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Proton Conductivity in Chitin System

Takashi Kawabata

Abstract

We have created and researched fuel cells using biomaterials as next-generation low-environmental-load energy. As is well known, chitin is a biomass that is discharged in large quantities as a marine product processing waste. We have focused on the chitin and have been studying the production of fuel cells and proton conductivity using it. It was revealed that chitin can be used as an electrolyte membrane for fuel cells under humidified conditions and becomes a proton conductor. It was found that the presence of water molecules is important for the appearance of proton conduction in chitin system. This study presents the utility value of chitin in new fields and provides insight into the proton conduction mechanism of chitin-based biomaterials.

Keywords: Chitin, chitosan, fuel cell, proton conductor, electrolyte

1. Introduction

In the olden days of biomaterials, prostheses and medical alternatives have been mainly developed. However, there are reports that biomaterials play a wider range of roles today and can be used in the field of electronic devices such as sensors. In other words, biomaterials are not limited to medical materials, but are becoming more valuable than materials such as plastics and metals that we usually use.

We have fabricated fuel cells based on chitin and investigated its proton conductivity in chitin systems. It is well known that the chitin is superior biomass emitted from marine products and is obtained from crabs and shrimp shells. It is also famous that chitin has excellent biocompatibility and can be easily decomposed in the environment. For a long time, most research on chitin focused on biocompatibility and ion adsorption capacity. For example, Malette *et al.* have studied the curative effect of chitosan on the vulnery [1]. Sandford *et al.* reported the useful substituent effect of chitosan to skin [2, 3]. Nair and Madhavan have suggested the method for the elimination of Hg in solution using chitosan, and Peniche-covas *et al.* have investigated the efficiency of adsorption of Hg [4, 5]. Recent studies seem to focus specifically on biocompatible medical application and biomass. Romana *et al.* have suggested that chitin-PLA laminated composite becomes a candidate for medical applications such as implants [6]. Mohamoud *et al.* have shown that insects can be used as an alternative low-cost chitin source, and bio-convert chitin directly to ethanol by using strain of *M. circinelloides* [7].

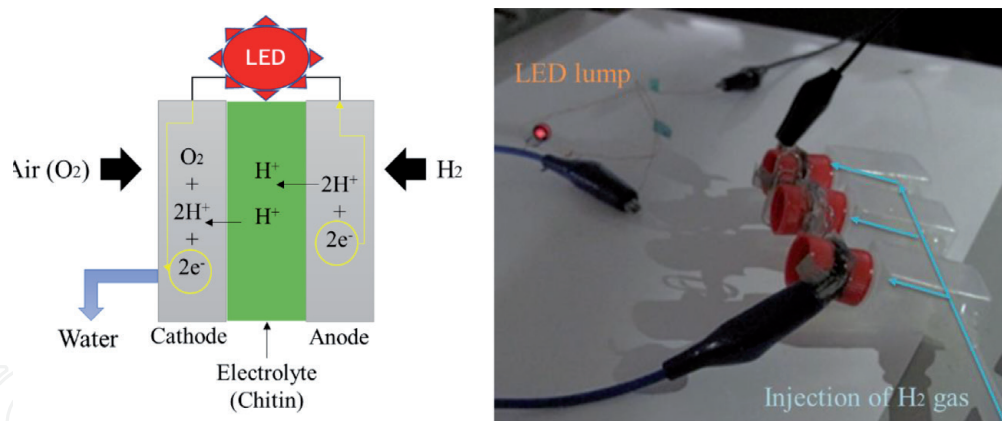


Figure 1. Schematic diagram of fuel cell used for demonstration (left) and photograph of turning up LED lamp by chitin fuel cell (right).

However, there were few reports in the field of energy such as using chitin in fuel cells. Biomaterials such as DNA, protein and polysaccharide are abundant in nature, and they are disassembled in environment by microbial. Active use of biomaterials is expected to have less environmental impact and manufacturing costs than chemical processes.

We have revealed that the chitin is proton conductor and available for electrolyte of fuel cells (**Figure 1**) [8]. Moreover, it was found that appearance of proton conductivity in chitin demand water molecules, and the acetyl group plays important role in injection water molecule into chitin. These suggestions are basis on relationship between results of impedance measurement and water content measurement with humidified condition. In appearance of proton conductivity in chitin, it is considered that one more important factor is exist of amino acetyl group. Effects of amino acetyl group have been revealed by comparing to proton conductivity in chitosan which is basic structure of chitin. Considering proton conduction system of chemical polymer Nafion® which is used the most for fuel cell, it is deduced that the amino and acetyl group in chitin involves forming hydration supporting proton transport. Although, it is found that power density and proton conductivity in chitin are lower than the Nafion®.

Therefore, in order to improve proton conductivity, there is room for further investigation of the relationship between the appearance of proton conductivity in chitin and water molecules. These understandings are expected to present the necessary and important factors for applying polysaccharides with little change in basic structure to electrolyte membranes.

2. Experimental

2.1 Sample preparation

Chitin films were prepared with the purified chitin of under 5% of deacetylation degree, obtained from crab (Sugino Machine Limited). This purified 2%(w/v) chitin slurry was well dispersed in distilled water and the chitin sheets were prepared by suction filtration using Teflon membrane filter (ADVANTEC, Co.) [8–10]. **Figure 2** shows the photograph of the chitin film. The thickness of the film is approximately 0.07 mm.

The chitin fiber specimens were prepared by purifying chitin obtained from the tendon of crab's legs. Based on the article of Prosky *et al.*, the purification

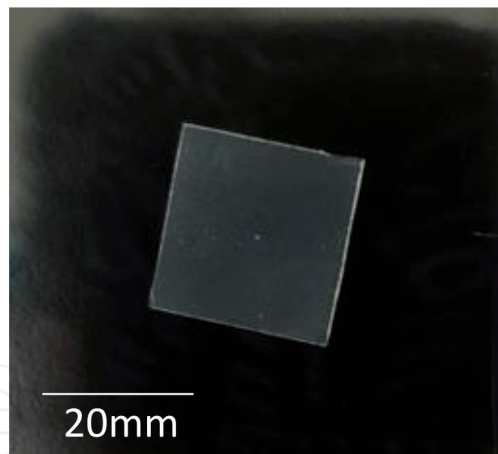


Figure 2.
 Photograph of chitin sheet [11].

method was performed using a group of enzymes including α -amylase and protease obtained from *Streptomyces griseus* (Wako Pure Chemical Industries, Ltd.) [8–10]. The oriented chitosan was prepared by oriented chitin to deacetylation treatment with 25%(w/v) sodium hydroxide under reflux conditions for 5 hours.

2.2 Fabrication of the fuel cell based on chitin and operating condition

Figure 3 shows the shape of the fuel cell based on the chitin electrolyte. As show in **Figure 3**, the chitin electrolyte was inserted between Pt-C electrodes (anode and cathode). The current was collected from the current collector plates. The hydrogen and oxygen gases were introduced from the up and down sides of the fuel cell, respectively. In the fuel gas flow, the relative humidity, temperature and gas-flow ratio were controlled by the humidified gas-flow control system of Auto PEM (Toyo Corporation) at room temperature. The H_2 gas flow rate and the air flow rate are 0.1 L/min and 0.25 L/min, respectively [8].

2.3 Impedance and water contents measurements

The water contents were measured from the relative humidity dependence of the weight of chitin using the electronic analytical balance (OHAUS Inc.) and the number of water molecules per a chitin molecule was calculated from the obtained water contents and molecular weights of water and mono-chitin [8]. The water content n was calculated using the following equation,

$$n = \frac{(w - d) / Mw}{d / Mc} \quad (1)$$

This time, w and d show each weight of wet and dry sample. Mw is molecular weight of water. Mc is molecular weight of mono-chitin or mono-chitosan.

The measurement of electrical conductivity was carried out using precision LCR meter (E4980A, Agilent Technologies Inc.). The relative humidity and temperature were controlled by the humidified gas-flow control system (Auto PEM). In the impedance measurement, the electrical conductivities perpendicular to the surface and parallel to the surface in chitin sheet were measured. In the case of chitin fiber specimens, impedance measurements were performed for specimens along the fiber direction and normal to the fiber direction, respectively [8–10].

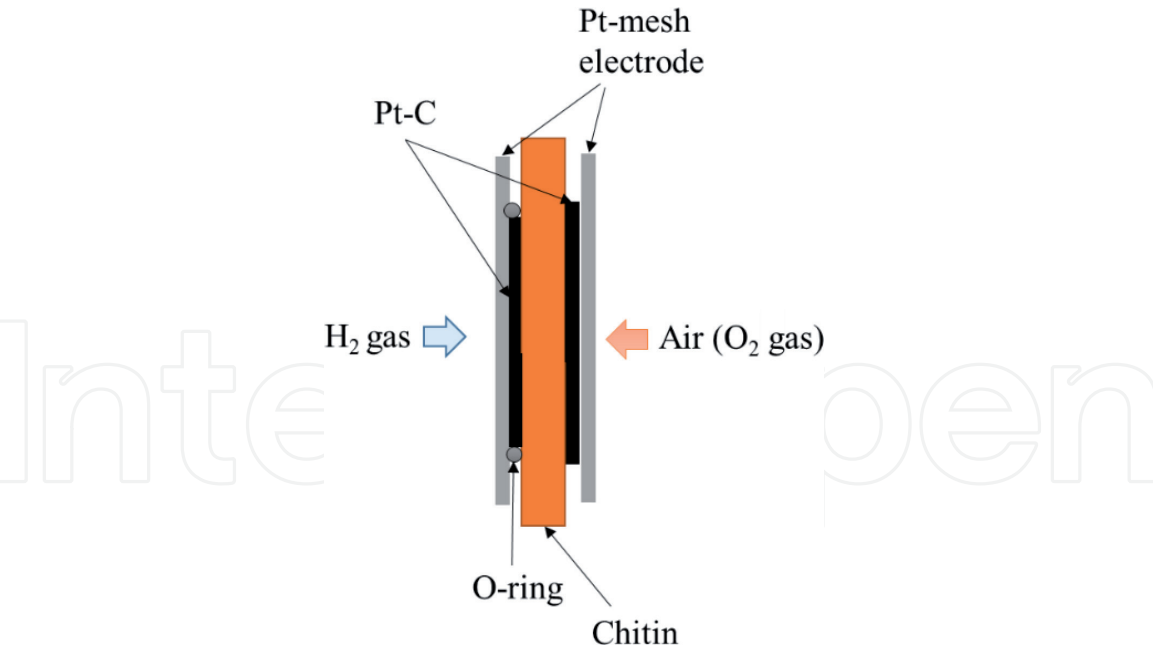


Figure 3.
Fuel cell based on the chitin.

3. Result and discussion

3.1 Power density in chitin and chitosan fuel cells

So far, we have revealed that power density in the fuel cell based on chitin or chitosan [8]. **Figure 4** shows *i*-*V* characteristics of the fuel based on the chitin. As shown in **Figure 4**, chitin electrolyte shows typical *i*-*V* curve and is also a polysaccharide material, but it has a high output, an open circuit voltage of 0.76 V and a power density of 1.35 mW/cm². The red dot in **Figure 4** shows the *i*-*V* characteristics when injecting unhumidified H₂ gas, but it can be seen that the current obtained is very low. Chitosan did the same test, but its maximum power density was 0.032 mW/cm², which was lower than that of chitin. These results indicate that chitin and chitosan become the proton conductor with humidified condition. Moreover, it is expected that these differences are due to difference between chitin and chitosan, that is, the deacetylation degree of the chitin system.

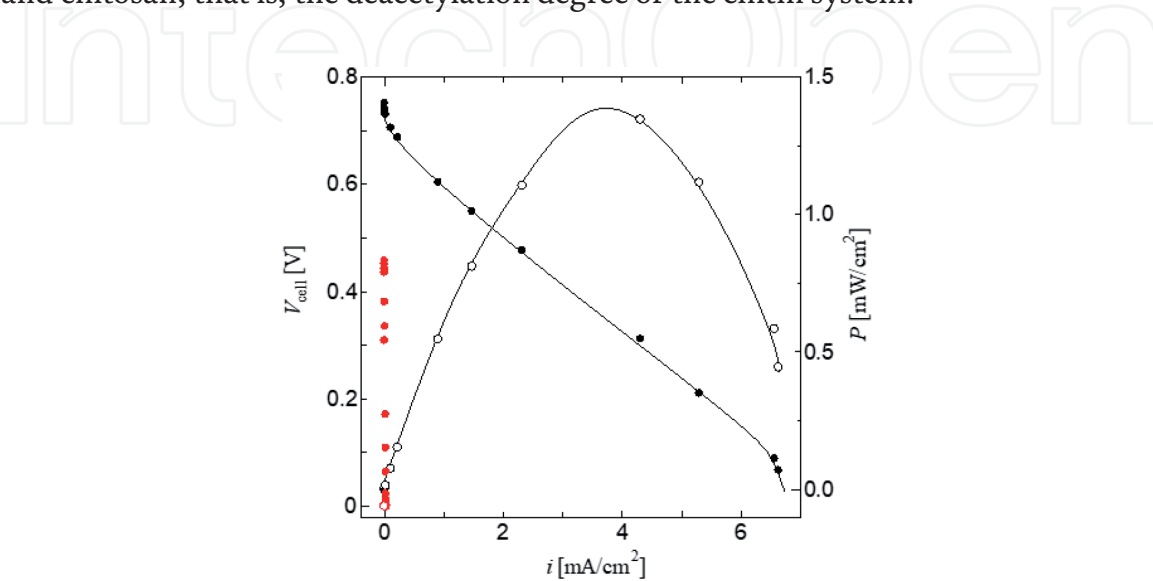


Figure 4.
**i*-*V* characteristics of fuel cell based on chitin electrolyte. Red and black dots show relation between open circuit voltage and current density. Black and red circle show power density.*

3.2 Proton conductivity in chitin system

Regarding the proton conductivity in chitin and chitosan, which have already revealed, these values in sheet specimens show approximately $10^{-4} \sim 10^{-1}$ S/m [1]. The proton conductivity of the chitin system sheet increases monotonically with increasing humidity, and the value of chitin is tens of times higher, especially when the relative humidity is changed from 60% to 100%. In the case of chitosan, its value changes approximately 10 times higher. Further, we focused on acetyl group in chitin, and have revealed that relationship between proton conductivity in chitin system and the deacetylation by using Fourier transform infrared spectrometer (FT-IR). **Figure 5** shows the FTIR spectrum of chitin used in the experiment [10]. It was found that the acetyl group plays important role for appearance of proton conductivity in chitin system because the degree of deacetylation gave conductivity of anomalous behavior [10].

Furthermore, we have approached the proton conductivity in chitin system by using measurement of water contents and comparing chemical component. First, we have used sheet and fiber specimen of chitin, and measured the degree of swelling by microscopic observation after immersion experiment in water. As a result, it was confirmed that the sheet specimen was isotropically swelled in both the cross section and the in-plane, and the fiber specimen was anisotropically swelled by approximately 20% in both the fiber cross section and the fiber direction. From the above, it was clear that the chitin system introduced water molecules, so we made a comparison based on the water content and chemical component. The results obtained by these researches indicated that injection of water molecule and existence of acetyl group for promotion it, that is necessary to appearance of the proton conductivity in chitin system. However, it has not been completely understood that water molecule how to behave in chitin system yet.

3.3 Percolation conductivity in chitin

In order to clarify the role of water molecules in chitin, we obtained the volume fraction of water molecules with respect to chitin molecules from the results of the relative humidity dependence of the hydration number, and investigated the relationship with proton conductivity. Yamada *et al.* measure the resistance value that changes by gradually increasing the volume fraction of the conductor material in the non-conductor material [12]. As a result, Yamada *et al.* report that the resistance

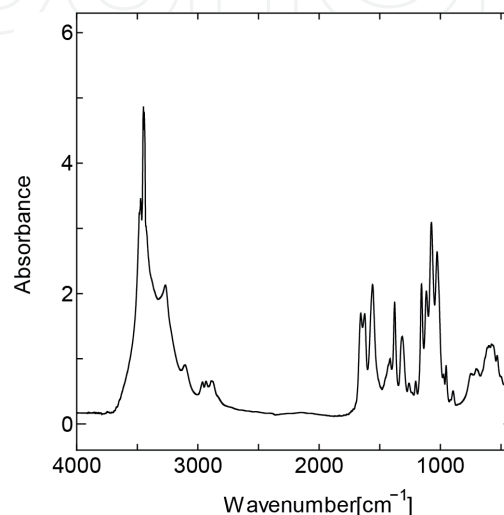


Figure 5.
 FT-IR spectra of chitin sample [10].

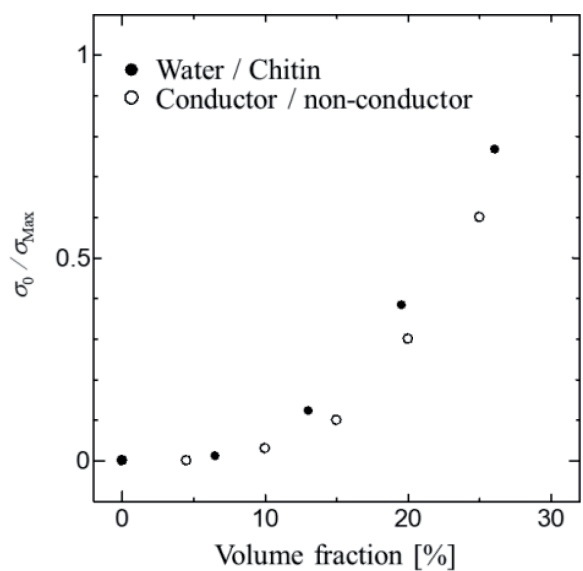


Figure 6.
Relationship between volume fraction of water molecules and percolation conduction in chitin [11].

value becomes constant at a volume fraction of about 30%. It is well known that the crystal structures of chitin and chitosan have been clarified for a long time and many reports have been published [13–19]. Sawada *et al.* report on the crystal structure of β -chitin dihydrate. We have found from water content experiments of chitin that each constituent unit has two water molecules, and that the proton conductivity is saturated during this dihydrate formation [8, 9]. Moreover, it has already confirmed that XRD diffraction pattern of our chitin sample is consistent with pattern of general chitin. Based on these results, the volume fraction of water molecules contained in the crystal lattice was estimated with reference to the report by Sawada *et al* [14–16]. **Figure 6** shows the relationship between the volume fraction of water molecules in chitin hydrate and the proton conductivity. The relationship between the volume fraction and the conductivity of the conductor in the non-conductor of **Figure 6** is a value calculated from the resistance value reported by Yamada *et al.* As can be seen in **Figure 6**, water molecules in chitin behave very much like conductors in non-conductors. In other words, this result indicates that water molecules in chitin function as a proton transport pathway.

3.4 Activation energy and proton pathway

Investigation of proton transport pathways in chitin is important for the future development and development of polysaccharide electrolyte membranes. So far, it has been shown that chitin has proton conductivity, and it is important that the introduction of water molecules behaves like a conductor for the proton conductivity. In addition, since the structure of chitin hydrate has been clarified, we approached the proton conduction pathway of chitin by measuring impedance using an oriented sample. As a result, it was confirmed that chitin and chitosan have orientation dependence of proton conductivity [8, 9]. From this result, the temperature dependence of the proton conductivity of the chitin system was investigated. **Figure 7** shows the proton conductivity in the chitin fiber direction when only the temperature factor is changed while maintaining a constant wet weight. As shown in **Figure 7**, the relationship between the reciprocal of temperature and the proton conductivity of chitin shows an Arrhenius-like linear change. This result indicates that the proton conductivity of chitin has thermal activity. **Table 1** shows the activation energy of proton conductivity derived from the Arrhenius equation

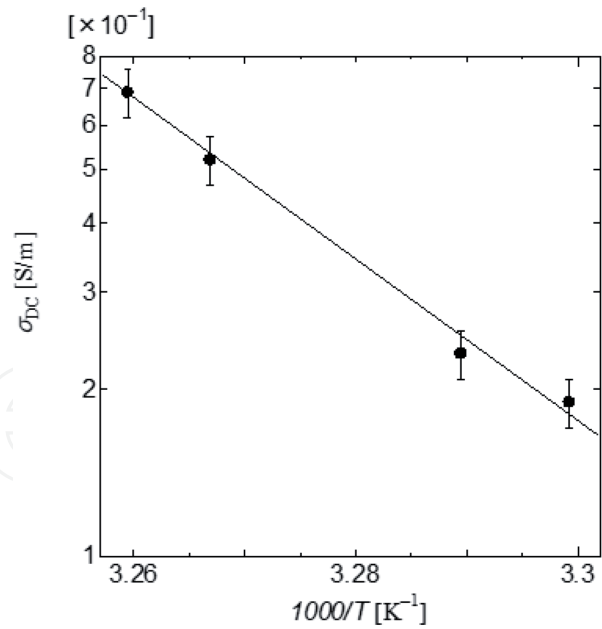


Figure 7.
Arrhenius plot of proton conductivity in chitin [11].

	Fiber direction (eV)	Fiber vertical direction (eV)
Chitin	0.55	0.30
Chitosan	0.57	0.58

Table 1.
Activation energy of proton conduction in the chitin system.

in each fiber direction of chitin and chitosan. Arrhenius equation is represented by following equation:

$$\sigma = \sigma_0 \exp\left(-\frac{\Delta E}{kT}\right) \tag{2}$$

Here, σ and σ_0 are proton conductivity and proton conductivity when frequency is 0, k and T are boltzmann constant and temperature, ΔE is activation energy.

As shown in **Table 1**, the activation energy of chitin-based proton conduction changed depending on the fiber direction in the case of chitin, and no change was observed in the case of chitosan. In general, a decrease in activation energy indicates a decrease in energy required for proton transport, and is therefore expected to contribute to the realization of high proton conductivity. Considering this, it is considered that the decrease in activation energy of chitin in the vertical direction of the fiber is appropriate. However, in the oriented sample, the activation energy of chitin in each fiber direction seems to be inconsistent, considering that the proton conduction of chitin in the fiber direction is the highest. Since the activation energy is not the only element required for proton conduction, the following equation:

$$\sigma = zne\mu \tag{3}$$

Here, z and n are ion valence and number of proton transport pathway, e and μ are charge density and mobility. Since the charge of the proton is +1 and $z = 1$, the charge concentration e is that the amount of water of crystallization is e ,

assuming that the proton conduction is through the water of crystallization of the chitin crystal. Furthermore, from Eq. 3, considering that the mobility μ is related to the activation energy, the value of the proton conductivity σ on the left side is determined, so that the high proton conductivity in the fiber direction of the oriented chitin is determined. It is suggested that it is brought about by the number n of proton transport pathways. Taking these things into consideration, we gained insight into the relationship between the crystal structure of chitin and chitosan hydrates and the proton transport pathway from the hydrogen bond distance.

Figure 8 shows the hydrogen bonds formed in chitin hydrate. In **Figure 8**, each color line shows hydrogen bonds, pink is about 2.6 Å of water-chitin molecule, yellow is 2.98 Å, and light blue is between chitin and chitin. Further, broken line shows the hydrogen bond formed along the fiber direction of chitin, and the rigid line shows the hydrogen bond formed in the direction perpendicular to the fiber. As shown in **Figure 8**, among the hydrogen bonds formed in chitin hydrate, the hydrogen bonds between the water molecule and chitin are formed at a distance of about 2.6 Å in the fiber vertical direction (a -axis direction). On the other hand, hydrogen bonds with a distance of 2.6 Å and 2.98 Å are alternately formed in the fiber direction. **Figure 9** shows the results in the case of chitosan. This result suggests that the proton transport pathway of chitosan is mediated by the hydrogen bond of 3.0 Å, which is the yellow dotted line in **Figure 9**, which is common in both the fiber direction and the fiber vertical direction. From these results, it is considered that the relationship between the proton conductivity of chitin and chitosan and the activation energy is due to the hydrogen bond distance of approximately 3.0 Å, which is common to both samples, as a bottleneck. It is expected that the high proton conductivity generated in the fiber direction of oriented chitin will be realized by increasing the number of pathways.

From the above results, the proton conduction of chitin having high proton conductivity is expected as shown in **Figure 10**. Proton conduction in chitin is considered to be realized by the Grosus mechanism in consideration of the relationship between the result of percolation conduction and the hydration structure. In the proton conduction, the crystal water becomes an oxonium ion by the proton, and the proton is passed to the adjacent water molecule by repeating the breaking and rearrangement of the hydrogen bond. In addition, as shown in **Figure 10**, it is considered that the high proton conductivity of chitin in the fiber direction was caused by the increase in the number of pathways due to the hydrogen bond of the bottleneck and the vertical path with low activation energy. On the other hand,

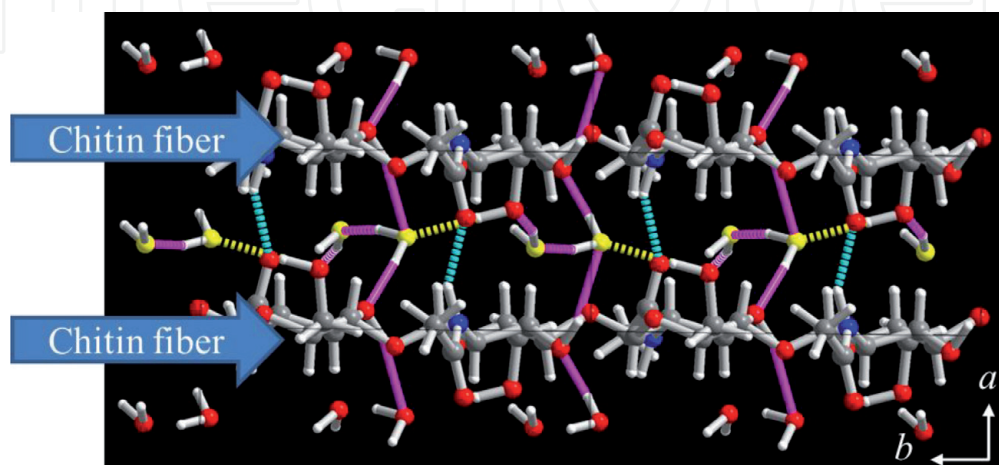


Figure 8. a - b plane of the crystal structure of chitin hydrate [11, 14–16]. White, gray, blue and red balls show hydrogen, carbon, nitrogen and oxygen.

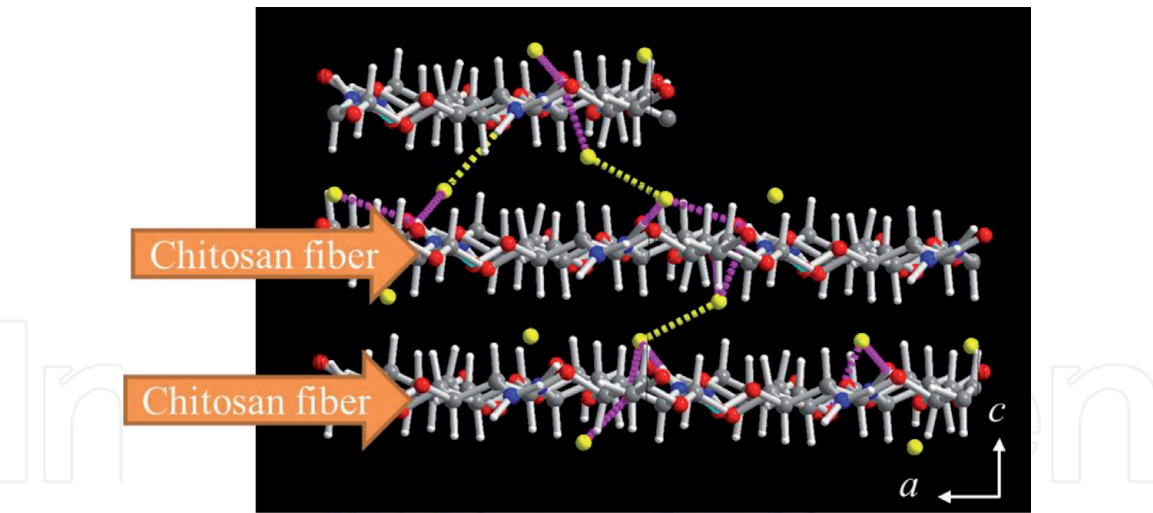


Figure 9.
a-c plane of the crystal structure of chitosan hydrate [11, 17–19]. White, gray, blue and red balls show hydrogen, carbon, nitrogen and oxygen. Yellow ball shows oxygen derived from water molecule.

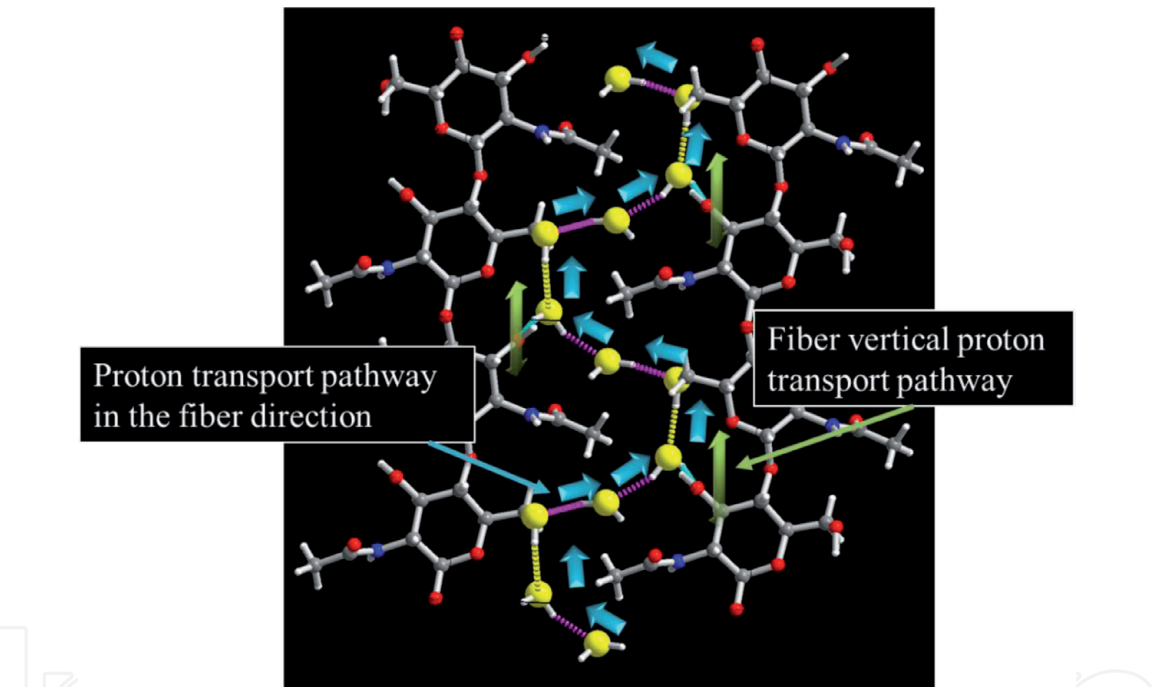


Figure 10.
Schematic diagram of proton transport pathway in chitin [11, 14–16].

the decrease in the proton conductivity in the vertical direction of the fibers of the oriented chitin can pass through the low activation energy pathway in the vertical direction, but the bottleneck is difficult to utilize, so that the number of pathways is reduced.

3.5 Creation of fuel cells using oriented chitin

The high proton conductivity of chitin appeared in the oriented sample and in the fiber direction. From this result, fuel cell using an oriented chitin sample was prepared. **Figure 11** shows schematic diagram of the fuel cell when oriented chitin is used and its *i-V* characteristics. As shown in **Figure 11**, the fuel cell using oriented chitin showed a much higher power density than the sheet sample, and a maximum of 33 mW/cm² was obtained. In other words, chitin indicates that the output can be

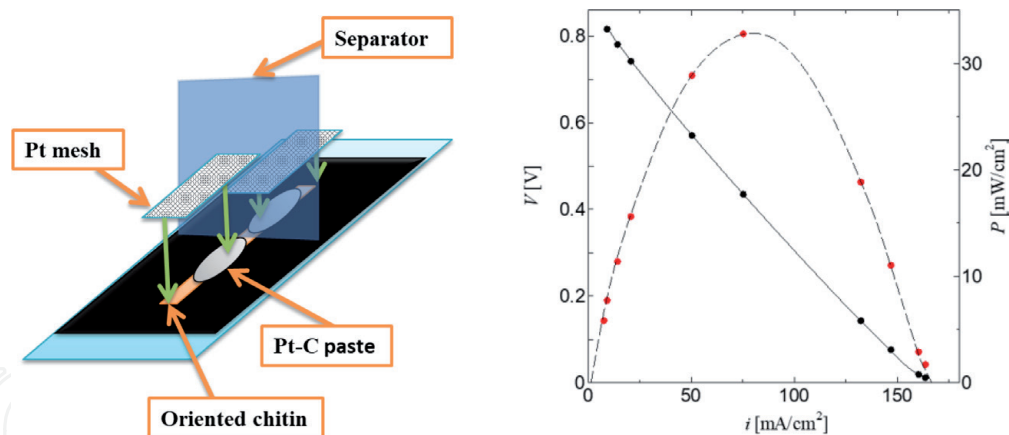


Figure 11. Schematic diagram of fuel cell using oriented chitin (left) and its i - V characteristics (right) [11].

improved by nearly 24 times by using the structure. In the future, it is expected that the key to practical use will be the improvement of output by chemical modification and the development of technology for producing oriented chitin at low cost.

4. Conclusions

Since chitin functions as an electrolyte membrane for fuel cells, it has been clarified that it is a proton conductor. It was found that the presence of water molecules is very important for the appearance of proton conductivity in chitin, and that these water molecules behave like conductors in chitin hydrate to conduct protons. Furthermore, it was suggested that the orientation dependence of the proton conductivity appearing in the oriented chitin is due to the bottleneck caused by the different hydrogen bond distances with the water molecules formed in the chitin depending on the position. It was also indicated that the high proton conductivity of oriented chitin appears by increasing the number of pathways by utilizing the bottleneck and the pathway in the fiber vertical direction, which is the low activation energy pathway. When a fuel cell using the fiber direction of oriented chitin having high proton conductivity was prepared, an improvement in proton conductivity of nearly 24 times was observed. In the future, chitin orientation methods and chemical approaches are expected to provide a foothold for more practical polysaccharide-based electrolyte membranes and to clarify new value in the energy field.

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Conflict of interest

The authors declare no conflict of interest.

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