COMPUTATIONAL STUDY OF PROTON TRANSFER IN RESTRICTED SULFONIC ACID FOR PROTON EXCHANGE MEMBRANE FUEL CELL

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A dissertation submitted in partial fulfillment of the
requirements for the award of the degree of
Master of Science (Chemistry)

Faculty of Science
Universiti Teknologi Malaysia

JUNE 2014

DEDICATION

To my beloved mom and dad

ACKNOWLEDGEMENT

First of all, I thank Allah S.W.T. for giving me opportunity to embark on my Master degree and for completing this long and challenging journey. My gratitude goes to my beloved supervisor, Dr. Hasmerya Maarof, who had guide me all the way and given me full support and all the guidance as well as the advices while completing this project. My appreciation for her time and patience would not be able to express in words.

Special thanks to my seniors and our research group members who have been there to help and guide me in the progress of completing this project report. They had given me worthy advices and suggestions for my research and have provided assistance at various occasions. Their tips and advises are very useful indeed.

Last but not least, I would like to express my token of appreciation to my beloved supportive family especially my parents. The supports and encouragement given during this duration of final year project was so much motivating. This piece of victory is dedicated to both of you. Alhamdulillah.

ABSTRACT

Interest in the use of fuel cell as highly efficient, clean energy conversion device has been rapidly increasing over the past twenty years. Currently, proton exchange membrane fuel cells (PEMFC) are regarded as the paramount type of fuel cell due to their wide range of applicability. Perfluorosulfonic acid (PFSA) ionomer Nafion® by DuPont remains the typical membrane in PEMFC under development today, despite well recognized drawbacks which include limitations in thermal stability. Recent studies have found that although the polymer-zeolite composite membranes have lower value of proton conductivity than Nafion®, polymer-zeolite composites show a more stable performance at high temperature. In this study, the proton transfer mechanism of zeolite functionalized sulfonic acid with water molecules is investigated using density functional theory (DFT) calculation at PM3/ONIOM(B3LYP/6-311G(d,p):PM3) level of theory. The systems were constructively built up by modifying the crystal structure of Linde Type A (LTA) zeolite functionalized sulfonic acid side chains, by varying the degree of separation of sulfonic acid side chains (2T, 3T and 4T) as well as the alkyl chain length (n=3, 5, 7) in order to study the effect of proton transfer at different distance and different chain length. Extensive searches for minimum energy conformations from 1 to 6 explicit water molecules revealed that 2T distance gives the best results for propyl sulfonic acid side chain, meanwhile 4T distance gives the best result for pentyl and heptyl sulfonic acid side chains, indicated by the minimum water molecules required to initiate second proton dissociation. The results have shown several agreements with previous *ab initio* calculation regarding polymeric fragments where partial dissociation of the protons in the fragments occurs at water contents of less than 3 H_2Os/SO_3H. Furthermore, we found that water distributions that facilitate a higher degree of dissociation and separation of the protons are important factors in stabilizing the fragments.

ABSTRAK

Kepentingan dalam penggunaan sel bahan api sebagai peranti penukaran tenaga yang sangat cekap dan bersih telah semakin meningkat dalam tempoh dua puluh tahun yang lalu. Pada masa ini, membran pertukaran proton sel bahan api (PEMFC) dianggap sebagai jenis yang paling utama kerana penggunaannya yang meluas. Ionomer asid perfluorosulfonik (PFSA) Nafion® oleh DuPont digunakan sebagai membran biasa dalam PEMFC hingga ke hari ini dan masih dalam penambahbaikan, walaupun terdapat kelemahan, termasuklah kurang kestabilan terma. Kajian terbaru mendapati bahawa walaupun membran komposit polimer-zeolit mempunyai nilai kekonduksian proton yang lebih rendah daripada Nafion®, komposit polimer-zeolit menunjukkan prestasi yang lebih stabil pada suhu tinggi. Dalam kajian ini, mekanisma pemindahan proton zeolit asid sulfonik dengan molekul air disiasat menggunakan pengiraan teori ketumpatan berfungsi (DFT) pada tahap PM3/ONIOM(B3LYP/6-311G(d,p):PM3). Sistem telah disimulasikan dengan memodifikasi struktur kristal zeolit Linde Type A (LTA) dengan kumpulan berfungsi asid sulfonik, dengan mengubah jarak antara rantaian sisi asid sulfonik (2T, 3T dan 4T) dan panjang rantai alkil (n=3, 5, 7) untuk mengkaji kesan pemindahan proton pada jarak dan panjang rantaian yang berbeza. Kajian struktur tenaga minimum pada 1-6 molekul air, jelas menunjukkan bahawa jarak 2T memberikan hasil yang terbaik untuk rantaian propil asid sulfonik manakala jarak 4T memberikan hasil yang terbaik untuk rantaian pentil dan heptil asid sulfonik, di mana minimum molekul air diperlukan untuk memulakan penceraian proton kedua. Hasil kajian mendapati beberapa persamaan dengan pengiraan *ab initio* pada kajian sebelum ini terhadap struktur polimer di mana penceraian separa proton dalam sistem berlaku pada kandungan air kurang daripada 3 H_2Os/SO_3H. Tambahan pula, kami mendapati bahawa pengagihan air yang memudahkan tahap penceraian dan pemisahan proton yang lebih tinggi adalah faktor penting dalam menstabilkan sistem.

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LIST OF SYMBOLS/ABBREVIATIONS

Ψ	-	Wavefunction
λ	-	Wavelength
$\hat{H}$	-	Hamiltonion operator
E	-	Total energy of particle
∇	-	Laplacian operator
V	-	Potential energy
x	-	Distance
m	-	Mass
r, θ, ϕ	-	Spherical coordinate
N	-	Normalization constant
PFSA	-	Perfluorosulfonic acid
PEM	-	Proton Exchange Membrane
PEMFC	-	Proton Exchange Membrane Fuel Cell
MEA	-	Membrane Electrode Assembly
DFT	-	Density Functional Theory
B3LYP	-	(Becke, three parameter, Lee-Yang-Par)
GTO	-	Gaussian Type Orbital
HF	-	Hartree Fock
PM3	-	Parameterized Model 3
STO	-	Slater Type Orbital
QM	-	Quantum Mechanics
MM	-	Molecular Mechanics
ZDO	-	Zero Differential Overlap

CHAPTER 1

INTRODUCTION

1.1 Background of Study

Apparently, environmental and energy saving issue have become one of crucial issue for human worldwide. In order to solve these problems, many efforts have being done to replace fossil fuels with other energy sources such as its connotation clean fuel. Fuel cells are on the edge of creating an enormous revolutionary change in the field of electricity due to their special properties. By definition, fuel cell is an electrochemical apparatus that convert the chemical energy of fuel without fuel combustion to electrical energy. Hence, in a fuel cell system, the chemical energy related to electrochemical reaction of the fuel with oxidant directly change into the water, electricity and heat.

Proton exchange membrane fuel cells (PEMFCs) have been discovered as capable power source for applications in transportation, stationary and portable device requiring clean, quiet and portable power [1]. The other major advantages include current prototype efficiency of up to 64%, high energy densities compared to batteries and the ability to operate on clean fuels while emitting no pollutants [2]. Despite these superiorities, diffusion of PEMFC technology into the market place is being limited by the cost and reliability issues [3]. According to Kreuer, research into fuel cells has grown exponentially over the last 15 years [4]. The key components in the fuel cell system are the proton exchange membranes (PEMs) itself [5]. In the case of polymer fuel cell, the major breakthrough in technology that have allowed significant improvement in the overall performance of PEMFC has been the modifications of Nafion® by Dupont.

In 1970s, a chemically stable cation-exchange membrane based on sulfonated poly-tetrafluoro-ethylene was first developed by Dupont as Nafion® leading to a large scale use of this membrane in the chor-alkali production industry and energy storage or conversion system (fuel cell). This Nafion® membrane was selected as a standard membrane for polymeric electrolyte fuel cell [6]. However, it has a number of drawbacks that need to be overcome, which is the high cost, due to its complicated system construction, the durability, and the poor performance at temperature above 80°C due to the loss of water. Besides, the CO poisoning at the anode and environmental hazards related with its dispose have caused the development of new membrane which include organic and inorganic hybrid membrane by using silica as support material [7]. This critical situation leads to the appropriate preservation and sustainable development strategies attempt to the production of green materials which are safer to users and more environmental friendly.

Performance, durability and cost are the three major properties known as "iron triangle" that need to be taken care of in order to have excellent proton exchange membrane. Hence, researches have to focus to obtain the proton exchange membrane with high conductivity, low electroosmotic drag coefficient, good chemical and thermal stability, good mechanical properties and low cost [5]. Although hydrophobic silica particles are not proton conductors, inclusion of the hygroscopic silica particles in composite solid electrolytes is primary single functional that is for water retention. Clearly, bifunctional particles, being both hydrophilic and proton conducting are preferred to be used as proton conducting material. Thus, zeolite could be one of the suitable materials with the preferred properties due to its crystalline aluminasilicate with a uniform pore size [8]. Hamdan [9] also states that nano zeolites are potential candidates to be used as proton conducting membrane instead of silica due to their significant moderate proton conductivity, excellent water retention at high temperature and molecular sieving capabilities. In addition, although the polymer-zeolite composite membranes have the lower values of proton conductivity than Nafion, polymer-zeolite composites show a more stable performance at high temperature [5]. In fact, nearly every application of zeolites has been driven by environmental concerns, or plays a significant role in reducing toxic waste and energy consumption [10].

1.2 Problem Statement

This decade, it is evidenced how our planet is being threatened by local and global environment problems as well as the consumption and supply of energy. PEMFC are one of the most promising clean energy technologies under development. The fuel cell membrane can be synthesized using different materials such as Nafion® or zeolite functionalized sulfonic acid used for PEMFC purposes. However, there is no fundamental computational study focusing on the proton transfer mechanism which occurs in zeolite PEM system which have been reported to be a better and cost effective performance material compared to Nafion® [8]. Therefore, simulation using density functional theory (DFT) calculation would help us to understand the role of each functionalized group and would eventually create a new possibility to use other type of compounds which can lead to the improvement of PEMFC material.

1.3 Objectives of Study

The aim of this research is to identify optimum condition of zeolite functionalized sulfonic acid for minimally hydrated PEMs. Thus, to achieve this aim, the related objectives are identified as follows:

1) To observe the mechanism of proton transfer in restricted sulfonic acid for PEMFC.
2) To study the effect of chain length to the proton transfer in restricted sulfonic acid for PEMFC.
3) To study the effect of sulfonic acid side chain distance to the proton transfer in sulfonic acid for PEMFC.

1.4 Scope/Limitation of Study

This study only focused on the proton transfer mechanism in restricted sulfonic acid with alkyl chain up to 7 carbons (heptyl) for PEMFC. In addition, the selection of the basis set for the DFT calculation will reflect not only the accuracy, but also the time consumed for computing the job. It is evidenced that DFT method give a faster calculation compared to *ab initio*, but the accuracy of results still depends on the type of basis set used. Therefore, a few points stated above were taken into account in order to complete this project within time.

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