfer in these environments require *ab initio* quantum mechanical calculations based on density functional theory (DFT). Complicating traits for these calculations are the structural complexity and the rarity of proton transfer events. The former defines a need for simplified model systems. The latter enforces the use of advanced computational techniques that permit an efficient sampling of rare events [24–28].

Ab initio simulations in PEM based on density functional theory were employed by Paddison and Elliott to study correlation effects and proton exchange at hydrated sidechains attached to a single polymer strand [29–32]. These approaches ignored, however, vital correlation effects that arise in conformations of 2D interfacial arrays of SGs. As we will discuss below, such effects dramatically influence hydrogen-bond formation, acid dissociation, and flexibility of SGs at hydrated interfaces.

A trifluoromethane sulfonic acid monohydrate (TAM) solid was explored in Ref. [33]. The regular structure of the crystal provides a proper basis for controlled *ab initio* molecular dynamics. These simulations revealed the transition of the native crystal structure, with localized positions of protonic charges, to an activated state with two delocalized protons. The energy of formation for the activated state is approximately 0.3 eV. These results suggest that an appropriate flexibility of anionic sidechains could be vital for high proton mobility in PEMs under conditions of minimal hydration and high anion density. Furthermore a drift of the Zundel-ion was observed, which suggests its role as a relay group for proton shuttling between hydronium ions or sulfonate anions. Molecular simulations based on the EVB approach, applied for instance by Petersen and Voth [34] or Spohr et al. [35] or continuum dielectric approaches [11,36] have dwelled as well on the role of acid-functionalized SGs on proton conduction mechanisms in water-filled pores of PEMs. However, these approaches utilize empirical correlations between interfacial structure and mechanisms of proton transport.

Our *ab initio* calculations presented in Ref. [37] targeted explicitly at understanding of structural correlations and dynamics at acid-functionalized interfaces between polymer and water in PEMs. Interfacial arrays consisting of the shortest SGs, i.e. $\text{CF}_3\text{SO}_3\text{H}$ and $\text{CH}_3\text{SO}_3\text{H}$, were considered under conditions of minimal hydration, i.e. with one H_2O per group. The main parameter in those calculations was the nearest neighbor distance of C atoms, d_{CC} . In this publication, we employ this model to explore the role of chemical architecture and packing density of sidechains on acid dissociation, interfacial correlations, and conformational transitions at the interface.

2. Model system and parameters

The model system introduced in Ref. [37] emerges from the self-organized morphology of the membrane at the microscopic scale that is shown in Fig. 1(a). It mimics microscopic interfacial elements that are likely to control proton conduction in hydrated PEMs under conditions of low hydration. The random array of hydrated and ionized sidechains is tethered to the surface of aggregated hydrophobic polymer backbones. Relevant structural properties include the shape, thickness, persistence length of aggregates, as well as the chemical properties and packing density of sidechains attached to their surface. In order to obtain a computationally feasible model for *ab initio* calculations, it is assumed that to a first approximation the highly correlated interfacial dynamics of sidechains, protons and water decouples from the dynamics of the polymeric aggregates. The supporting

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