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CHEMICAL DEGRADATION OF NAFION MEMBRANES UNDER PEMFC AS INVESTIGATED BY DFT METHOD

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ABSTRACT

CHEMICAL DEGRADATION OF NAFION MEMBRANES UNDER PEMFC AS INVESTIGATED BY DFT METHOD. An exsitu method has been developed to performance of Nafion's membrane in PEMFC (Proton Electrolyt Membrane Fuel Cells), caused by the chemical degradation of ·OH and ·H radicals. The change of the chemical structure occurring during the degradation were primarily calculated of the relative energy of reactions by DFT (Density Functional Theory) method approach in the Gaussian software. This study aims to determine whether DFT method with functional B3LYP, PBEPBE, and B3PW91 and base sets 6-311++G can be used in determining the relative energy of a reaction and knowing the difference in role between ·OH and ·H in the degradation process of the main chain Nafion with the final group are $-CF_2H$, $-CF=CF_2$ and -COOH. The three functionalities applied showed that the ·OH radical has more role than the ·H radical in the degradation process of the Nafion main chain. In the $-CF_2H$ group was shown the relative energy value of reaction 2 is lower than reaction 5, in the $-CF=CF_2$ group was shown the relative energy value of reaction 8* is lower than reaction 11 and in the -COOH group the relative energ value of reaction 14 is lower than reaction 16. By knowing the relative energy of the Nafion main chain degradation reaction with a certain final group and the role of certain radical compounds in the degradation process, the DFT method with functional B3LYP, PBEPBE and B3PW91 and base sets 6-311++G can recommend various modifications of the Nafion as a fuel cell membrane, particularly in increasing of membrane performance.

Keywords: Nafion, PEMFC, DFT, ·OH radical, ·H radical

ABSTRAK

DEGRADASI KIMIA MEMBRAN NAFION PADA PEMFC MENGGUNAKAN METODE DFT. Suatu metode eksitu telah dikembangkan untuk menampilkan degradasi secara kimia membran Nafion pada PEMFC (Proton Electrolyt Membrane Fuel Cells) yang disebabkan oleh radikal ·OH dan ·H. Perubahan struktur kimia yang terjadi selama degradasi dihitung berdasarkan energi relatif reaksi menggunakan pendekatan metode DFT (Density Functional Theory) pada software Gaussian. Kajian ini bertujuan untuk menentukan apakah metode DFT dengan fungsional B3LYP, PBEPBE dan B3PW91 dan basis set 6-311++G dapat digunakan untuk menentukan energi relatif reaksi dan mengetahui perbedaan peranan radikal ·OH dan ·H pada proses degradasi rantai utama Nafion dengan gugus akhir $-CF_2H$, $-CF=CF_2$ dan –COOH. Aplikasi ketiga fungsional menunjukkan bahwa radikal ·OH lebih berperan dibanding radikal ·H pada proses degradasi rantai utama Nafion. Pada gugus akhir $-CF_2H$ ditunjukkan bahwa nilai energi relatif reaksi 2 lebih rendah dibanding pada reaksi 5, pada gugus akhir $-CF=CF_2$ nilai energi relatif reaksi 8* lebih rendah dibandingkan pada reaksi 11 dan pada gugus akhir -COOH nilai energi relatif reaksi 14 lebih rendah dibanding pada reaksi 16. Dengan mengetahui energi relatif reaksi degradasi rantai utama Nafion dengan gugus akhir tertentu dan peranan radikal tertentu pada proses

degradasi, metode DFT dengan fungsional B3LYP, PBEPBE dan B3PW91 dan basis set 6-311++G dapat merekomendasikan berbagai modifikasi Nafion sebagai membran sel bahan bakar, khususnya dalam meningkatkan performa membran.

Kata kunci: Nafion, PEMFC, DFT, radikal ·OH, radikal ·H

INTRODUCTION

The energy crisis is the most popular issue discussed by the world community. The crisis occurred because fuel consumption continues to increase while natural resources cannot be renewed. Energy crisis management considers environmental friendly, high efficiency, abundant availability, ease of operation and low cost [1,2]. One alternative energy predicted by many scientists as future energy revolution is fuel cell. Fuel cells are electrochemical devices that convert chemical energy into electrical energy through electrochemical reactions. The device is one of the main objects of renewable energy development [3]. In its application there are various types of fuel cells namely Alkaline Fuel Cells (AFC), Proton Exchange Membrane Fuel Cells, also called Proton Electrolyte Membrane Fuel Cells (PEMFC), Phosphoric Acid Fuel Cells (PAFC), Molten Carbonate Fuel Cells (MCFC), Solid Oxide Fuel Cells (SOFC), and Direct Methanol Fuel Cells (DMFC) [4,5]. The most widely used type of fuel cell is the Proton Exchange Membrane Fuel Cells (PEMFC) [6]. PEMFC is considered as the most promising energy source for the future by reason of high efficiency and low hazardous gas emissions [1,2].

An important component of PEMFC which is the focus of most researchers is the membrane. The reason for developing the membrane is its function to deliver H^+ ions from anode to cathode and prevent electrons from reaching the cathode. Its development efforts are focused on improving performance, both in stability and membrane resistance. This encourages various modifications and innovations from various fields of science in more widespread commercialization effort. One of the most widely used commercial membranes is Nafion, produced by DuPont. Nafion performance is still constrained by degradation, both mechanically and chemically [7]. Chemical degradation is considered as a major factor in decreasing membrane performance caused by ·OH, ·H and ·OOH radicals [8, 9] Research on chemical degradation of Nafion needs to be done both practically and theoretically to get optimal results. The theoretical study that is considered effective in studying the mechanism of Nafion degradation is chemical computing.

Research conducted by Yu, et al. [9] examines the effect of the environment on the mechanism of Nafion degradation in quantum mechanics. The method used is DFT with functional B3LYP and M06 for certain cases while the base set is applied 6-311**G. The results of study showed that at ''OH condition Nafion was more easily degraded in the main chain. Whereas at fuelcell condition chemical degradation Nafion was more likely to occur inside chains by ·H radical. In this work, the role of ·OH and ·H radicals on the degradation process of Nafion with different final groups (–CF_2H, -CF= CF_2 and -COOH) through the relative energy values calculated using the DFT method with functional of B3LYP, PBEPBE B3PW91 and basis set 6-311++G which has never been done before. The entire calculation is run with the Gaussian software with a Windows operating system. This method could provide accurate relative energy of nafion degradation which is difficult to determine in experimental work. Then, it could be use for recomendation in modifying various fuel cell membrane designs, especially the use of Nafion membranes in PEMFC.

EXPERIMENTAL METHOD

The study uses a set of Personal Computers with Windows operating systems, software used Gaussian 03 Rev c.02 and GausView 4.1 [10] and the method used is the density functional theory (DFT) approach. Calculation of total energy using functional such as B3LYP [9,11], PBEPBE [12] and B3PW91 [11,13] and base set 6-311++ G [13,14]. The algorithm used in the DFT method, B3LYP, and PBEPBE functionals was written in Eq. 1, 2 and 3, respectively. Functional of B3PW91 means Becke exchange, Perdew and Wang correlation while PW91 means Perdew-Wang 199.

$$E_{DFT} = E_{NN} + E_T + E_v + E_{coul} + E_{exch} + E_{corr} \quad \text{..... (1)}$$

$$E_{XC} = 0.2*E_X(HF) + 0.8*E_X(LSDA) + 0.72*DE_X(B88) + 0.81*E_C(LYP) + 0.19*E_C(VWN) \quad \text{..... (2)}$$

$$E_{XC} = 0.2*E_X(HF) + 0.8*E_X(LSDA) + 0.72*DE_X(B88) + 0.81*E_C(LYP) + 0.19*E_C(VWN) \quad \text{..... (3)}$$

Determination of the estimated shape of the molecule was begun with the determination of the molecular structure, then the determination of the structure geometry was done using the Gauss View 4.1 program. Determination of initial geometry describe the approximate structure that will be determined optimal geometry. The geometry structure was depicted in the GaussView 4.1 software, structure saved and inputted with the Gaussian Job

format, GIF. GaussView 4.1 has new animation capabilities and displays molecular vibrations in accordance with normal modes. Gauss View generates files that will be run by Gaussian 03W. The results of Gaussian 03W that can be visualized by GaussView include; geometry, vibration, orbitals, electron density and electrostatic potential.

The molecular model was run using the Gaussian 03W program by entering the functions of B3LYP, PBEPBE, and B3PW91. Molecular thermochemistry was determined by entering freq and structure optimization was done by entering opt. In this simulation was used base set of 6-311++G. Calculations were saved in .out format.

Reaction energy was obtained by calculating the energy difference. The correction factors in the calculation of frequency vibrations are 0.976 for B3LYP, 0.991 for PBEPBE, and 0.963 for B3PW91 [14]. The correction factor is factor of the Zero Point Energy for each Gaussian calculation molecule and is accumulated with the total energy calculated. Data obtained from the calculation results obtained total energy data in Hartree units (conversion in electron volts, eV), frequencies and Zero-point correction (Hartree/Particles) [14,15].

RESULT AND DISCUSSION

The general structure of Nafion consists of main chain and side chain. The Nafion main chain has three final cluster models namely -CF_2H, -CF_2=CF_2 or -COOH. The three types of final groups are then taken the last five carbon atoms in the calculation, so that each molecule is written into CF_3-CF_2-CF_2-CF_2-CF_2H, CF_3-CF_2-CF_2-CF=CF_2, dan CF_3-CF_2-CF_2-CF_2-COOH. The molecules degrade when reacting with ·OH and ·H radicals. The total energy degradation was calculated and ΔE reaction was determined. Calculation of total energy used Gaussian software. The total reaction energy obtained from subsequent calculations was determined by the relative energy of the reaction by calculating the difference between the product energy and the reactant reaction energy. This calculation include the correction factor and frequency as well as unit conversions.

The main chain of the Nafion final group - CF_2H is assumed to be a CF_3-CF_2-CF_2-CF_2-CF_2H compound. The reaction of CF_3-CF_2-CF_2-CF_2-CF_2H with ·OH radical occurs in four stages with the overall results of the mechanism of reaction 1 to reaction 4, as shown in Figure 1. Based on the data in Table 1 show that reaction 1 obtained low relative reaction value. All three functionally show reaction 1 can take place spontaneously. The relative energy value of the functional PBEPBE is 0.166 eV which indicates that the reaction cannot take place spontaneously. Functional of B3LYP have relative energy values that are close to the comparator.

The reaction of CF_3-CF_2-CF_2-CF_2-CF_2H with ·OH radical occurs in four stages with the overall results of

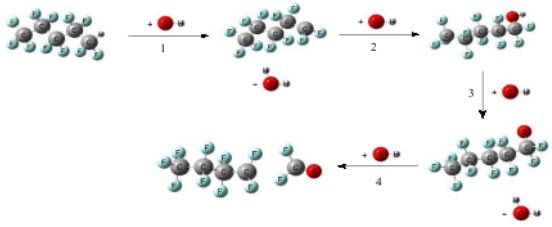

Figure 1. Reaction of -CF_2H final group on Nafion with ·OH radical

CF_3-CF_2-CF_2-CF_2-CF_2H + ·OH → CF_3-CF_2-CF_2-CF_2-$\dot{C}F_2$ + H_2O Reaction 1

CF_3-CF_2-CF_2-CF_2-F_2 + ·OH → CF_3-CF_2-CF_2-CF_2-CF_2OH Reaction 2

CF_3-CF_2-CF_2 CF_2-CF_2OH + ·OH → CF_3-CF_2-CF_2-CF_2-CF_2 + H_2O Reaction 3

CF_3-CF_2-CF_2-CF_2-CF_2 + ·OH → CF_3-CF_2-CF_2-F_2 + CF_2=O Reaction 4

Figure 2. Reaction of -CF_2H final group on Nafion with ·OH radical

CF_3-CF_2-CF_2-CF_2-CF_2H + ·OH → CF_3-CF_2-CF_2-CF_2-$\dot{C}F_2$ + H_2 Reaction 5

CF_3-CF_2-CF_2-CF_2-F_2 + H_2 → CF_3-CF_2-F_2 + CF_2=CF_2 Reaction 6

Table 1. Relative energy of the final group reaction on Nafion (-CF_2H) with ·OH and ·H radicals

Interaction groups with radicals	Reaction	B3LYP	PBEPBE	B3PW91	Reference[9]
-CF_2H and ·OH	Reaction 1	-0.271	-0.699	-0.305	-0.640
	Reaction 2	-4.040	-4.515	-4.868	-4.540
	Reaction 3	0.138	**0.698**	-0.291	0.060
	Reaction 4	-0.288	-1.024	**-0.931**	-0.700
-CF_2H and ·H	Reaction 5	-0.114	**0.166**	-0.044	-0.110
	Reaction 6	1.251	1.342	1.317	1.360

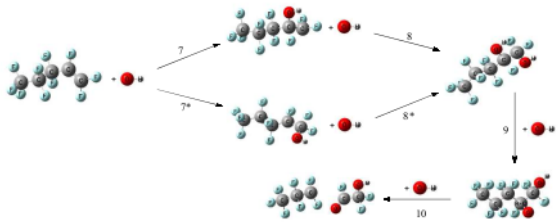

Figure 3. Reaction of the group -$CF=CF_2$ with ·OH radical

CF_3-CF_2-CF_2-$CF=CF_2$ + ·OH → CF_3-CF_2-CF_2-CF_2OH-$\dot{C}F_2$ Reaction 7

CF_3-CF_2-CF_2-$CF=CF_2$ + ·OH → CF_3-CF_2-$\dot{C}F_2$-CF_2-CF_2OH Reaction 7*

CF_3-CF_2-CF_2-CF_2OH-F_2 + ·OH → CF_3-CF_2-CF_2-CFOH-CF_2OH Reaction 8

CF_3-CF_2-CF_2-F_2-CF_2OH + ·OH → CF_3-CF_2-CF_2-CFOH-CF_2OH Reaction 8*

CF_3-CF_2-CF_2-CFOH-CF_2OH + ·OH → CF_3-CF_2-CF_2-CF-CF_2OH + H_2O Reaction 9

CF_3-CF_2-CF_2-CF-CF_2OH → CF_3-CF_2-F_2 + O=CF-CF_2OH Reaction 10

the reaction mechanism 5 to reaction 6 , as shown in Figure 2. Based on the data in Table 1 shows that in reaction 6 relatively uniform energy was obtained with positive value, this means the reaction is not spontaneous. In both reactions, it was shown that there was significant role of the ·H radical, especially in reaction 5, meaning that the ·H radical had a significant effect on the degradation process of the first stage compared to the second stage.

The reaction mechanism in the final group of -$CF=CF_2$ with the ·OH radical, that is ·OH attacks the double-bonded carbon in final group, as shown in Figure 3. The reaction of final group Nafion -CF_2=CF_2 with ·OH radical occurs in 4 stages. The first and second stages have two possible reaction pathways, but spontaneous reaction paths are considered. Based on the data in Table 2, the results for reaction 7 of the three functional show spontaneous reactions with relatively lower energy compared to reaction 7*. The similiar thing happened in the second stage reaction with two alternative reaction pathways, reaction 8 and 8*, with the lowest ΔE are in functional B3LYP and PBEPBE. All relative energy values indicate values that are close to comparators in all three functions. The role of ·OH in the -CF_2 = CF_2 group occurred in the second stage, with the lowest relative reaction energy value in reaction 8* in two functional groups, namely B3LYP and PBEPBE according to the comparator of -4.55 eV. The value is significantly different in B3PW91 functional that is equal to -1.716 eV, this shows that the ·OH radical has a significant influence on reaction 8*.

The reaction mechanism in the final group of -CF= CF_2 with ·H radical occur in two stages, as shown in Figure 4. The ·H radical is generally the same as ·OH, attacking the final group, which is carbon double bond.

Tabel 2. Relative energy of the final group reaction on Nafion (-CF = CF2) with ·OH and ·H radicals

Interaction group with radicals	Reaction	B3LYP	PBEPBE	B3PW91	Reference[9]
-$CF=CF_2$ and ·OH	Reaction 7	**-1.811**	-2.318	-1.999	-2.180
	Reaction 7*	-1.336	-1.862	1.387	-1.750
	Reaction 8	-3.627	-4.164	-4.512	-4.120
	Reaction 8*	-4.101	-4.620	-1.716	-4.550
	Reaction 9	**-0.634**	-0.887	-0.500	-0.300
	Reaction 10	**0.421**	0.325	-1.693	-0.360
-$CF=CF_2$ and ·H	Reaction 11	-1.951	**-2.965**	1.580	-1.910
	Reaction 12	1.151	**1.850**	-0.992	1.210

Figure 4. Reaction of the group -CF=CF_2 with ·OH radical

CF_3-CF_2-CF_2-CF=CF_2 + ·OH → CF_3-CF_2-CF_2-CF_2-$\dot{C}F_2$ + H_2 Reaction 11

CF_3- CF_2-CF_2-CF_2-F_2 + H_2 → CF_3-CF_2-F_2 + CF_2=CF_2 Reaction 12

Figure 5. Reaction of the group -COOH with ·OH radical

CF_3-CF_2-CF_2-CF_2-COOH + ·OH → CF_3-CF_2-CF_2-CF_2-$\dot{C}(OH)_2$ Reaction 13

CF_3-CF_2-CF_2-CF_2-$C(OH)_2$ → CF_3-CF_2-CF_2-F_2 + O=$C(OH)_2$ Reaction 14

Based on the data in Table 2 show that the relative energy value of the ·H radical reaction with the final group -CF=CF_2 in reaction 11 is more dominant spontaneously than reaction 12. In functional PBEPBE, the relative energy value of the reaction is different from the comparator and the other two functional. In B3LYP functional show that reaction 11 has lower relative energy reaction, so that the ·H radical play more important role reaction 11 than reaction 12.

The reaction mechanism in the final group of -COOH with ·OH radicals occur in two stages, as shown in Figure 5. Based on the data in Table 3 show that all three functions used have the lowest relative energy value of reaction at reaction 14. In functional B3LYP, reaction 13 has the relative energy of the reaction different from the comparator. The difference in the relative energy value of the reaction is due to differences in the basis set used, where this study used 6-311++G while Yu et al. [9] used 6-311G**. The use of basis sets 6-311++G emphasize the diffusion function, which is basis function with larger spatial level or large size version of s and p functions. The base set is used because the diffusion function is carried out on molecules that have atoms with unpaired electrons (radicals). The modeling of Nafion structural products in the reaction 13 during the ongoing degradation process has radical molecular transition structure, so the reaction 13 has lower value than the comparator. This indicate that the ·OH radical play significant potential effect in reaction 14 rather than reaction 13.

The reaction mechanism in the final group of -COOH with ·H radical occur in two stages, as shown in Figure 6. Based on the data in Table 3 shows the two-stage reaction mechanism of the Nafion of final group -

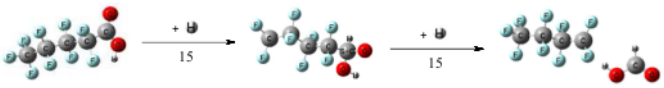

Figure 6. Reaction of the group -COOH with ·H radical

CF_3-CF_2-CF_2-CF_2-COOH + ·H → CF_3-CF_2-CF_2-CF_2-$H\dot{C}OH$ Reaction 15

CF_3-CF_2-CF_2-CF_2-HCOH → CF_3-CF_2-F_2 + (OH)HC=O Reaction 16

Tabel 3. Relative energy of the final group reaction on Nafion (-COOH) with ·OH and ·H radicals

Interaction group with radicals	Reaction	B3LYP	PBEPBE	B3PW91	Reference[9]
-COOH and ·OH	Reaction 13	-0.216	-0.923	-0.575	-0.100
	Reaction 14	-0.583	-1.285	-2.054	0.950
-COOH and ·H	Reaction 15	-2.983	-0.045	-1.999	-0.300
	Reaction 16	-3.234	0.775	-2.849	-0.440

COOH with ·H radical has negative relative energy value. Both stages take place spontaneously. Reactions 15 and 16 show the lowest relative energy value are in B3LYP functional. In PBEPBE functional are obtained different value, which is positive value in reaction 16. The difference in results on PBEPBE functional is expected due to the existence of system that should be polarized but cannot be calculated due to the use of a 6-311++G basis set which emphasizes diffusion systems. This is consistent with comparative data and B3LYP functional data in reaction 16 which have relatively lower energy than reaction 15. All three calculation data show more spontaneous results for reaction 16 than reaction 15. The results mechanism reaction of ·H radical in the final group of -COOH is more involved in reaction 16 than reaction 15.

In the degradation reaction of main chain Nafion in final group of -CF_2H group, the role of each radical was known from the relative energy value of reaction. The relative energy of reaction 2 for three functional is lower than the relative energy of reaction 5, as shown in Table 1. It mean that the ·OH radical has more influence on the Nafion degradation process with final group -CF_2H. In degradation reaction of Nafion main chain with final group of -$CF{=}CF_2$, it was known that the role of each radical from the relative energy value of reaction from comparing the reaction 8* with reaction 11, as shown in Table 2. Comparison of the three functional show reaction 2 has lower energy value compared to reaction 11, this indicate that the ·OH radical more influence on the degradation process of the Nafion with final group of -$CF{=}CF_2$. In the degradation reaction of Nafion main chain with final group –COOH, it was known the role of each radical of the relative energy value of the reaction by comparing reaction 14 with reaction 16, as shown in Table 3. The comparison show the three functional in reaction 14 has lower values compared with reaction 16, meaning that the ·OH radical has more influence on the degradation process of Nafion with final group of -COOH. Generally, it was found that in Nafion degradation with final groups of CF_2H, -$CF{=}CF_2$ and -COOH, ·OH radical attack was more destructive for Nafion. The same result were found in previous study using different functional [9]. Hence, it was suggested that reducing Nafion degradation would be modify the use of catalysts that minimize ·OH radical formation or concider other final groups that are more resistant to ·OH radical attack.

CONCLUSION

Chemical degradation is considered as a major factor in decreasing membrane performance caused by ·OH and ·H radicals. The theoretical study that is considered effective in studying the mechanism of Nafion degradation is chemical computation. The DFT method with B3LYP, PBEPBE, and B3PW91 functional and base sets 6-311++G can be used in determining the relative energy of Nafion main chain degradation with –CF_2H, -$CF{=}CF_2$ and -COOH final group by ·OH and ·H radicals. In the whole of chemical degradation process of Nafion, ·OH radical play more important role than ·H radical.

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