



Molecular Dynamics Study of Ionomer Adsorption at a Carbon Surface in Catalyst Ink



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ABSTRACT

Ionomer adsorption at the surface of a graphite sheet in a solvent-saturated environment was examined using molecular dynamics simulations. The amount of ionomer adsorbed on the graphite surface greatly depended on the equivalent weight (EW) of the ionomer and the alcohol content in the solvent. The maximum ionomer coverage was obtained in water-rich solvent for low EW ionomer, while the addition of alcohol to the solvent was necessary to enhance adsorption of high EW ionomer. The ionomer coverage at the surface with ionized functional groups was lower than that of the bare graphite surface, which indicated a significant effect of the electrostatic repulsive interaction between negatively charged functional groups and sulfonic acid groups on the ionomer adsorption. The effect of the alcohol content and EW of the ionomer on ionomer coverage still remained even in the presence of strong electrostatic interactions between sulfonic acid groups and the functionalized carbon surface.

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1. Introduction

Polymer electrolyte fuel cells (PEFCs) are promising power sources for automotive use. The reduction of cost is the most significant issue for the large-scale commercialization of PEFC vehicles [1–4]. A membrane electrode assembly (MEA), which consists of a polymer electrolyte membrane (PEM), catalyst layers (CLs), microporous layers (MPLs), and gas diffusion layers (GDLs), is the central component of a PEFC. The CL is a random porous medium, which is attached directly to the PEM. It generally consists of Pt nanoparticles dispersed on porous carbon supports and proton conducting ionomer. Pt loadings of current CL designs incur a major portion of the material costs in PEFCs [4]. Therefore, it is of vital importance to reduce Pt usage in the CLs without sacrificing PEFC performance.

A sulfonated tetrafluoroethylene copolymer is typically used as the proton-conducting ionomer in a CL. The ionomer is essential for proton transport, while an excess amount of ionomer inhibits both electrochemical reaction and mass transport of reactant gases [2,5–12]. The optimum design of ionomer structure and

distribution in CL is strongly desired to achieve an inexpensive PEFC with lowered Pt loading in the CLs.

Despite the importance of structure control of the ionomer in the CL, the mechanism of structure formation of the ionomer has been elusive for years because of the complexities and large number of controlling parameters in the fabrication process. The fabrication process of the CL includes an ink preparation process and a coating process. In the former process, the materials composing the CL are mixed and dispersed in the solvent. A blend of water and alcohol is typically used as a dispersion medium for Pt-supported carbon and ionomer. The composition of the dispersion medium, the choice of alcohol, solid contents, and mixing conditions are major controlling parameters in the ink fabrication process. The catalyst ink is deposited on a substrate or directly onto a PEM. The screen printing, die coating, or spray-coating is a major choice for the deposition method. The CL structure is finally formed after drying the deposited CL ink at elevated temperature.

Many studies have been conducted to determine the mechanism of structure formation of the CL and its impact on PEFC performance. Uchida et al. aimed to control the segregation of ionomer in catalyst ink by controlling the dielectric constant with various organic solvents [13]. They pointed out that the optimum segregation of ionomer was obtained in the solvent with dielectric constant from 3 to 10. Similar results were reported by Shin et al.

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and Fernandez et al. [14,15]. Ngo et al. investigated ionomer morphology in catalyst ink and its impact on PEFC performance with different alcohol contents using the Cryo-TEM technique [16]. They found that ionomer morphology was dominated by the solubility parameter and dielectric constant of the solvent. In their study, PEFC performance increased with increasing solubility parameter and dielectric constant of the catalyst ink, which corresponds to a decrease in alcohol content in the solvent. Although their study provides useful insights into the structure formation of ionomer in catalyst ink, the observed trend is contrary to previous studies by other researchers [13–15].

Recently, more fundamental studies had been undertaken for a better understanding of CL ink structure formation. Koestner et al. investigated the impact of alcohol content of the solvent on ionomer adsorption at highly oriented pyrolytic graphite (HOPG) using *in situ* liquid atomic force microscopy (AFM) [17,18]. They concluded that ionomer adsorption on the carbon surface was dominated by electrostatic interaction between the HOPG surface and negatively charged sulfonic head groups of the ionomer, which was controlled by the dielectric constant of the solvent. Although their findings provided useful insight into the adsorption behavior of an ionomer single rod on the carbon surface, the influence of aggregation of ionomer rods was not considered because of the highly diluted ionomer solution in their experiments.

Ma et al. investigated the amount of adsorbed ionomer on carbon materials by measuring the ionomer concentration in the supernatant solution that was obtained by the centrifugal separation of the catalyst ink by ^{19}F nuclear magnetic resonance spectroscopy (NMR) [19]. According to their results, ionomer was primarily adsorbed on Pt/C following a Langmuir isotherm at low concentration. The amount of adsorbed ionomer was dominated by the chemical properties of the Pt/C surface. Shibayama et al. applied a contrast-variation-small-angle neutron scattering (CV-SANS) method to study the detailed structure of catalyst ink [20,21]. Two domains of ionomer in the catalyst ink were revealed, the ionomer shell domain with thickness of ca. 10 nm adsorbed on the outer surface of carbon aggregates, and the free ionomer domain floating between carbon aggregates. They also pointed out the importance of nonadsorbed ionomer for formation of proton-conducting pathways in the CL. Recently, more direct observation of catalyst ink structure was achieved by applying a cryogenic scanning electron microscopy (Cryo-SEM) method.

Takahashi et al. observed two sizes of the Pt/C aggregates in catalyst ink surrounded by an interconnected ionomer network [22]. According to their results, the ionomer played a key role in the formation of small Pt/C aggregates. The alcohol content in the solvent influenced the number of small aggregates, and as a result, this affected the proton conductivity, gas permeability, and catalytic activity of the CL. These experimental studies clearly indicated the importance of controlling the amount of ionomer adsorbed on the Pt/C surface based on a fundamental understanding of ionomer adsorption at the Pt/C surface to optimize the CL performance. Although the surface property of Pt/C and alcohol content of the solvent were two major parameters that determined ionomer adsorption at the Pt/C surface, the detailed mechanism of the adsorption process is still controversial.

Molecular dynamics (MD) simulation is a valuable theoretical technique to predict structural or transport properties with consideration of molecular-level interactions. It has been applied to examine the molecular structure of ionomer and its influence on the proton transport in the bulk membrane [23–31], the molecular structure of ionomer and water at the interface of Pt/C in CLs [32–36], and reactant gas permeation through the thin ionomer [37–40]. Malek et al. performed a simulation based on coarse-grained molecular dynamics to study the self-organized microstructure formation of catalyst ink [41,42]. The simulation led to a phase-segregated structure consisting of aggregated carbon particles surrounded by ionomer. The morphology of the ionomer depended on the dielectric constant of the solvent and surface properties of the carbon aggregates. Although their simulation provided important insights into the structure formation of the ionomer in catalyst ink, the molecular structures of ionomer, carbon, and solvent were not explicitly considered in the simulation, so that the detailed mechanism of ionomer adsorption at the carbon surface is still not clear.

In the present study, we performed atomistic molecular dynamics simulations of ionomer adsorption on a carbon surface in catalyst ink. Three ionomers with different concentrations of sulfonic head groups were employed in this study. First, we investigated the morphology of the ionomer in the bulk solution to study fundamental structural pictures of ionomer dispersed in the solvent. Thereafter, we performed MD simulations, inserting the graphite carbon sheet to study ionomer adsorption on the carbon surface. We analyzed ionomer coverage on the carbon surface with

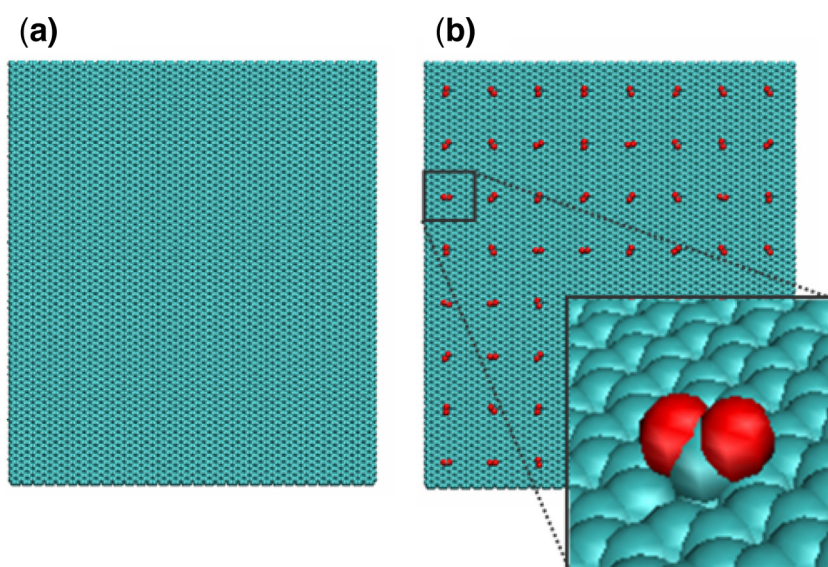


Fig. 1. Illustration of graphitized carbon sheet (a) and graphitized carbon sheet with 64 ionized carboxylate ion groups (b).

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