Hemoglobin Components as Cathode Electrode Catalyst in Polymer Electrolyte Fuel Cells

Muneyuki Tsuda
Department of Applied Physics, Osaka University, Suita, Osaka 565-0871, Japan

Wilson Agerico Diño
Department of Applied Physics, Osaka University, Suita, Osaka 565-0871, Japan
Japan Science and Technology Agency, Kawaguchi, Saitama 332-0012, Japan and
Physics Department, De La Salle University, Taft Ave., Manila 1004, Philippines

Hiroshi Nakanishi and Hideaki Kasai*
Department of Applied Physics, Osaka University, Suita, Osaka 565-0871, Japan.
(Received 25 September 2004; Accepted 18 October 2004; Published 23 October 2004)

We consider hemoglobin (Hb) components for possible use as cathode electrode catalyst in polymer electrolyte fuel cells (PEFCs). We choose iron-porphyrin (FeP) and (imidazole)FeP [(Im)FeP] as a representative heme complex of the Hb active site, and investigate their catalytic activities for O₂ dissociation using ab initio calculations based on density functional theory (DFT). The imidazole ligand suppresses the donation/back-donation of electrons between Fe and O₂, resulting in the weakening of the Fe-O₂ bond and the strengthening of the O-O bond. Therefore, the catalytic activity of FeP is higher than that of (Im)FeP. [DOI: 10.1380/ejssnt.2004.226]

Keywords: Polymer electrolyte fuel cells; Cathode electrode; Biological molecules-proteins; Iron; Oxygen; Chemisorption; Molecule-solid reactions; Catalysis; Density functional calculations; Biophysics, medical physics, and biomedical engineering

From an environmental viewpoint, much attention has been focused on polymer electrolyte fuel cells (PEFCs) as an alternative electronic power source of the future. However, PEFCs are too expensive for widespread use because of the large amount of platinum used for both anode and cathode electrode catalysts. Many researchers have tried to design alternative catalysts to platinum, e.g., platinum-based alloys and platinum-group metals, for many years [1]. Regardless of their great efforts, however, both cheaper and more active materials than platinum have not been discovered yet. New breakthroughs for catalyst-design may be possible using ideas other than such conventional ideas as mentioned above.

It is well known that hemoglobin (Hb) can transport oxygen and carbon dioxide in the vascular systems of animals. Heme, which has been considered as the active site of Hb, is constructed from at least one iron-porphyrin (FeP) complex. We think that the catalytic activity of FeP may be used for cathode electrode application of PEFCs. We consider hemoglobin (Hb) components for possible use as cathode electrode catalyst in polymer electrolyte fuel cells (PEFCs). We choose iron-porphyrin (FeP) and (imidazole)FeP [(Im)FeP] as a representative heme complex. We choose FeP and (imidazole)FeP [(Im)FeP] as a representative heme complex. Imidazole is representative of a histidine amino acid which binds to heme.

We perform all calculations based on density functional theory (DFT) [2, 3] with the Becke-Perdew-Wang (B3PW91) exchange-correlation functional [4, 5] and the Dunning-Hay-Wadt basis sets (LANL2DZ) [6–9], as implemented in the Gaussian 03 [10]. All populations and charges are presented by Natural Bond Orbital Analysis (NBO) [11].

---

*Corresponding author: kasai@dyn.ap.eng.osaka-u.ac.jp

Table 1 gives structural parameters and vibrational frequencies for the optimized geometries of FeP, (Im)FeP and their O₂ adducts, without any symmetry constraints. B3PW91/LANL2DZ level calculations can account for the experimental heme-O₂ adduct geometries and vibrational frequencies [12–15]. Our results correspond to singlet ground states for Fe-O₂ and (Im)FeP-O₂. Free O₂ molecule has two π* electrons and produces bent Fe-O-O configurations, where all of the Fe-O-O angles are close to the 120° expected for the sp² hybridization (cf. heme-CO adduct). ν(Fe-O₂) (674 cm⁻¹) of FeP-O₂ is more than that of (Im)FeP-O₂ (609 cm⁻¹), and ν(O-O) (1211 cm⁻¹) of FeP-O₂ is less than that of (Im)FeP-O₂ (1225 cm⁻¹). This indicates that the imidazole ligand weakens the Fe-O₂ bond and strengthens the O-O bond. (Rovira et al. [16], however, suggested a different tendency from ours using Car-Parrinello molecular dynamics.)

Table 2 gives Fe(3d) orbital populations and Fe charges of FeP and (Im)FeP before and after O₂ binds. When O₂ binds to Fe, the O₂ donates electrons to the unoccupied Fe(3dₓ₂−z₂) and the electrons of the occupied Fe(3dₓ₂) back donates to O₂. Fe(3dₓ₂−z₂) population (0.470) of (Im)FeP is more than that of FeP (0.111), and Fe(3dₓ₂) population (1.885) of (Im)FeP is less than that of FeP (1.950). Thus, both donation [0.686: FeP → 0.347: (Im)FeP] to Fe(3dₓ₂) and back-donation [0.645: FeP → 0.475: (Im)FeP] from Fe(3dₓ₂−z₂) are suppressed by the imidazole ligand. Dawson et al. [17] suggested that a strong electron donation from the negatively charged ligand of cytochrome P450 may facilitate the O-O bond cleavage. In the present study, however, their suggestion may not be applied since the donation (1.183: FeP charge of FeP, 0.870: Fe charge of (Im)FeP) from imidazole induces the suppression of both donation and back-donation between Fe and O₂, and the reinforcement of the O-O bond. The result has a close relation to the vibrational frequencies (see Table 1).

Figure 1 shows the calculated potential energy profile for O₂ dissociation from FeP-O₂ adduct. The reaction ini-
TABLE I: Structural parameters and vibrational frequencies for the optimized geometries of iron-porphyrin (FeP), (imidazole)FeP [(Im)FeP], and their O₂ adducts. * Average distance of four Fe-N(pyrrrole) bonds. † Fe-N(imidazole) distance. ‡ B3LYP with Ahlrichs VDZ basis sets. § Fe(TPP)-O₂ (TPP: tetraphenylporphyrin). ‖ Fe(TpivP)(1,2-Me₂Im)-O₂ (TpvP: picket fence porphyrin, Me₂Im: dimethylimidazole). ¶ Fe(Pc)-O₂ (Pc: phthalocyanato).

| Compound       | Fe-Oₓ | O-O  | Fe-O-O | Fe-Np | Fe-Nₓ ^{\text{Im}} | ν(Fe-O₂) | ν(O-O) | δ(Fe-O-O) |
|----------------|-------|------|--------|-------|-------------------|----------|--------|-----------|
|                | [Å]   | [Å]  | [deg]  | [Å]   | [Å]               | [cm⁻¹]   | [cm⁻¹] | [cm⁻¹]    |
| FeP            |       |      |        |       |                   |          |        |           |
| FeP-O₂         | 1.714 | 1.315| 121.990| 2.01  |                   | 674      | 1211   | 349       |
| Ref. [12] (calc.) ‡ | 1.715 | 1.314| 122.386| 2.01  |                   | 702      | 1159   | 347       |
| Ref. [13] (exp.) § |       |      |        |       |                   | 508      | 1195   | 349       |
| (Im)FeP        |       |      |        |       |                   | 2.004    | 1.917  |           |
| (Im)FeP-O₂     | 1.777 | 1.314| 122.106| 2.009 |                   | 1.998    | 609    | 1225      |
| Ref. [12] (calc.) ‡ | 1.776 | 1.311| 122.9  | 2.023 |                   | 2.024    | 623    | 1176      |
| Ref. [14] (exp.) § |       |      |        |       |                   | 1.99     | 2.29   |           |
| Ref. [15] (exp.) ¶ |       |      |        |       |                   |          |        |           |

TABLE II: Fe(3d) orbital populations and Fe charges of iron-porphyrin (FeP) and (imidazole)FeP [(Im)FeP] before and after O₂ binds.

|          | FeP before | FeP after | after-before | FeP before | FeP after | after-before | (Im)FeP before | (Im)FeP after | after-before |
|----------|------------|-----------|--------------|------------|-----------|--------------|----------------|--------------|-------------|
| 3dₓᵧ     | 0.636      | 0.780     | 0.144        | 0.637      | 0.780     | 0.143        | 0.780          | 0.143       |            |
| 3dₓz     | 1.950      | 1.918     | -0.032       | 1.915      | 1.937     | -0.022       | 1.937          | -0.022      |            |
| 3dₓz     | 1.950      | 1.305     | -0.645       | 1.885      | 1.410     | -0.475       | 1.410          | -0.475      |            |
| 3dₓz⁻²    | 1.975      | 1.965     | -0.010       | 1.982      | 1.975     | -0.007       | 1.975          | -0.007      |            |
| 3dₓ      | 0.111      | 0.797     | 0.686        | 0.470      | 0.817     | 0.347        | 0.817          | 0.347       |            |
| Cₓpصيب | 1.183      | 0.964     | -0.219       | 0.870      | 0.775     | -0.095       | 0.775          | -0.095      |            |

In summary, we confirmed the O-O bond breaking abilities of FeP and (Im)FeP, which are active sites of Hb. Since imidazole ligand strengthens the O-O bond, the FeP cleaves the O-O bond more easily than (Im)FeP. Nevertheless, the activation barrier for O₂ dissociation from FeP-O₂ adduct is too high to utilize for cathode electrode application in PEFCs. This implies that just FeP cannot be of practical use of a catalyst. However, we think that this problem may be overcome by designing FeP-based materials, which are equivalent to, in terms of catalytic activity, well-known platinum catalyst [29].

This work is partly supported by the Ministry of Education, Culture, Sports, Science and Technology of Japan (MEXT) Special Coordination Funds for Promoting Science and Technology (Nanospintronics Design and Realization), the 21st Century Center of Excellence (COE) Program ‘Core Research and Advance Education Center for Materials Science and Nano-Engineering’ supported by the Japan Society for the Promotion of Science (JSPS) the New Energy and Industrial Technology Development Organization (NEDO) Materials and Nanotechnology Program, and the Japan Science and Technology Agency (JST), Research and Development Applying Advanced Computational Science and Technology Program. Some of the calculations presented here were carried out using the computer facilities of the Japan Atomic Energy Research Institute (JAERI) and the National Institutes of Natural Sciences (NINS).
FIG. 1: Calculated potential energy profile given in eV for O$_2$ dissociation from iron-porphyrin-O$_2$ (FeP-O$_2$) adduct. Distances are shown in Å. Atomic colors are brown for Fe, blue for N, gray for C, white for H, and red for O.

FIG. 2: Calculated potential energy profile given in eV for O$_2$ dissociation from (imidazole)iron-porphyrin-O$_2$ [(Im)FeP-O$_2$] adduct. Distances are shown in Å. Atomic colors are brown for Fe, blue for N, gray for C, white for H, and red for O.

[1] N. M. Markovi. and P. N. Ross Jr., Surf. Sci. Rep. 45, 117 (2002).
[2] P. Hohenberg and W. Kohn, Phys. Rev. 136, B864 (1964).
[3] W. Kohn and L. J. Sham, Phys. Rev. 140, A1133 (1965).
[4] A. D. Becke, J. Chem. Phys. 98, 5648 (1993).
[5] J. P. Perdew and Y. Wang, Phys. Rev. B 45, 13244 (1992).
[6] T. H. Dunning, Jr. and P. J. Hay, in Modern Theoretical Chemistry, Ed. H. F. Schaefer, III, Plenum, New York, pp. 1-28 (1976).
[7] P. J. Hay and W. R. Wadt, J. Chem. Phys. 82, 270 (1985).
[8] W. R. Wadt and P. J. Hay, J. Chem. Phys. 82, 284 (1985).
[9] P. J. Hay and W. R. Wadt, J. Chem. Phys. 82, 299 (1985).
[10] M. J. Frisch et al., Gaussian 03, Revision B.05, Gaussian, Inc., Pittsburgh PA, 2003.
[11] A. E. Reed, L. A. Curtiss and F. Weinhold, Chem. Rev. 88, 899 (1988).
[12] K. M. Vogel, P. M. Kozlowski, M. Z. Zgierski and T. G. Spiro, J. Am. Chem. Soc. 121, 9915 (1999).
[13] L. M. Proniewicz, I. R. Paeng and K. Nakamoto, J. Am. Chem. Soc. 113, 3294 (1991).
[14] G. L. Woolery, M. A. Walters, K. S. Suslick, L. S. Powers and T. G. Spiro, J. Am. Chem. Soc. 107, 2370 (1985).
[15] K. Bajdor, H. Oshio and K. Nakamoto, J. Am. Chem. Soc. 106, 7273 (1984).
[16] C. Rovira, P. Ballone and M. Parrinello, Chem. Phys. Lett. 271, 247 (1997).
[17] J. H. Dawson, R. H. Holm, J. R. Trudell, G. Barth, R. E. Linder, E. Bunnenberg, C. Djerassi and S. C. Tang, J. Am. Chem. Soc. 98, 3707 (1976).
[18] C. Peng, P. Y. Ayala, H. B. Schlegel and M. J. Frisch, J. Comput. Chem. 17, 49 (1996).
[19] C. Peng and H. B. Schlegel, Isr. J. Chem. 33, 449 (1994).
[20] A. Eichler and J. Hafner, Phys. Rev. Lett. 79, 4481 (1997).
[21] M. Tsuda, W. A. Diño, H. Nakanishi and H. Kasai, submitted.
[22] W. A. Diño, H. Kasai and A. Okiji, Phys. Rev. Lett. 78, 286 (1997).
[23] W. A. Diño, H. Kasai and A. Okiji, J. Phys. Soc. Jpn. 67, 1517 (1998).
[24] W. A. Diño, H. Kasai and A. Okiji, Surf. Sci. 418, L39 (1998).
[25] W. A. Diño, H. Kasai and A. Okiji, Surf. Sci. 493, 278 (2001).
[26] W. A. Diño, J. Phys.: Condens. Matter 14, 4379 (2002).
[27] H. Kasai, W. A. Diño and R. Muhida, Prog. Surf. Sci. 72, 53 (2003).
[28] M. Okada, K. Moritani, A. Yoshigoe, Y. Teraoka, H. Nakanishi, W. A. Diño, H. Kasai and T. Kasai, Chem. Phys. 301, 315 (2004).
[29] M. Tsuda, W. A. Diño, H. Nakanishi and H. Kasai, in preparation.

http://www.sssj.org/ejssnt (J-Stage: http://ejssnt.jstage.jst.go.jp)