Structural characteristics of gluconolactone/gluconic acid aqueous solution used for bio battery by molecular dynamics

Shigeki Matsunaga
National Institute of Technology, Nagaoka College, Nagaoka 940-8532, Japan
E-mail: matsu@nagaoka-ct.ac.jp

Abstract. The structural characteristics of gluconolactone/gluconic acid aqueous solution as a model for the anode of biofuel cells are investigated by molecular dynamics. The molecular structure of components of the solution and the atomic charges are optimized by the density functional theory (DFT) using Gaussian09. The distribution of constituent ions of the solution is investigated by a radial distribution function. The shape change of gluconic acid anions in the solution and the frequency distribution of each ion are also examined.

1. Introduction
In recent years, biofuel cells have been drawing attention. Glucose is one of the promising energy resources used in biofuel cells because it is obtained by degrading cellulose, which is abundant in nature. Biofuel cells are also expected as the next generation portable chemical battery that is safe and can be used by the human body. In a recent report, enzyme fuel cells achieved 10 times the energy storage of lithium-ion batteries [1]. At the anode of a biofuel cell, glucose is oxidized to produce gluconolactone, as,

\[
C_6H_{12}O_6 \rightarrow C_6H_{10}O_6 + 2H^+ + 2e^- .
\]  

(1)

Then, gluconolactone dissolves in water to give gluconic acid, but in the aqueous solution it ionizes and exists as an anion, as,

\[
C_6H_{10}O_6 + H_2O \rightarrow C_6H_{12}O_7^- \rightarrow C_6H_{11}O_7^- + H^+
\]  

(2)

Therefore, the aqueous glucose solution at the anode of a biofuel cell contains many components, including buffer solutions. There are many molecular dynamics (MD) studies on glucose aqueous solution, but few MD studies dealing with multicomponent systems. In recent years, we have systematically carried out MD studies of multicomponent aqueous solutions. [2-5]. In addition, we have conducted research on aqueous solutions of glycolic acid and lactic acid used in biofuel cells [6-8].

In this study, as part of a series of studies, we would like to consider the structural characteristics of glucose-oxidized gluconolactone/gluconic acid aqueous solution as a model for the anode of biofuel cells.

2. Optimization of molecules
The molecules and their ions used in MD have been optimized in advance using Gaussian09, i.e. the arrangement and charge of atoms within the molecule have been determined. For this purpose, B3LYP/6-31+G(d,p) level density functional theory (DFT) is applied in the cavity of the IEF-PCM solvent field [9].
The obtained molecules and ions are shown in Fig. 1 (a) – (c). Interestingly, although gluconic acid is a linear molecule, its anion has an arcuate structure.

The vibrational spectra of gluconolactone and gluconic acid anion are shown in Fig. 2 from top to bottom, respectively. In the region of 3000 1/cm or more, the mode corresponding to the O-H expansion and contraction can be seen. A large peak due to stretching of C = O exists at about 1700 1/cm. In the area of 500-1500 1/cm, vibrational modes of C-O stretching can be seen. Furthermore, in the region below 500 1/cm, C-H bending vibrations are observed. The vibrational mode differences between the gluconolactone and gluconate anions reflect the structural differences in these molecules. The frequency modes of the gluconic acid anion have more and complex peaks than those of gluconolactone in both the low and high frequency region.
3. Simulation procedure
The basic procedure of MD simulation is briefly described below, which is similar to our previous paper [3,4,5]. The solution contains solvent water, gluconolactone, gluconic acid anion, K+, H+, OH-. The solvent water molecule TIP4P is treated as a rigid body model. The pair potential functions of TIP4P water are expressed as charged Leonard Jones (L-J) type potential, as follows [10,11],

$$\phi_{ij}(r) = \frac{z_iz_je^2}{r} + 4\epsilon \left( \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^{6} \right)$$

In equation (3), $i$ and $j$ represent the components, $z_i$ is the charge of constituent $i$, and $e$ is the elementary charge. The interactions $K^+K^+$, $K^+\text{TIP4P}$ are expressed as [12],

$$\phi_{ij}(r) = \frac{z_iz_je^2}{r} + \frac{C}{r^9} - \frac{D}{r^6}$$

The interaction between the remaining components is given by [13,14],

$$\phi_{ij}(r) = \frac{z_iz_je^2}{r} + \frac{A}{r^{12}} - \frac{B}{r^6}$$

MD is carried out at NPT, i.e. the number of components, pressure and system temperature are constant at 1 atm and 298K. The number of molecules is 3140, 2775 H$_2$O, 35 gluconolactone, 65 gluconic acid anion, 100 K$^+$, 100 OH$^-$, 65 H$^+$, i.e. 2 mol/L gluconolactone and gluconic acid anion, which is adjusted so that the charge neutral condition is satisfied. The ratio of gluconolactone and gluconic acid anion was determined from experimental data [15]. The one time step of MD is 0.1fs. The Ewald method is used
to calculate the charge interaction. SEIGRESS (Fujitsu) is used in the main MD calculation [16]. In MD, gluconolactone and gluconic acid anion are calculated under the condition that the bond length is constant, i.e., the SHAKE algorithm [17]. The snapshot of MD cell is shown in Fig. 3.

Figure 3. The snapshot of MD cell. C: brown, O: pink, H: white, K: purple.

Figure 4. The bond angle between carbon atoms in gluconic acid anion.
In order to confirm the shape of gluconic acid anion in the solution, the bond angle between carbon atoms was investigated. The obtained bond angle distribution is shown in Fig.4, where the numbers correspond to the carbon atoms in Fig.1(c). Almost all bond angles between carbon atoms are distributed in the range of 100° to 130°. Only a few bonds are found near 90° and 180°. This indicates that the arcuate shape of the gluconic acid anion is retained in the solution.

Figure 5(a) $g_{ij}(r)$ between O_water and C, H, and O in gluconolactone (glu) and gluconic acid anion (gla).

Figure 5(b) $g_{ij}(r)$ between H_water and C, H, and O in gluconolactone (glu) and gluconic acid anion (gla).
The distribution of water molecules around the gluconolactone and the gluconic acid anion in the solution is examined by the radial distribution function \( g_{ij}(r) \). The obtained results are shown in Fig 5(a) and (b). In these figures, \( g_{ij}(r) \) for water and gluconolactone is larger than that for water and gluconic acid anion. This result suggests that gluconolactone attracts water molecules more than gluconic acid anion. In Fig 5(a), the first peak position of \( g_{ij}(r) \) for O_water and O and H in gluconolactone and gluconic acid anion is at about 3.3 Å, which corresponds to the distance between gluconolactone and gluconic acid anion and their first hydration shell. In the same way, their second peak at around 6.1 Å corresponds to the distance to the second hydration shell.

The diffusion coefficient of the \( i \)-th component in the solution can be calculated from the mean square displacement (MSD) as follows [18],

\[
D_i = \lim_{t \to \infty} \frac{1}{6t} \langle |\mathbf{r}_i(t) - \mathbf{r}_i(0)|^2 \rangle.
\]  (6)

MSD obtained by MD is shown in Fig 6. The estimated diffusion coefficient \( D_i \) of each component is summarized in Table 1. \( D_i \) of water is very close to the literature value [19]. \( D_i \) for gluconolactone and gluconic acid anion is comparable to that for glucose in water [20].

| constituent           | \( D_i \left( \times 10^{-5} \text{ cm}^2/\text{s} \right) \) |
|-----------------------|------------------------------------------------------|
| gluconolactone        | 0.59                                                 |
| oxalic acid anion     | 0.47                                                 |
| K⁺                    | 1.09                                                 |
| water                 | 2.15                                                 |

Table 1. Diffusion coefficients obtained from MSD.

Figure 6. MSD of O in water, C in gluconolactone, C in gluconic acid anion, and K⁺.
Finally, we calculate the frequency dependent diffusion coefficient $D_i(\nu)$, which is expressed as [18],

$$D_i(\nu) = \frac{1}{3} \int_0^\infty \langle \vec{v}_i(t) \cdot \vec{v}_i(0) \rangle \cos(2\pi \nu t) \, dt,$$

where $\langle \vec{v}_i(t) \cdot \vec{v}_i(0) \rangle$ represents the velocity auto-correlation function (VAF) for the $i^{th}$ component.

As shown in Fig. 7, the low-vibration infrared region is attributed to the cage effect by the surrounding water molecules, i.e., the hydration shell. The structural difference between gluconolactone and gluconic acid anion can be clearly seen in the frequency range of 400 to 1200 [1/cm]. The bond length is fixed and only bending is allowed in the molecules in MD calculation, however the high frequency distributions over 500 [1/cm] corresponding to the stretching modes are obtained. These results can be produced by interactions between atoms in different molecules, or intermolecular interactions.

![Figure 7. $D_i(\nu)$ for C in gluconic acid anion, C in gluconolactone, and O in water.](image)

4. Conclusion
MD was performed on an aqueous solution of gluconolactone and gluconic acid anion as a model for the biofuel cell anode. The arrangement and charge of atoms of gluconolactone and gluconic acid anion have been previously determined using Gaussian09. It is interesting to note that the obtained gluconic acid has a chain shape, but the gluconic acid anion has an arc shape. The bond angles between carbons in gluconic acid anion were distributed from 100° to 130° during MD. From the radial distribution function obtained by MD, two layers of hydration shell were found around gluconolactone and gluconic acid anion. The diffusion coefficient obtained from MSD well reproduced the experimental value in the literature. The distribution of $D_i(\nu)$ shows the cage effect due to surrounding water molecules and the difference in the structures of gluconolactone and gluconic acid anion.
Acknowledgments
I would like to express my thanks to Professor S. Tamaki for his helpful comments and encouragement on this study. Part of the results in this study was obtained using the supercomputing facilities at Research Institute for Information Technology, Kyushu University. This study received financial support from the Uchida Energy Science Promotion Foundation.

References
[1] Zhu Z, Tam T K, Sun F, You C, and Zhang Y -H P 2014 Nature Comm. 5 3026 (pp 1 – 8)
[2] Matsunaga S 2017 J. Mol. Liq. 226 90-95
[3] Matsunaga S 2016 Int. J. Mol. Sci. 17 45 (pp 1 - 18)
[4] Matsunaga S 2015 Mol. Sim. 41 913-917
[5] Matsunaga S and Tamaki S 2014 J. Sol. Chem. 43 1771-1790
[6] Matsunaga S 2018 IOP Conf. Ser.: Mater. Sci. and Eng., 369(1) 012014(1-6)
[7] Matsunaga S 2018 AIP Conf. Proc. 1981 020115(1-4)
[8] Matsunaga S 2019 Polymer Eng. & Sci. 59(12) 2474-2478
[9] Foresman J B and Frisch Æleen 1998 Exploring Chemistry with Electronic Structure Methods, 2nd ed. (Pittsburg: Gaussian, Inc)
[10] Jorgensen W L, Chandrasekhar J, Madura J D, Impey R W and Klein M L 1983 J.Chem. Phys. 79 926-935
[11] Mahoney M W and Jorgensen W L 2000 J. Chem. Phys. 112 8910-8922
[12] Peng Z, Ewig C S, Hwang M-J, Waldman M and Hagler A T 1997 J. Phys. Chem. A 101 7243-7252
[13] Mayo S L, Olafson B D and Goddard III W A 1990 J. Phys. Chem. 94 8897-8909
[14] Rappe A K, Casewit C J , Colwell K S, Goddard III W A and Skiff W M 1992 J. Am. Chem. Soc. 114 10021-10035
[15] Fabre L, Flèche G, Fuertes P, Gallezot P, and Perrard A 2000 Catalysis Letters 68 41–44
[16] FUJITSU Technical Computing Solution SCIGRESS. https://www.fujitsu.com/global/solutions/business-technology/tc/sol/scigress/index.html Accessed 4 September 2020
[17] Ryckart J-P, Ciccotti G, and Berendsen H J C 1977 J. Comp. Phys. 23 327-341
[18] Hansen J-P and McDonald I R 1986 Theory of Simple Liquids, 2nd Ed., (London: Academic Press)
[19] Mills R 1973 J. Phys. Chem. 77,(5) 685-688
[20] Ribeiro Ana C F, Ortona O, Simões S M N, Santos C I A V, Prazeres P M R A, Valente A J M, Lobo V M M, and Burrows H D 2006 J. Chem. Eng. Data 51 1836-1840