QM/MM dynamics of Proton Transport in Chitosan/Phosphotungstic Acid Composite Membrane for Direct Methanol Fuel Cell

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Abstract-The aim of this research is to study proton transport in DMFC using chitosan/phosphotungstic acid (CS/PWA) composite membrane as Proton Exchange Membrane (PEM). Model of proton transport mechanism was proposed in order to investigate the proton transport rationality in CSPWA composite membrane, which is indicated by energy models. QM/MM dynamics method on the basis of CP2K code was used to calculate energy of the models. Results showed that the model of proton transport mechanism produced energy gradient. Interaction model of proton (H^+ ion) and CS/PWA hydrated membrane has minimum QM/MM energy than the other models. The value of QM/MM energy of H^+-CS/PWA hydrated is -312.717135970308 a.u.

Index Terms-Proton transport, QM/MM dynamics, Chitosan, Phosphotungstic acid, Composite membrane, DMFC.

INTRODUCTION

Proton transport (PT) plays an important role in Direct Methanol Fuel Cell (DMFC). PEM that connects reaction between the cathode and the anode decided the ability of membrane to transport proton from the cathode to the anode. CS is a copolymer of glucosamine and N-acetylglucosamine which has many excellent properties such as biocompability, nontoxicity, chemical and thermal stability, thus it has been widely studied as a promising membrane materials. PWA ($H_3PW_{12}O_{40}$), possess a unique discrete ionic structure and exhibits extremely high proton conductivity. Experimental study reported that modification of biopolymer chitosan (CS) and complex agent phosphotungstic acid (PWA) formed composite membrane which produces proton conductivity of membrane 2.4 x 10^{-2} S cm^{-1} at temperature 80°C [1].

In theoretical study, proton (H^+) react to the surrounding water form hydroinum ion (H_3O^+), then the hydronium ion transport to the Nafion polymer membrane by hopping mechanism [2]. Interaction detail between chitosan and phosphotungstic acid in composite membrane not reported yet theoretically. However, despite extensive study, the molecular-level details of membrane morphology, proton hopping, and small molecule transport are poorly understood, because the dynamical processes at subnanometer and subnanosecond scales are not readily accessible to experiments [2]. Therefore, studies of rationality proton transfer in membrane have been paid more attention for both experimental and theoretical research.

In this paper, we investigate energy QM/MM of the proton transport model in mechanism of CS/PWA composite membrane. The following QM/MM dynamics are carried with CP2K code, which provides a general framework for DFT using a mixed Guassian and plane waves approach and classical pair and many-body potentials [3]. CP2K code is a open source molecular dynamics program to perform atomistic and molecular simulations.

MATERIAL AND METHODS

The model used to QM/MM calculation are fragment of one molecule chitosane and phosphotungstic acid, two molecule water, one hydronium ion (H_3O^+) and one proton (H^+). The models are shown in Figure 1. The primary software that used to calculate QM/MM method is CP2K package that consist of CP2K code and data (version 2.2.426-6). Additional softwares used are Avogadro (version 1.0.3-5), Bluefish Editor (version 2.2.2-1) and Visual Molecular Dynamics (VMD) version 1.9.1. All software are open source that ran in Linux operation system. The type of Linux is Ubuntu 12.04 LTS (Precise Pangolin) 64 bit. The hardware used is a Notebook that has specification i.e. Random Acces Memory 4GB DDR3, inte core i5, and NVidia GeForce 720M.

Preparation for calculate QM/MM started by build model using Avogadro. Avogadro software also used to minimize the structure model to remove bad contacts and reach closet local minima, that process called minimize energy. The next step, optimize geometry models using CP2K with run type job GEO_OPT. The last step,

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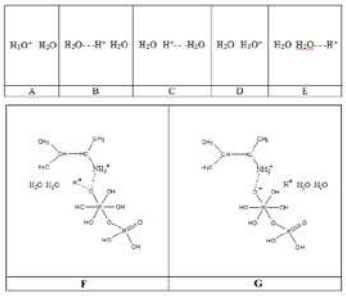

Figure 1. The 2D Model of proton transport mechanism in CS/PWA composite membrane.

simulate QM/MM method to get excited-state dynamic by using CP2K code. The QM/MM parameter that used i.e. ensemble NVT (number of atom, volume dan temperature) constant, temperature 298 K, cell volume 12 x 12 x 12 Å, canonical through velocity rescaling (CSVR) thermostate type, Goedecker- Teter-Hutter (GTH) pseudopotential, Becke-Lee-Yang-Parr (BLYP) functional, GTH and GPW (Gaussian and Plane Wave) basis set, and boundary condition 0.5 femtosecond. The result of QM/MM method visualized by VMD software.

RESULTS AND DISCUSSION

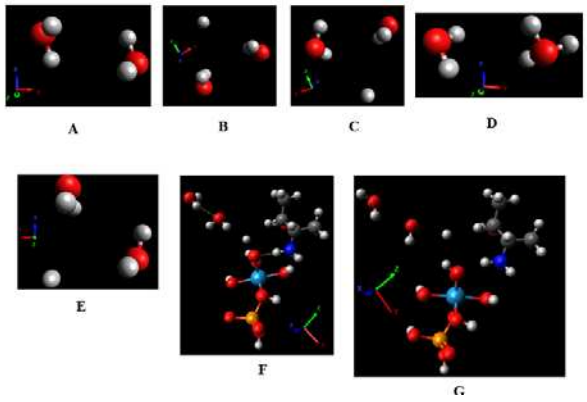

Figure 2. The 3D model of proton transport mechanism in CS/PWA composite membrane (red: oxygen, white: hydrogen, grey: carbon, deep blue: nitrogen, sea blue: tungsten, and orange: phosphate).

The modeling mechanism of proton transport followed step in Figure 1. 3D model have been build and minimized by Avogadro are shown in Figure 2. In that case conjugate base from amina protoned (NH_3^+) from chitosane dan ion WO^- from phosphotungstic acid are defined as quantum box, which will be simulated with Quantum Mechanics (QM), and the others with Molecular Mechanics (MM). It should be pointed out that water are excluded out of the QM region. Model A consist of one hydronium ion and one molecule water, B consist of propagation loss of H^+ ion from the ion hydronium and one molecule water, C consist of one molecule water and interaction of H^+ and water, D consist of one molecule water and one hydronium ion, E consist of one molecule water and interaction of H^+ and water, F consist of two molecule water and interaction of H^+-monomer CS/PWA, and G consist of monomer CS/PWA that has loss H^+ and two molecule water.

Figure 3 shown that position of H+ ion, hydronium ion, molecule water, and interaction of H+ and fragment CS/PWA give different interaction and resulted different QM/MM energy. Model A to F give energy gradient form high to low energy, its mean that dynamics of proton transport will be rationality occur from high energy to low energy. Model F has minimum QM/MM energy than the other models. It's mean that interaction of CS/PWA composite membrane and proton rationality occur and the proton interact electrostatically. The value of QM/MM energy of H+-CS/PWA hydrated is -312.717135970308 a.u. Model G give energy higher than F, its about 0.010248465 a.u, because of the model stability is H+ ion interact to atom O of W-O bond in PWA fragment (model F). Model G shown that proton back interact to the free water.

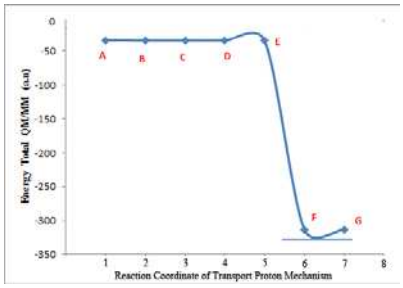

Figure 3. Graphic of QM/MM total energy in different model

CONCLUSION

The result of this research are model of proton transport mechanism in CSPWA composite membrane rationality occur. The interaction of proton in form H+ ion and CS/PWA membrane has lowest QMMM energy of the other model. The QMMM energy of H^+-CS/PWA hydrated is -312.717135970308 a.u., its energy shown that this model most stable configuration structure.

REFERENCES

[1] Cui, Z., Liu, C., Lu, T., dan Xing, W.,"Polyelectrolyte complexes of chitosan and phospotungstic acid as proton-conducting membranes for direct methanol fuel cells". Journal of Power Sources, 167, 94-99, 2007.

[2] Devanathan, R., Idupulapati, N., Bear, M.D., Mundy, C.J., dan Dupuis, M., "Ab Initio Molecular Dynamics Simulation of Proton Hopping in a Model Polymer Membrane", *Journal of Physial Chemistry*, 117, 16522−16529, 2013.

[3] Zhang, G. and Xie, S., "Temperature and Electric Field Effect on Proton Transfer in Adenine-thymine", *Bull. Korean Chem. Soc*., Vol. 35, No. 12, 2014.