

**Ab Initio Study of Proton Transfer and Hydration on Phosphorylated Nata de coco****Sitti Rahmawati<sup>1,2</sup>, Cynthia Linaya Radiman<sup>2</sup>, and Muhamad Abdulkadir Martoprawiro<sup>2,\*</sup>**<sup>1</sup>Chemistry Study Program, Mathematics and Sciences Division, Faculty of Teacher Training and Educational Sciences, Tadulako University, Jl. Soekarno Hatta Km 9 Palu 94118 Indonesia<sup>2</sup>Inorganic and Physical Chemistry Division, Faculty of Mathematics and Natural Sciences, Bandung Institute of Technology, Jl. Ganesha 10 Bandung 40132 Indonesia

Received May 9, 2017; Accepted August 10, 2017

**ABSTRACT**

This research aims to calculate energetics parameters, hydrogen bonding, characteristics local hydration, and proton transfer in phosphorylated nata de coco (NDCF) membrane using ab initio method. The minimum energy structure of NDCF membranes and the addition of  $n$  water molecules ( $n = 1-10$ ) determined at the B3LYP/6-311G\*\* level indicates that proton dissociation requires a minimum of four water molecules. Dissociated protons stabilize with the formation of (hydronium, Zundel, Eigen) ions. Calculation of the interaction energy with  $n$  water molecules indicates an increasingly negative change in energy ( $\Delta E$ ) and enthalpy ( $\Delta H$ ), and hence an increasingly positive interaction with water molecules. This interaction facilitates the transfer of protons in the membrane matrix. Calculation of the rotational energy at the center of C-O indicates that the pyranose ring structure, with a maximum barrier energies of  $\sim 12.5$  J/mol, is much more flexible than the aromatic backbones of sulfonated poly(phenylene) sulfone (sPSO<sub>2</sub>) and the polytetrafluoroethylene (PTFE) backbones in perfluorosulfonic acid ionomers (PFSA). These energy calculations provide the basis that the flexibility of the pyranose ring and the hydrogen bonding between water molecules and phosphonate groups influence the transfer of protons in the membrane of NDCF.

**Keywords:** proton transfer; ab initio; nata de coco**ABSTRAK**

Penelitian ini bertujuan untuk menghitung parameter energetika, ikatan hidrogen, karakteristik hidrasi lokal, dan transfer proton pada membran nata de coco terfosfatasi menggunakan metode ab initio. Struktur energi minimum untuk nata de coco terfosfatasi dan penambahan  $n$  molekul air ( $n = 1-10$ ) yang ditentukan dengan metode B3LYP/6-311G(d) menunjukkan bahwa untuk disosiasi proton minimal dibutuhkan empat molekul air. Proton yang terdisosiasi distabilkan dengan terbentuknya ion-ion hidronium, Zundel dan Eigen. Perhitungan energi interaksi dengan  $n$  molekul air menunjukkan perubahan energi ( $\Delta E$ ), dan perubahan entalpi ( $\Delta H$ ) yang semakin negatif. Hal ini menunjukkan interaksi dengan molekul air makin kuat. Interaksi ini dapat mempermudah transfer proton dalam matriks membran. Perhitungan energi rotasi pada pusat C-O menunjukkan bahwa struktur cincin piranosa jauh lebih fleksibel dibandingkan struktur aromatik polifenilen sulfon tersulfonasi (sPSO<sub>2</sub>), dan struktur politetrafluoroetilen (PTFE) dalam ionomer asam perfluorosulfonat (PFSA): energi penghalang terbesar dari cincin piranosa  $\sim 12,5$  J/mol. Perhitungan energi tersebut memberikan dasar bahwa fleksibilitas dari cincin piranosa dan ikatan hidrogen antara molekul air dengan gugus fosfonat mempengaruhi transfer proton pada membran NDCF.

**Kata Kunci:** transfer proton; ab initio; nata de coco**INTRODUCTION**

Fuel cells are a promising energy source hoped to alleviate the future energy crisis. A variety of different fuel cells are currently being studied and developed, each with their own advantages, weaknesses, and potential applications. In general, fuel cells generate energy efficiently (40–80%) and are environmentally friendly [1-3]. Fuel cells are also capable of continuous energy conversion as long as they are fed a sufficient supply of natural gas, hydrocarbons, or alcohol. Of the

various approaches, the Proton Exchange Membrane Fuel Cell (PEMFC) is one of the most promising, being both highly efficient and environmentally friendly. PEMFC utilizes a solid polymer membrane as an electrolyte [4-7].

In most current literature, a perfluorocarbon based electrolyte membrane called Nafion is used in PEMFCs. The continued popularity [5] of Nafion is due to a number of advantageous properties; mechanical robustness, stability at the operating temperature of fuel cells (approximately 80 °C), and stability in the

\* Corresponding author. Tel : +62-81221222424  
Email address : muhamad@chem.itb.ac.id

proximity of chemicals with high proton conductivity (0.08 S/cm) [3,8-10]. On the other hand, Nafion cannot be reused, leading to a high environmental and production cost [8] of the PEMFC. In addition, Nafion is susceptible to dehydration, leading to a fall in proton conductivity at high temperatures [2,11-12].

These shortcomings have led to a search for alternatives to Nafion as an electrolyte in fuel cells, capable of operating at higher temperature, with higher mechanical robustness, but with a proton conductivity level approaching Nafion. Studies on phosphorylated bacterial cellulose (nata de coco) have been synthesized and characterized [4]. Phosphorylated nata de coco has been shown to possess proton conductivity approaching that of Nafion 117. The chemical structure of phosphorylated nata de coco differs from that of Nafion; the hydrophobic and hydrophilic domains contained in phosphorylated nata de coco are what facilitate proton transfer through a cluster network. Due to water in the media, protons and hydroxyl ions are in balance. The formation of ester cellulose eases the transfer of protons in the membrane matrix, as  $H^{\delta+}$  from the  $-O^{\delta-}H^{\delta+}$  in phosphate rings are easily detached and quick to react with water producing ionized water.  $O^{\delta-}$  also interacts with ionized water, resulting proton transfer and increasing the conductivity of the phosphorylated nata de coco membrane. In addition, hydrophilic and phosphate rings are able to form intermolecular hydrogen bonds and between water molecules. The rate at which the electrolyte membrane bonds with water will determine the proton transfer rate [13].

A number of models and simulations were developed to comprehend the hydration process and proton transfer in the membrane. The classical molecule dynamics (MD) and *ab initio* molecular dynamics (AIMD) methods were used to determine proton mobility as a function of hydration conditions and sulfonated function rings [14-15]. Studies on SSC PFSA membrane fragments show that the formation of hydrogen bonds between water molecules is highly dependent on acid ring connectivity. The study also shows that Zundel ions ( $H_5O_2^+$ ) play an important role in facilitating proton transfers in low hydration conditions. The results of *ab initio* computation on sPSO<sub>2</sub> ionomers show that, as a whole, proton transfer occurs in various structures within sPSO<sub>2</sub>, with meta-meta conformity generally preferred over orto-orto conformity. sPSO<sub>2</sub> ionomers are more effective in producing moving protons in low-water conditions [16]. A study of proton transfer energetics in phosphoric acid clusters shows that the (second) energy barrier of proton transference and its endothermic properties fall with an increase in the size of phosphoric acid clusters [17]. In line with these findings, this study will evaluate proton transfer in bacterial cellulose membranes (phosphorylated nata de coco); the structure

of hydrogen bonds between molecules, and how the structure reacts to the gradual addition of  $n$  water molecules at various points in the bacterial cellulose structure.

## EXPERIMENTAL SECTION

### Instrumentation

Devices research used in this study consists of hardware and software. Super computer hardware in the form of High Performance Computer (HPC) systems at ITB Bandung. This facility is an integrated computer facilities consisting of 20 modules, each of which has two hexacore intel X5650 (Hyper threading per core subject which produce a total of 24 cores per module) RAM 16 GB and 320 GB Hard Disk capacity. The software used is a Linux-based operating systems with input in the form of z-matrix structure and computational calculations using GAUSSIAN 09 for Linux, and ChemCruff, Jmol, GaussView used to make the initial coordinates of the molecular structure and visually see the output.

### Computation Method

The quantum mechanical *ab initio* method was used to compute the interaction energy between phosphorylated nata de coco molecules. All electronic structural calculations utilized the Gaussian09 software. Previous studies indicated of the minimum energy structure, the electronic structure, and geometry optimization are determined at the quantum mechanical *ab initio* method, indicated the migration of protons in the interaction of acetic acid-water and ammonia [18].

### Initial structure and geometric optimization

The first procedure was the creation of initial structure coordinates (z-matrix) of the molecules in the phosphorylated nata de coco polymer membrane. The bonds' lengths, relative orientations, and dihedral orientations are required to calculate the z-matrix. Next, geometric optimization of the polymer membrane molecule was conducted using the DFT/B3LYP method with the 6-311G (d) basis set. This optimization was generated until the most stable conformity structure of the phosphorylated nata de coco molecule. The final energy obtained from this optimization indicates the lowest energy level with the most structurally stable molecule with minimum intra-atom repulsion.

### Energy calculation

The optimized z-matrix structure for each phosphorylated nata de coco structure (its monomers,

dimers, trimers, etc.) was used to calculate energy, by adding a water molecule in the same position. The DFT method with the B3LYP function and the 6-311G(d) basis set was used to generate these calculations. The change in energy between dimers, trimers, etc. was then obtained from the various optimized conformation structure energy calculations. These calculations heavily influence subsequent results in this study [16].

To investigate changes in proton transfers and hydrogen bonding in the vicinity of the phosphoric acid groups in low water conditions, water molecules were added one by one (i.e. +  $n$  H<sub>2</sub>O, where  $n = 1-10$ ) to the optimized structures generated in the previous steps. Finally, optimizing the results of this process, obtained the interaction energy between water molecules and the phosphonate groups. The binding strength (due to hydrogen bonding) was evaluated at the B3LYP/6-311G(d) level and subsequently corrected for zero-point energy (ZPE) and basis set superposition error (BSSE) as has been done by Wang and Paddison systems sulfonated poly phenylene sulfone. [16]. The calculation of energy changes ( $\Delta E$ ) using the formula of equation 1, the same principle used to calculate the enthalpy changes ( $\Delta H$ ) and free Gibbs energy change ( $\Delta G$ ). The rotational energy barriers with the method described above as then conducted to determine the flexibility of the pyranose ring backbone.

$$\Delta E = E_{\text{NDCF}-n\text{H}_2\text{O}} - E_{\text{NDCF}} - E_{\text{H}_2\text{O}} \quad (1)$$

## RESULT AND DISCUSSION

### Minimum Energy Structures

Phosphorylated nata de coco is a polymer that contain of  $\beta$ -1,4 bonds D-glucose phosphonate units (monomer). Interaction energy changes of phosphorylated nata de coco are determined by added one water molecule to its monomer (two, three, four and five) on the same position. The results of various

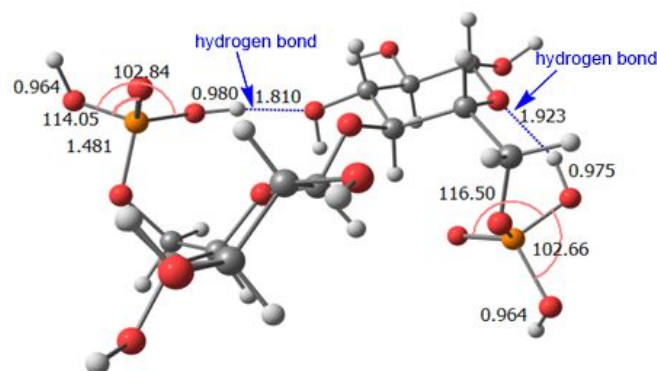
structure optimizations are Interaction energy changes of the monomers and water showed no significant changes, about -12.55 kcal/mol [19]. These results tell that two monomer structures can represent longer phosphorylated nata de coco polymer in the interaction energy calculation with water molecule [20].

The structure of phosphorylated nata de coco is comprised of several hydroxyl ions and phosphonate groups ( $-\text{PO}_3\text{H}_2$ ), which has been shown to affect local hydration and properties of the proton transfer. The minimum energy structure of phosphorylated nata de coco, determined through the B3LYP/6-311G(d) method elaborated upon above, is shown in Fig. 1.

For the conformation shown in Fig. 1, the hydrogen bond between the phosphonate ( $-\text{PO}_3\text{H}_2$ ) and hydroxyl ( $-\text{OH}$ ) groups is comparable to the hydrogen bond in phosphoric clusters, namely 1.810 Å [17], classified as medium hydrogen bonds [20].

### Backbone Conformation

Aside from intra molecular interaction, the B3LYP/6-311G (d) method was also used to calculate the interaction between pyranose rings by rotation at



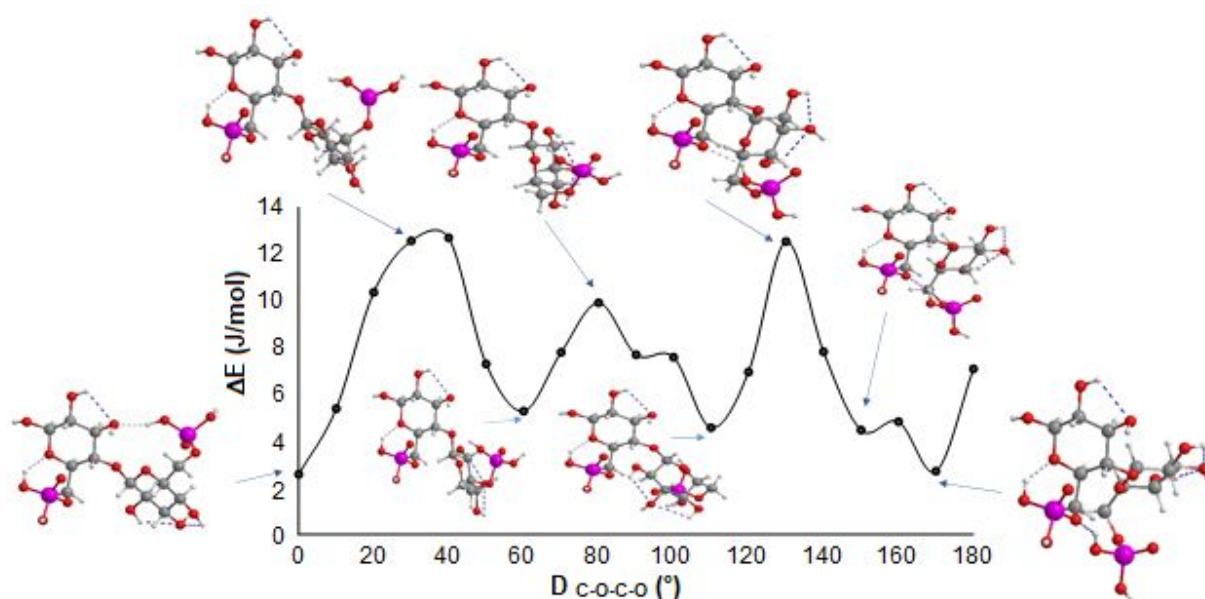
**Fig 1.** Structural optimization of phosphorylated nata de coco dimers (B3LYP/6-311G(d))

**Table 1.** Results of the structure optimization of the phosphorylated nata de coco dimer +  $n$  water molecules (B3LYP/6-311G (d) method)

+ $n$ H <sub>2</sub> O	-P <sub>1</sub> (OH) r <sub>O-H</sub> (r <sub>47-49</sub> ) Å	-P <sub>1</sub> (OH) r <sub>O-H</sub> (r <sub>48-50</sub> ) Å	-P <sub>2</sub> (OH) r <sub>O-H</sub> (r <sub>52-54</sub> ) Å	-P <sub>2</sub> (OH) r <sub>O-H</sub> (r <sub>53-55</sub> ) Å	Dc-o-c-o
0	0.975	0.964	0.980	0.964	-81.688
1	0.991	0.964	0.981	0.964	-81.697
2	0.994	0.964	0.982	0.990	-81.490
3	0.992	0.995	0.965	0.995	-84.285
4	0.993	0.996	1.010	0.991	-79.068
5	0.992	1.011	1.011	0.990	-81.425
6	0.995	1.008	1.012	0.998	-70.133
7	1.007	1.013	1.023	0.999	-79.406
8	1.008	1.014	0.986	1.013	-80.616
9	1.007	1.021	0.997	1.020	-79.229
10	1.006	1.021	1.019	0.997	-84.729

**Table 2.** Binding energy for the optimized phosphorylated nata de coco dimer +  $n$  water molecules

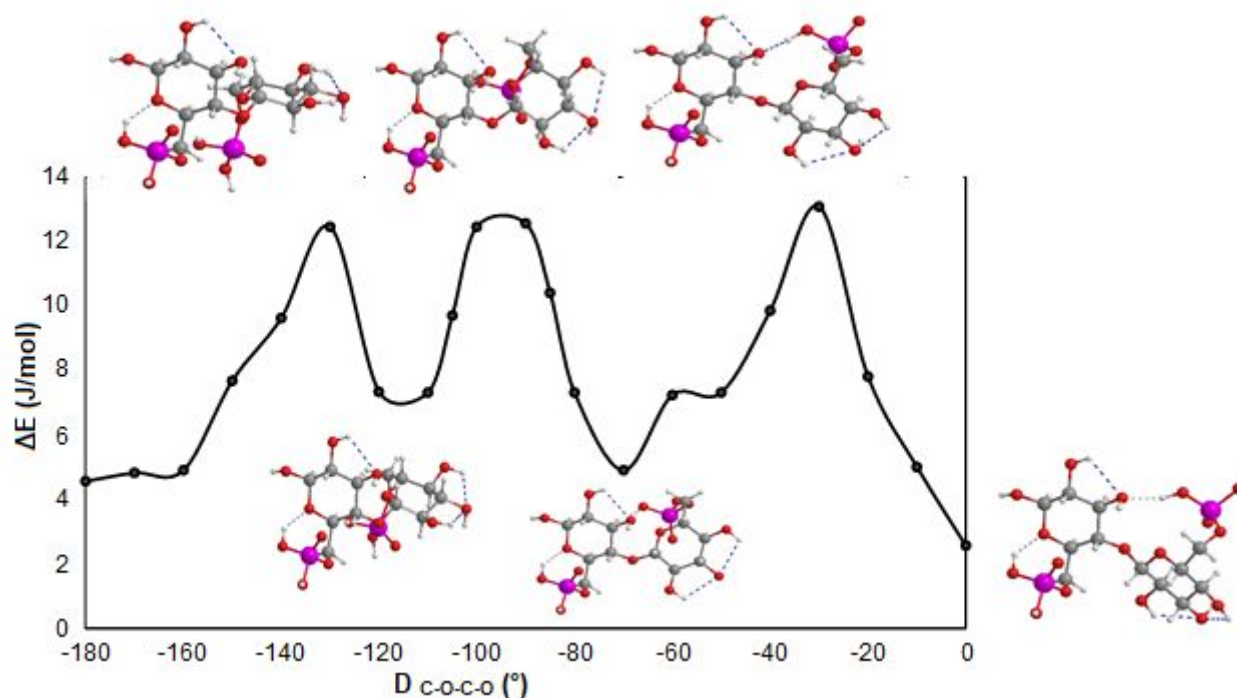
+ $n$ H <sub>2</sub> O	$\Delta E_{ZPE}$ (kcal/mol)	$E_{BSSE}$ (Hartree)	$\Delta E$ (kcal/mol)	$\Delta H$ (kcal/mol)	$\Delta G$ (kcal/mol)	average value (kcal/mol)/H <sub>2</sub> O		
						$\Delta E$	$\Delta H$	$\Delta G$
0								
1	-14.637	-2510.228	-15.173	-15.766	-5.132	-15.173	-15.766	-5.132
2	-34.046	-2586.595	-35.204	-36.389	-14.641	-17.602	-18.195	-7.320
3	-47.618	-2662.927	-49.066	-50.843	-19.360	-16.355	-16.948	-6.453
4	-59.861	-2739.169	-61.378	-63.747	-21.981	-15.344	-15.937	-5.495
5	-69.156	-2815.504	-70.189	-73.151	-26.113	-14.038	-14.630	-5.223
6	-83.127	-2891.856	-84.739	-88.294	-28.224	-14.123	-14.716	-4.704
7	-101.487	-2968.174	-103.928	-108.075	-36.763	-14.847	-15.439	-5.252
8	-116.048	-3044.509	-118.250	-122.989	-45.542	-14.781	-15.374	-5.693
9	-129.988	-3120.850	-133.108	-138.440	-45.591	-14.790	-15.382	-5.066
10	-145.917	-3197.184	-149.089	-155.013	-52.948	-14.909	-15.501	-5.295

**Fig 2.** Relative rotational energy along central C–O bonds in phosphorylated nata de coco dimers obtained at B3LYP/6-311G(d)

the C–O bond. Structural parameters, including the dihedral degree of rotation for the C–O bond ( $D_{C-O-C-O}$ ) and the O–H bond length ( $-\text{PO}(\text{O} \cdots \text{H})_2$ ) is shown in Table 1. Electronic energy, zero point energy, change in internal energy, Gibbs free energy, and change in enthalpy are shown in Table 2.

The interaction between the phosphonate ( $-\text{PO}(\text{O} \cdots \text{H})_2$ ) and hydroxyl groups and the interaction of pyranose rings significantly affects conformation. Each phosphate groups in the phosphorylated nata de coco dimer is expected to interact with neighboring hydroxyl and pyranose rings or with its hydroxyl unit. Consequently, the pyranose ring tends to rotate about its C–O bond to minimize the steric effect. The determination of the global minimum energy of the phosphorylated nata de coco dimer structure in Fig. 2 and 3 show that the two pyranose rings are regulated by an advantageous barrier energy configuration. The potential energy surface (PES) scans have been

conducted with the B3LYP/6-311G(d) method for the rotation of pyranose rings about the C–O bond for negative and positive  $180^\circ$ . As seen in Fig. 2 and 3, barrier energy peaks when the two pyranose rings are perpendicular and falls when in parallel. Similarly, rotational energy peaks when the conformances of the two pyranose rings are perpendicular. The average and maximum barrier energies of phosphorylated nata de coco dimers was found to be approximately 5.3 and 12.5 J, respectively, far below the observed barrier energy of PFSA fragments and sPSO<sub>2</sub>. This shows that the backbone of pyranose rings are more flexible (less stiff) compared to PTFE backbones and sPSO<sub>2</sub> [16,21-22]. A possible explanation is that the majority of the hydrogen bonds formed in phosphorylated nata de coco are unaffected by rotation along central C–O bonds.



**Fig 3.** Relative rotational energy along central C–O bonds in dimer phosphorylated nata de coco obtained at B3LYP/6-311G(d)

### Proton Transfer and Hydration

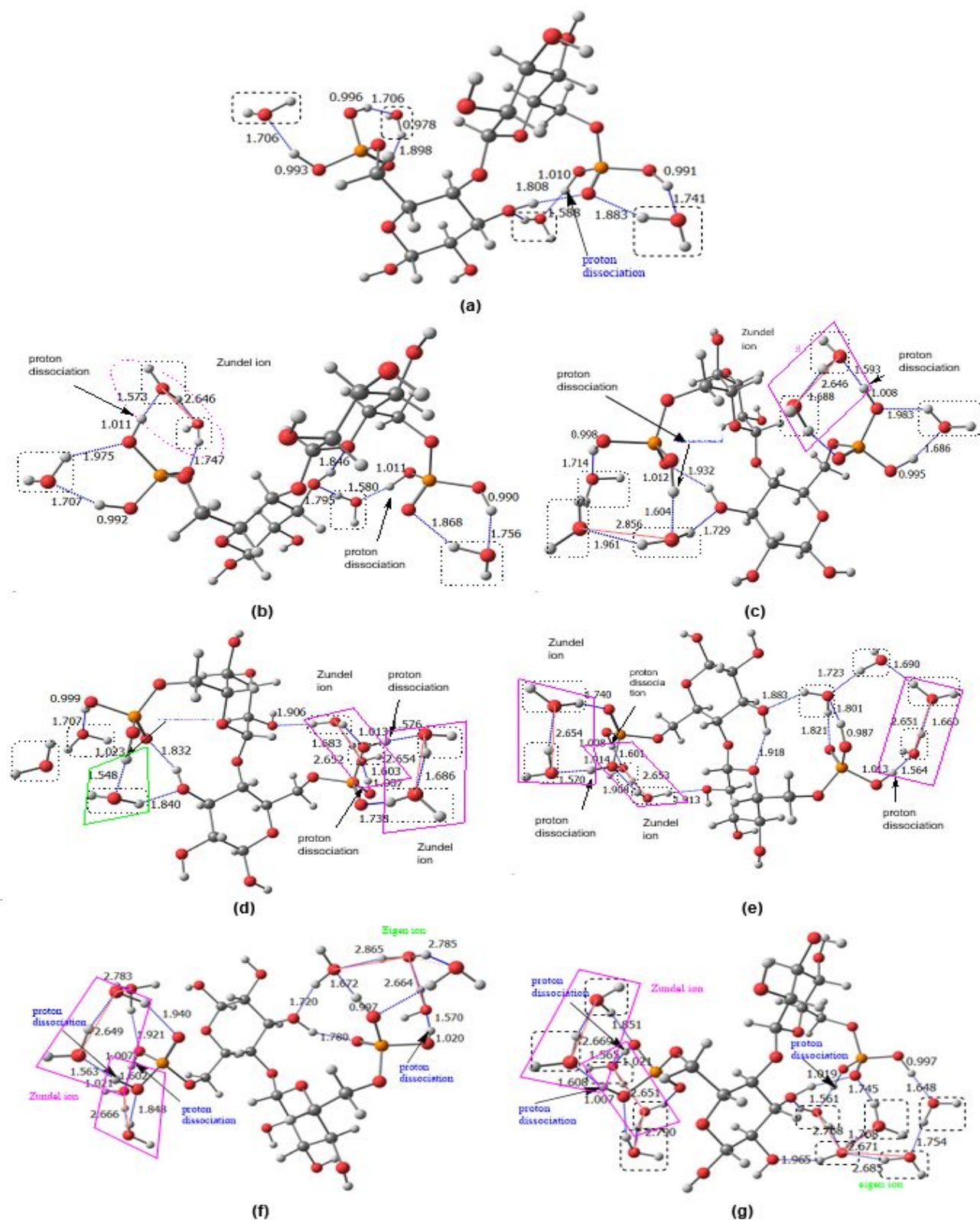
To investigate proton transfer near the phosphate ring ( $-\text{PO}(\text{O}\cdots\text{H})_2$ ) at a low degree of hydration, water molecules were added one by one to the phosphorylated nata de coco dimer. Utilizing the B3LYP/6-311G (d) method, multi hydration phosphorylated nata de coco dimers were obtained from various structures with  $n$  molecule air ( $n = 1-10$ ), with the resulting conformances shown in Fig. 4.

The optimization results obtained from energy data of each structure, so it can be calculated change in energy, enthalpy change and the Gibbs free energy change using equation 1. Table 2 displays data from the energy calculation results and BSSE computation that corrects the bonding energy between molecules. An increasingly negative change in energy, Gibbs free energy and enthalpy indicates a stronger interaction with water molecules. The values of  $\Delta E$ ,  $\Delta G$  and  $\Delta H$  show the stability parameters of a system's thermodynamics; the more negative the reaction will tend to be stable because the reaction takes place spontaneously. The addition of one water molecule to the system lowers the change in energy, enthalpy change and the change in Gibbs free energy ( $\Delta E$ ,  $\Delta G$  and  $\Delta H$ ), so that the intensity of the interaction between the phosphorylated nata de coco dimers with the water molecule also increases. The values of  $\Delta E$ ,  $\Delta G$  and  $\Delta H$  indicate the thermodynamic stability parameters of a system, the more negative the

reaction will tend to be stable because the reaction is spontaneous. The addition of one water molecule to the system lowers the system, so that the intensity of the interaction between the phosphorylated nata de coco dimers with the water molecule also increases, encouraging the transfer of protons in the membrane matrix as the  $\text{H}^{\delta+}$  from  $-\text{O}^{\delta-}\text{H}^{\delta+}$  in the phosphate ring is able to easily dissociate and is free to interact with water to produce protonated water.  $-\text{O}^{\delta-}$  will also interact with other protonated water molecules leading to increased proton transfer and increasing the conductivity of the phosphorylated nata de coco membrane. Intermolecular interaction between polymer chains will fall and interaction between phosphate groups and water will subsequently rise [13]. The average value of  $\Delta E$ ,  $\Delta G$  and  $\Delta H$  for the interaction between water molecule and nata de coco dimer increased gradually at addition of 1-2 water molecules, decreased gradually up to addition of five water molecules, and were relatively constant for the next addition of water molecules.

This is consistent with previous research suggesting that proton dissociation is tied to the proportion of water and phosphoric acid in the system; phosphorylated nata de coco is comprised of hydrophobic and hydrophilic domains allowing proton transfer to occur through cluster networks. With water in the media, a balance between protons and hydroxyl ions is established [13].





**Fig 4.** Fully-optimized (B3LYP/6-311G (d)) minimum energy structures of phosphorylated nata de coco dimer with  $n$  water molecules: (a)  $n = 4$ ; (b)  $n = 5$ ; (c)  $n = 6$ ; (d)  $n = 7$ ; (e)  $n = 8$ ; (f)  $n = 9$ ; (g)  $n = 10$ . The proton dissociation occurs when four water molecules were added

The bonding energy tends to be similar, with a rise in bonding energy corresponding to increased hydration. The local hydration of the phosphorylated nata de coco dimer was considerably different from that of PFSA and sPSO<sub>2</sub>; in sPSO<sub>2</sub> proton dissociation occurred with the addition of a minimum of three water molecules ( $d_{\text{O-H}} = 1.02$  and  $1.06 \text{ \AA}$ ), while in PFSA a minimum of five water molecules ( $d_{\text{O-H}} = 1.01$  and  $1.02 \text{ \AA}$ ) was required [16,21-22]. In phosphorylated nata de coco dissociation ( $d_{\text{O-H}} = 1.01 \text{ \AA}$ ) was observed with the addition of four water molecules, with the dissociated proton stabilizing into a hydronium ion as seen in Fig. 4a. With the addition of five and six water molecules, the two dissociated protons stabilized into Zundel and hydronium ions as seen in Fig. 4b. The existence of a Zundel ion resulted in a minimum bonding energy, hence encouraging proton transfer as Zundel ions function as a mediator in the proton transfer process. With the addition of seven and eight water molecules, the three dissociated protons formed two Zundel ions and one hydronium ion as seen in Fig. 4c. Finally, with the addition of nine and ten water molecules, one Eigen ion and two Zundel ions were formed as a result of the dissociation seen in Figure 4d. The hydronium ion forms an Eigen ion through the hydrogen bonds formed with three water molecules with an average O-H distance of  $2.56 \text{ \AA}$ . The formation of an Eigen ion indicates that the proton has migrated to the second hydration layer [23].

## CONCLUSION

Optimization results from the B3LYP/6-311G (d) calculation shows that proton dissociation requires a minimum of four water molecules. Dissociated protons are stabilized with the formation of hydronium, Zundel, and Eigen ions. The gradual addition of  $n$  water molecules (with  $n = 1-10$ ) leads to increasingly negative changes in energy ( $\Delta E$ ) and enthalpy ( $\Delta H$ ), indicating stronger interaction with water molecules. This interaction may encourage proton transference in the membrane matrix. Rotational energy calculations show that the pyranose ring structure is significantly more flexible than the aromatic sPSO<sub>2</sub> structure and the poly tetra fluoro ethylene (PTFE) structure in perfluoro sulfonic acid (PFSA) ionomer. The highest rotational barrier energy of the pyranose rings were  $\sim 12.5 \text{ J/mol}$ . These energy calculations provide the basis that the flexibility of the pyranose ring and the hydrogen bonding between water molecules and phosphonate groups influence the transfer of protons in the membrane of phosphorylated nata de coco.

## ACKNOWLEDGEMENT

The authors are grateful for financial support of the scholarship *Beasiswa Pendidikan Pascasarjana Dalam Negeri* (BPP-DN), Ministry of Research, Technology and Higher Education of the Republic of Indonesia, the through Doctoral program Graduate School of Institut Teknologi Bandung, Indonesia.

## REFERENCES

- [1] Schuster, M., de Araujo, C.C., Atanasov, V., Andersen, H.T., Kreuer, K-D., and Joachim Maier, J., 2009, Highly sulfonated poly(phenylene sulfone): Preparation and stability issues, *Macromolecules*, 42 (8), 3129–3137.
- [2] Maiyalagan, T., and Pasupathi, S., 2010, Components for PEM fuel cells: An overview, *Mater. Sci. Forum*, 657, 143–189.
- [3] Zaidi, S.M.J., and Matsuura, T., 2009, *Polymer Membranes for Fuel Cells*, Springer, New York.
- [4] Wang, Y., Chen, K.S., Mishler, J., Cho, S.C., and Adroher, X.C., 2011, A review of polymer electrolyte membrane fuel cells: Technology, applications, and needs on fundamental research, *Appl. Energy*, 88 (4), 981–1007.
- [5] Smitha, B., Sridhar, S., and Khan, A.A., 2005, Solid polymer electrolyte membranes for fuel cell applications—A review, *J. Membr. Sci.*, 259 (1-2), 10–26.
- [6] Mecheri, B., D'Epifanio, A., Traversa, E., and Licoccia, S., 2008, Sulfonated polyether ether ketone and hydrated tin oxide proton conducting composites for direct methanol fuel cell applications, *J. Power Sources*, 178 (2), 554–560.
- [7] Song, A.K., Batista, C., Sarpeshkar, R., and Han, J., 2008, Rapid fabrication of microfluidic polymer electrolyte membrane fuel cell in PDMS by surface patterning of perfluorinated ion-exchange resin, *J. Power Sources*, 183 (2), 674–677.
- [8] Spry, D.B., and Fayer, M.D., 2009, Proton transfer and proton concentrations in protonated Nafion fuel cell membranes, *J. Phys. Chem. B*, 113 (30), 10210–10221.
- [9] Bae, B., Miyatake, K., and Watanabe, M., 2008, Sulfonated poly(arylene ether sulfone) ionomers containing fluorenyl groups for fuel cell applications, *J. Membr. Sci.*, 310 (1-2), 110–118.
- [10] Wilkinson, D.P., Zhang, J., Hui, R., Fergus, J., and Li, X., 2010, *Proton Exchange Membrane Fuel Cell Material Properties and Performance*, CRC Press, New York.

- [11] Neburchilov, V., Martin, J., Wang, H., and Zhang, J., 2007, A review of polymer electrolyte membranes for direct methanol fuel cells, *J. Power Sources*, 169 (2), 221–238.
- [12] Liu, Q., Song, L., Zhang, Z., and Liu, X., 2010, Preparation and characterization of the PVDF-based composite membrane for direct methanol fuel cells, *Int. J. Energy Environ.*, 1 (4), 643–656.
- [13] Radiman, C.L., and Rifathin, A., 2013, Preparation of phosphorylated nata-de-coco for polymer electrolyte membrane applications, *J. Appl. Polym. Sci.*, 130 (1), 399–405.
- [14] Cui, S., Liu, J., Selvan, M.E., Paddison, S.J., Keffer, D.J., and Brian J. Edwards, B.J., 2008, Comparison of the hydration and diffusion of protons in perfluorosulfonic acid membranes with molecular dynamics simulations, *J. Phys. Chem. B*, 112 (42), 13273–13284.
- [15] Habenicht, B.F., Paddison, S.J., and Tuckerman, M.E., 2010, The effects of the hydrophobic environment on proton mobility in perfluorosulfonic acid systems: An *ab initio* molecular dynamics study, *J. Mater. Chem.*, 20 (30), 6342–6351.
- [16] Wang, C., and Paddison, S.J., 2013, Hydration and proton transfer in highly sulfonated poly(phenylene sulfone) ionomers: An *ab initio* study, *J. Phys. Chem. A*, 117 (3), 650–660.
- [17] Vilciauskas, L., Paddison, S.J., and Kreuer, K-D., 2009, *Ab initio* modeling of proton transfer in phosphoric acid clusters, *J. Phys. Chem. A*, 113 (32), 9193–9201.
- [18] Wijaya, K., Tahir, I., and Harnowo, 2003, Study of double protons migration mechanism in supramolecular structures of acetic acid-water and acetic acid-ammonia by *ab initio* method, *Indones. J. Chem.*, 3 (2), 102-110.
- [19] Rahmawati, S., Radiman, C.L., and Martoprawiro, M.A., 2016, *Ab initio* study of phosphorylated nata de coco membrane structure, *Prosiding Seminar Nasional Sains dan Pendidikan Sains*, ISBN: 978-602-74182-0-2, 54–57.
- [20] Rahmawati, S., Radiman, C.L., and Martoprawiro, M.A., 2016, *Ab initio* calculation of hydration and proton transfer on sulfonated nata de coco, *Eur. J. Chem.*, 7 (4), 442–447.
- [21] Paddison, S.J., 2005, Molecular modeling of the short-side-chain perfluorosulfonic acid membrane, *J. Phys. Chem. A*, 109 (33), 7583–7593.
- [22] Paddison, S.J., and Elliott, J.A., 2006, On the consequences of side chain flexibility and backbone conformation on hydration and proton dissociation in perfluorosulfonic acid membranes, *Phys. Chem. Chem. Phys.*, 8, 2193–2203.
- [23] Paddison, S.J., 2003. Proton conduction mechanisms at low degrees of hydration in sulfonic acid-based polymer electrolyte membranes, *Annu. Rev. Matter. Res.*, 33, 289–319.