

Coarse-Grained Molecular Dynamics Simulation of Perfluorosulfonic Acid Polymer in Water–Ethanol Mixtures

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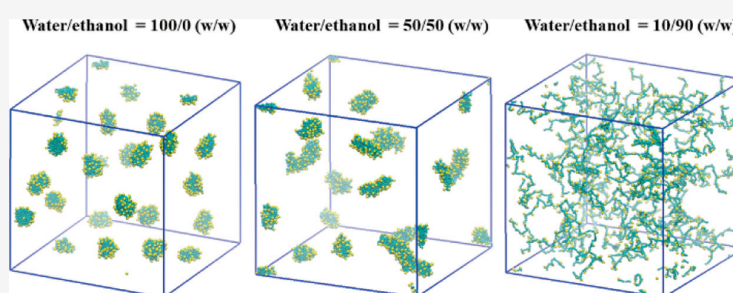
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ABSTRACT: The aggregation behavior of perfluorosulfonic acid (PFSA) ionomers in a solvent is crucial for the fabrication of catalyst inks for fuel cell applications. In this study, we extended a previous coarse-grained (CG) model of PFSA in water to water–ethanol mixtures following the concept of the Shinoda–DeVane–Klein force field. The constructed CG force field was adopted to investigate the ionomer structures in water–ethanol mixtures using molecular dynamics (MD) simulations. The CG–MD simulations demonstrated that PFSA ionomers form cylindrical-like particles in solutions with ethanol concentrations ≤ 50 wt % and random coil conformations at higher ethanol concentrations. The formation of the cylindrical structure at low ethanol concentrations was attributed to the presence of strong electrostatic interactions among the charged groups, while the more polymer/solvent interfacial attraction and larger conformational entropy of PFSA chains at high ethanol concentrations cause a highly solvated structure. The findings of this study will be highly beneficial for designing ionomer dispersions for catalyst ink fabrication.

1. INTRODUCTION

Perfluorosulfonic acid (PFSA) ionomers, such as FORBLUE i-SERIES and Nafion, have been widely used in proton exchange membranes for fuel cell applications.¹ A general chemical structure of PFSA ionomers comprising a hydrophobic polytetrafluoroethylene backbone and hydrophilic side chains terminated by sulfonic acid moieties is shown in Figure 1a. Their amphiphilic properties promote the nanoscale phase separation between the hydrophobic and hydrophilic domains in hydrated PFSA membranes. Therefore, the dissociated protons from sulfonic acid moieties can be transferred through these phase-separated hydrophilic domains. Thus, owing to their unique structure-driven multifunctionality, PFSA ionomers have been regarded as prototypical materials for energy-conversion devices.²

Recently, there has been an increasing interest in understanding the behavior of PFSA ionomers in the fuel cell catalyst layers (CL), wherein they provide the required mechanical integrity.^{3,4} Furthermore, ionomers in the CL play a crucial role in transporting reactants and products between ionomers and catalytic sites (e.g., Pt) on a carbon support.^{3,4} A lower ionomer content results in a larger electrical resistance, which can be attributed to the insufficient contact between ionomers

and Pt particles. In contrast, a higher ionomer concentration increases the surface contact; however, the thicker ionomer layer increases the oxygen transport resistance. Hence, it is necessary to control the ionomer structure to form a uniform and thin layer on the CL. The CL microstructure is fabricated by coating and drying catalyst ink, which is composed of Pt-supported carbon, ionomers, and dispersion solvent, on the electrode. The interactions among the catalyst, ionomers, and the solvent in the catalyst ink as well as the evaporation of the solvent affect the final structure and performance of the CL. Therefore, it is challenging to control the ionomer structure covering the catalyst surface uniformly. Because ionomers in polar solvents, such as water and alcohol, form cylindrical particles consisting of a central hydrophobic backbone core surrounded by ionic groups, avoiding the self-aggregation of

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