CHAPTER 5

CONCLUSION

Since polymer membrane and catalyst are essential for fuel cell performance, this research was carried out to investigate the microscopic properties contributed from their atomistic behavior. The simulations of modified fuel cell materials in various aspects i.e. Krytox-silica composite Nafion membrane, bombarded Nafion surface, synthesized Fe-N_x/C catalyst carbon, and N-containing alternative material, were carried out in this dissertation.

For MD simulations of 5% wt of Krytox-silica in Nafion and pure Nafion systems, study considering the effects of temperature and water content in the materials was accomplished. MD simulations at temperatures of 298, 333, 353, and 373 K with the associated water content of 1,766, 883, 527, and 354 molecules, respectively, were used and compared with published experimental data. The diffusion coefficient of H_3O^+ was used to analyze the proton diffusion efficiency. The effect of the amount of water molecules on the diffusion coefficient or proton conductivity was showed. A greater deviation in 5% wt of Krytox-Silica in Nafion from pure Nafion systems was observed. The RDF was used to follow molecular interaction. The hydrophilicity of the material was indicated by the interactions of SO_3^-- water, SO_3^-- H_3O^+, and H_3O^+-water. Strongly interaction of H_3O^+ and water molecule was found. During MD simulation, the Zundel-like ion was observed. The lower amount of

H_3O^+ distributed around SO_3^- than that water can describe SO_3^- could move easily between side chain or did not stay long time when compared with water distributed around SO_3^- or H_3O^+. In silica part, the strongly interaction of water and hydroxyl group of silica was observed which responds with hydrogen bond distance. This MD result can describe the possibility of absorbent acting of silica and the adding of 5% wt of Krytox-silica in Nafion could be used for fuel cell application at high temperature.

In surface modification aspect, simulations of Ar^+ beam bombardment on Nafion and deposition of plasma coating on carbon were accomplished by MD and MC simulations. The information achieved from MD simulation can reveal the chemical and physical change of Nafion with respect to Ar^+ initial energy and doses. The variation of Ar^+ kinetic energies of 0.5, 1.0, 1.5, 2.0, 2.5, and 3.0 eV, at a dose of $1x10^{14}$ ions/cm^2, was studied in MD simulation. While the variation of Ar^+ doses of $1x10^{14}$, $5x10^{14}$, and $1x10^{15}$ ions/cm^2 at 1.0 keV was designed to study the ion dose effect. The surface area of Nafion was found increase. The potentially breaks the C-S bond, leading to SO_3^- sputtering decreasing the hydrophilicity of the bombarded Nafion was observed. The percentage of potentially C-S bonds broken in the system for all Ar^+ energies are relating with the experimental SO_3^- sputtering measured by in-situ mass spectroscopy. In addition, the calculated results suggest a possible threshold at 2.0 keV. For MC simulation of plasma deposition on carbon model, iron and nitrogen plasma on carbon model indicated the different interaction among plasma species. The deposition of nitrogen within 3.5 Å of carbon model are in better distribution than that of iron.

From this result, nitrogen plasma should be sputtered at first step to activate surface for catalyst formation.

In the study of proton transfer in N-containing alternative material, the proton transfer barrier calculation and diffusion efficiency were carried out by using DFT method and DFT-MD simulations. To mimic the real proton transfer in the PEMFC working condition, electric field effect was included. The energy barriers of proton hopping and molecular orientation were investigated explicitly. The proton transfer energy barrier was found depended on the inter-molecular distance, structural orientation, and electric field direction, indicating by the change in potential energy profiles of proton transfer and trajectory from DFT-MD simulations. Higher proton diffusion coefficient was found in the system with the applied electric field in parallel to the transfer direction.