Journal of Applied Polymer SCIENCE

Anhydrous proton conductor consisting of pectin–inorganic composite material

Masanori Yamada, Takahiro Ogino

Department of Chemistry, Faculty of Science, Okayama University of Science, Ridaicho, Okayama 700-0005, Japan
Correspondence to: M. Yamada (E-mail: myamada@chem.ous.ac.jp)

ABSTRACT: An organic–inorganic proton conductive composite material consisting of a biopolymer was prepared by mixing the pectin, tetraethyl titanate, and imidazole. Although the pectin material without the composite dissolved in water, the pectin–inorganic composite material did not show water solubility. In addition, in the composite material, the pectin and imidazole formed an acid–base structure by an electrostatic interaction, and as a result, these composite materials showed a thermal stability at intermediate temperatures (100–200°C). Furthermore, these composite materials indicated the proton conductivity of 5.6×10^{-4} S cm^{-1} at 180°C under anhydrous conditions. The activation energy of the proton conduction under anhydrous conditions was 0.32–0.22 eV and these values were one order of magnitude higher than that of the typical humidified perfluorinated membrane, such as Nafion®. The organic–inorganic composite material consisting of a biocomponent may have the potential to be utilized as a novel proton conductor under anhydrous conditions. © 2015 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 2015, 132, 42433.

INTRODUCTION

Pectin, mainly consisting of α(1-4)-linked D-galacturonic acid, is one of the acidic biopolymers in the cell walls of all plant tissues and is a natural, nontoxic, biodegradable, and water-soluble material.[1,2] Additionally, the pectin-containing materials have been discarded as industrial waste, such as the secondary product of fruit juice or sunflower oil, in a food-processing factory.[3] Therefore, pectin is inexpensive and can be used as a functional polysaccharide material, such as an absorbent of metal ions,[4,5] drug delivery system,[6,7] and biodegradable hydrogel.[8] Additionally, since pectin has many functional groups, such as a carboxyl group, pectin can immobilize various molecules in these groups.[7,9–11] As a result, the pectin derivative with a functional group has been reported to be utilized as a proton and ion conductors at room temperature under humidified conditions.[9–12]

The polymer electrolyte fuel cell (PEFC), which generates electric power from hydrogen and oxygen and produces water as the product, is one of the clean energy conversion systems. Especially, the PEFC operation at intermediate temperatures (100–200°C) has been considered to provide many advantages, such as an improved CO tolerance of the platinum electrode, higher energy efficiency, and cogeneration.[13–17] Therefore, the proton conductor for the electrolyte in the PEFC has been investigated around the world. However, since the proton con-

duction of the typical humidified perfluorinated membrane, such as Nafion®, is based on the presence of the mobile water molecules in the membrane, the proton conductivity at >100°C abruptly decreases due to the evaporation of water from the membrane.[13–18] Therefore, the development of the proton conductor with a high proton conductivity under anhydrous or low humidity and intermediate temperature conditions is very important. These anhydrous proton conductors have been reported for the polybenzimidazole (PBI)–acid composite,[19,20] sulfonated poly (ether–ether–ketone) (SPEEK)-heterocycle,[21] ionic liquids,[22] fullerene derivatives,[23] and mono-dodecylphosphate (MDP)–benzimidazole.[24] However, these materials, consisting of an artificial molecule or polymer, require high cost for the synthesis of the polymer. Additionally, since these materials cannot degrade in the environment, these materials require a high disposal cost. Therefore, the utilization of a biopolymer as the proton conductive material has attracted attention.[18,25,26] As a result, the proton conductors, which consist of a biopolymer, such as chitosan,[25] alginic acid,[27] carrageenan,[28] starch,[29] and DNA,[30] have been reported. However, since these proton conductors are unstable in water and do not show a high mechanical property, these materials are difficult to use under practical conditions. On the other hand, the polymer–inorganic composite material by mixing the polymer and inorganic component, such as silica or titanate, shows a water insolubilization, a thermal stabilization, and a high mechanical strength.[31–33] Therefore, the addition of an inorganic component
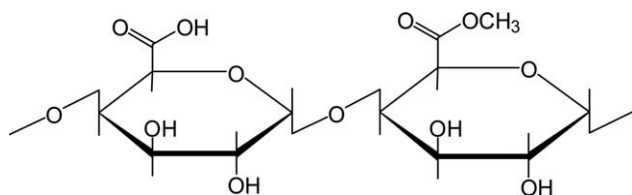
Scheme 1. Molecular structure of pectin.

to the biopolymer can improve these weak characteristics of the biopolymer. The preparations of the biopolymer–inorganic composite materials as anhydrous proton conductor are novel and important for the development of future PEFC technologies. Additionally, the utilization of a polysaccharide, such as pectin, as an anhydrous proton conductor is interesting and important for low cost and environmentally benign materials.

In this study, we prepared a pectin–inorganic composite material by the sol–gel reaction of tetraethyl titanate. The water-insoluble pectin–inorganic composite material showed a good thermal stability. In addition, the pectin–inorganic composite material showed the proton conductivity of 5.6×10^{-4} S cm^{-1} at 180°C under anhydrous conditions. Furthermore, the activation energy of the proton conduction was 0.32–0.22 eV. This value was one order of magnitude higher than that of a typical humidified perfluorinated membrane, such as Nafion®.

EXPERIMENTAL

Materials

The pectin (from citrus, molecular weight 2–3 $\times$ 10^5 g/mol) was purchased from Wako Pure Chemical Industries, Ltd., Osaka, Japan. Scheme 1 shows the molecular structure of pectin. The degree of esterification (DE) of pectin was estimated by the titration. As a result, DE of used pectin was 0.5 (50% esterificated). The tetraethyl titanate and imidazole (Im) were purchased from Tokyo Kasei Industries Ltd., Tokyo, Japan and Wako Pure Chemical Industries, respectively. Ion exchange resin Amberlite IR 120(H) was obtained from Supelco Inc., Bellefonte, PA. Solvents used were of an analytical grade in all the experiments described. Ultrapure water (Millipore Corporation, Billerica, MA) was used in this research.

Preparation of Pectin/Ti/Im Composite Material

The pectin, which is natural product, has existed sodium or potassium salts. Therefore, the pectin was changed from metal ion form to H$^+$ form by the ion-exchange column with ion-exchange resin Amberlite IR 120(H). The completeness of ion exchange of pectin was determined by the pH measurement.[30] The molar ratio (R) of pectin/Ti/Im composite material was determined by [Im]/[Pectin (monomer unit)]. The [Pectin (monomer)] and [Im] are molar concentration of sugar (monomer unit) in pectin and Im molecule, respectively. The aqueous pectin-Im mixed solution was prepared by the addition of Im to pectin solution (10 mg mL^{-1}). This mixed solution was incubated for 24 h at RT. The tetraethyl titanate (0–33 wt % for pectin) was quickly added in pectin–Im solution, vigorously mixed by the touch mixer for 30 s, and then incubated with the stirring at RT for 1 h. This pectin–Im–tetraethyl titanate mixed solution was centrifuged at 12,000 rpm for 2 s to remove the

precipitate. The supernatant was cast onto Teflon® plate, dried at RT for overnight, and then heated at 70°C for 1 h. In contrast, the dried tetraethyl titanate sample was prepared as follows: the tetraethyl titanate solution was mixed with water, incubated at RT for 24 h, dried at RT for overnight, and then heated at 70°C for 1 h.

The molar ratios ((mole of sugar unit)/(mole of Ti element)) of sugar unit and Ti element in pectin/Ti composite material were estimated from the ratio of C and Ti elements. The content of C was determined by the elemental analyses (CHN analysis) of composite material. The content of Ti was determined as follows: the pectin/Ti composite materials were immersed into 1 M HCl at 100°C for 3 h to hydrolyze the composite material. These Ti element-containing solutions were analyzed by the inductivity coupled plasma (ICP) atomic emission spectrophotometry (ICPS-7000 Ver. 2, Shimadzu Corp., Kyoto, Japan).

Characterization of Pectin/Ti/Im Composite Material

The infrared (IR) absorption spectra were measured by the attenuated total reflection (ATR) method with diamond prism using a Fourier transform infrared spectrometer (FT-IR 8400, Shimadzu Corp.). The IR spectrum was measured with the resolution of 4 cm^{-1}. The thermal stability of the pectin/Ti/Im composite material was analyzed by the thermogravimetric–differential thermal analysis (TG–DTA) (DTG-60, Shimadzu Corp.). The TG–DTA measurement was carried out at a heating rate of 10°C min^{-1} under a dry-nitrogen flow. Sample weights of TG–DTA measurements were normalized at 1 mg.

Tensile Strength of Pectin/Ti Composite Film

The pectin/Ti composite film was cut into 5 $\times$ 15 mm^2. The thickness of composite film was measured by a thickness gauge ID-C X series (Mitutoyo Corporation, Kanagawa, Japan). The thickness of film was 60–90 μm. The tensile stress and strain was measured using a digital force gauge ZTA-50N (Imada CO., Ltd., Aichi, Japan). The drawing speed of composite film was controlled at 10 mm min^{-1} by test stand MX2–500N (Imada CO., Ltd.). The temperature and relative humidity (RH) conditions at the tensile strength measurements were 25°C and 50 $\pm$ 5%, respectively. The initial length of the composite film was 5 mm. The values of tensile stress and strain were expressed as an average of five measurements.

Proton Conductive Measurement of Pectin/Ti/Im Composite Material

Proton conductivity of pectin/Ti/Im composite material was demonstrated by the a.c. impedance method in the frequency range from 4 Hz to 1 MHz using a chemical impedance analyzer 35320-80 (Hioki Co., Nagano, Japan) in a stainless-steel vessel from RT to 180°C under dry-nitrogen flow.[17,30] The pectin/Ti/Im composite material sandwiched between two gold electrodes (diameter: 5 mm). The direction of conductive measurement is perpendicular to the composite material. Before the measurements of proton conductions, the composite materials were dried at 180°C for 3 h in stainless-steel vessel to evaporate the water and volatile components from composite material. Additionally, all the experimental procedures in proton conductive measurements were carried out under dry-nitrogen flow. Conductivities of pectin/Ti/Im composite materials were
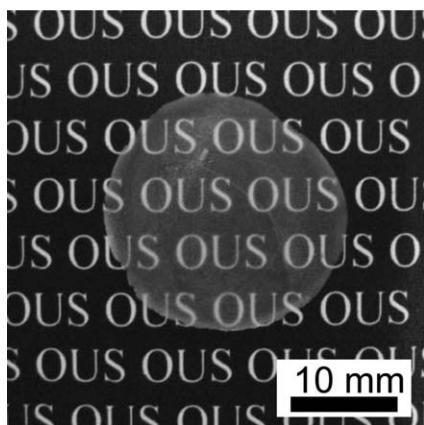
Figure 1. Photograph of pectin/33 wt % Ti composite membrane with a thickness of *ca* 30 μm.

determined from a typical impedance response (Cole–Cole plots). The resistances of the composite materials were obtained from the extrapolation to the real axis.

RESULTS AND DISCUSSION

Preparation of Pectin/Ti Composite Material

The pectin–Ti mixed solution was prepared by mixing the pectin solution and tetraethyl titanate solution. The mixed solution was centrifuged, casting the supernatant onto a Teflon® plate, and then dried. Figure 1 shows the photograph of the pectin/Ti composite film with the addition of 33 wt % tetraethyl titanate. The thickness of the pectin/33 wt % Ti membrane was *ca* 30 μm. The free-standing membrane is flexible. Additionally, although the pectin film without the mixing of tetraethyl titanate solved easily to water, this pectin/33 wt % Ti composite film did not show any solubility in water. The flexibility of the pectin/Ti composite film decreased with the increasing addition of tetraethyl titanate, and the composite film with the addition of ≥35 wt % tetraethyl titanate did not provide any flexibility. Therefore, for the functional material that is water insoluble and has flexible properties, we used the pectin/Ti composite material with the addition of 33 wt % tetraethyl titanate. On the other hand, the molar ratio ((mole of sugar unit)/(mole of Ti element)) of the sugar unit and Ti element in the pectin/Ti composite material was determined by an elemental analysis and ICP analysis. As a result, the molar ratios of the sugar unit and Ti element in the pectin/23 wt % Ti and pectin/33 wt % Ti composite materials were 17 and 9.9, respectively. The molar ratio of sugar unit and Ti element was different from that of the preparing ratio. However, the relative molar ratio of Ti element at pectin/23 wt % Ti and pectin/33 wt % Ti composite materials accorded. This is due to the difference of molecular size. Since the molecular size of pectin is larger than that of tetraethyl titanate, the part of pectin was not encapsulated into tetraethyl titanate network.

IR Spectra of Pectin/Ti Composite Materials

Figure 2 shows the IR spectra of (a) pectin without the addition of tetraethyl titanate, (b) pectin/23 wt % Ti composite material, (c) pectin/33 wt % Ti composite material, and (d) dried tetraethyl titanate. In the IR spectra of the dried tetraethyl titanate,

the absorption band at 548 and 650 cm^{-1}, related to the terminal Ti—O vibration,[34] appeared. Additionally, at 598 cm^{-1}, the absorption band, which was attributed to the bridging Ti—O vibration,[34] appeared. Furthermore, the absorption band at ca 2900 cm^{-1}, related to the stretching vibration of C—H in the alkyl chain,[35] was not obtained. This is due to the hydrolysis of the ethoxy group in the tetraethyl titanate molecule. These results suggested that the tetraethyl titanate condensed using our procedure and formed the Ti—O—Ti bonding. The IR spectra of the pectin/Ti composite material showed absorption bands at 548, 598, and 650 cm^{-1} which was based on the Ti—O vibration. In addition, the new absorption band at 630 cm^{-1} was obtained by the addition of the tetraethyl titanate to the pectin (see the arrow of spectrum (c) in Figure 2). A similar result, such as the appearance of a new absorption band at *ca* 630 cm^{-1} by mixing of the organic and inorganic components, has been reported by incorporation of the tetraethyl titanate into ethyl cellulose.[36] This is due to the formation of bonding between the pectin and Ti component in the composite material. These results suggested that the pectin material with the addition of tetraethyl titanate formed an organic–inorganic cross-linking structure with a three-dimensional network of Ti—O.

The pectin/Ti composite material with the addition of tetraethyl titanate of 33 wt % showed a water insolubility. Therefore, we prepared the pectin/Ti/Im composite material by the addition of 33 wt % tetraethyl titanate into the pectin–Im mixed solution. Figure 3 shows the IR spectra of (a) dried tetraethyl titanate powder, (b) pectin/Ti composite without the addition of Im ($R = 0$), (c) pectin/Ti/Im composite with the addition of Im ($R = 3$), (d) $R = 5$, (e) $R = 10$, (f) $R = 15$, and (g) Im molecules. The absorption band of the C=O stretching vibration[35]
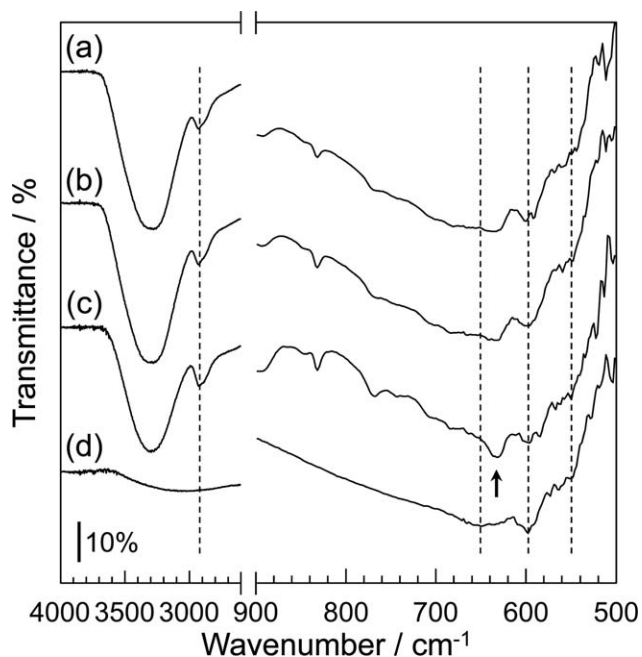

Figure 2. IR spectra of (a) pectin, (b) pectin/23 wt % Ti composite, (c) pectin/33 wt % Ti composite, and (d) dried tetraethyl titanate materials. The IR spectrum was measured at the resolution of 4 cm^{-1}. Triplicate experiments gave similar results.
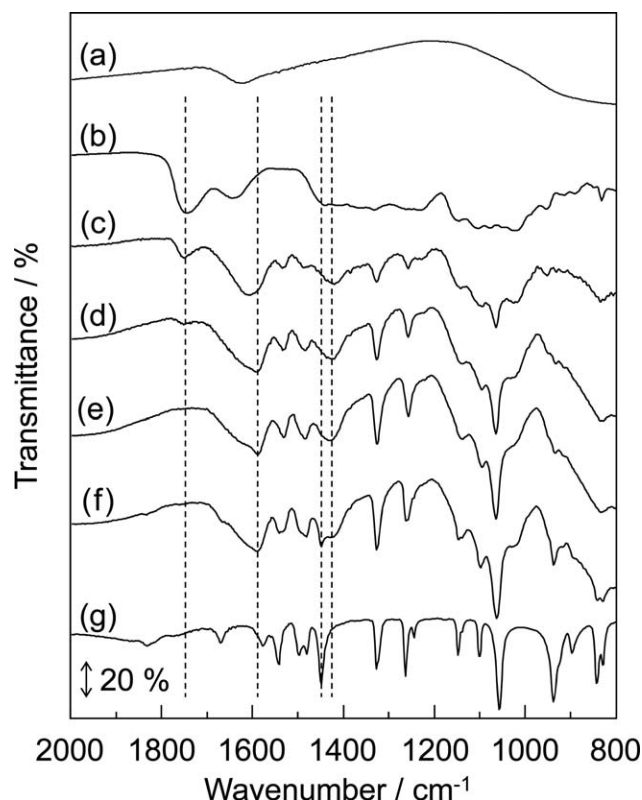
Figure 3. IR spectra of (a) dried tetraethyl titanate powder, (b) pectin without the composite, (c) pectin/Ti composite without the addition of Im ($R = 0$), (d) pectin/Ti/Im composite ($R = 3$), (e) $R = 5$, (f) $R = 10$, (g) $R = 15$, and (g) Im molecules. The composite material was prepared by the addition of 33 wt % tetraethyl titanate. The IR spectrum was measured at the resolution of 4 cm^{-1}. Triplicate experiments gave similar results.

in the —COOH group with the dimer structure in the pectin at 1743 cm^{-1} disappeared with the addition of the Im molecule. Additionally, when the Im molecule was added to the pectin/Ti composite material, the absorption bands at 1595 and 1420 cm^{-1}, related to the symmetric and asymmetric stretching vibration of —COO$^-$,[35–38] respectively, relatively increased. These results suggested that the —COOH group in pectin became deprotonated by the addition of the Im molecule and formed the —COO$^-$ group and free proton. Similar results, such as the formation of a free proton by the addition of a basic molecule into acidic polymer, have been reported for acid–base composite materials.[17,30] Furthermore, the absorption band at 1448 cm^{-1}, attributed to the aromatic C=N of the Im molecule,[35] relatively decreased with the addition to the pectin/Ti composite material. These results suggested that the free proton from the —COOH group in the pectin interacts with the nonprotonated —N= group of the Im molecule and forms the positively charged imidazole. Namely, the pectin/Ti/Im composite material produced the acid–base salts, including the imidazolium organic salts.

Mechanical Strength of Pectin/Ti Composite Material

The mechanical strength of a pectin/Ti composite material was measured by a tensile machine. The initial length of the membrane was 5 mm and the separation ratio was 10 mm min^{-1}. Figure 4 shows the stress–strain curves of (a) pectin membrane without the addition of tetraethyl titanate, (b) pectin/23 wt % Ti composite membrane, and (c) pectin/33 wt % Ti composite membrane. When the stress was applied to the pectin membrane without the tetraethyl titanate composite, the membrane broke at 1.8 MPa. This value increased with the addition of the tetraethyl titanate and showed 12 MPa at the addition of 33 wt % tetraethyl titanate. The stress of the pectin/33 wt % Ti composite membrane at the break point was six times higher than that of the pectin membrane. Additionally, the strain of the pectin membrane without the composite at the break point was 17%. This value decreased to *ca* 5% by the addition of tetraethyl titanate. These phenomena are due to the formation of a cross-linking structure between the pectin chains by the condensation reaction of tetraethyl titanate in the pectin/Ti composite material. Similar results, such as the increase in the physical property by the addition of an inorganic component into a biopolymer, have been reported for various organic–inorganic hybrid materials.[31–33,39]

Thermal Stability of Pectin/Ti/Im Composite Material

Figure 5(a,b) shows the thermogravimetric (TG) and differential thermal analyses (DTA) of (1) pectin without the composite, (2) pectin after the heat treatment at 180°C for 3 h, and (3) Im molecules, respectively. The pectin without the composite (line (1) in Figure 5) showed the TG weight loss of approximately
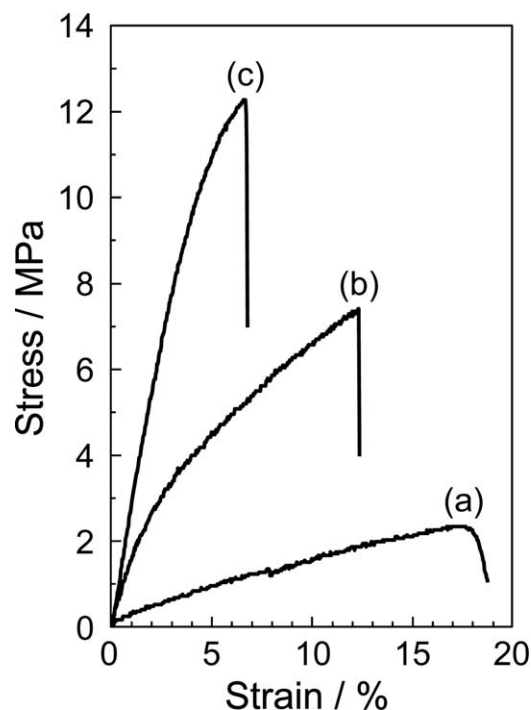

Figure 4. Stress–strain curves of (a) pectin without the addition of tetraethyl titanate, (b) pecin/23 wt % Ti composite, and (c) pectin/33 wt % Ti composite materials. These measurements were demonstrated at 25°C under $50 \pm 5\%$ RH conditions. The initial length of the membrane was 5 mm and the separation rate was 10 mm min^{-1}. Pentaplicate experiments gave similar results.
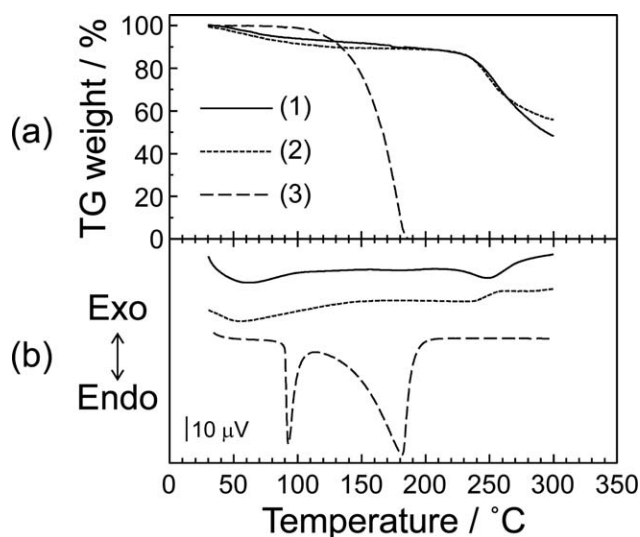
Figure 5. TG (a) and DTA (b) curves of (1) pectin without the composite, (2) pectin after the heat treatment at 180°C for 3 h, and (3) Im molecule. These measurements were done at the heating rate of 10°C min^{-1} under dry-nitrogen flow. Triplicate experiments gave similar results.

13% at 250°C. This is due to the evaporation of water from the pectin membrane. Additionally, the DTA curve of pectin indicated an endothermic peak which is related to the pyrolysis of pectin at 234.4°C. In contrast, the Im molecule without the composite (line (3) in Figure 5) showed two endothermic peaks due to its melting and evaporation at 89.7 and 134.3°C, respectively. Therefore, we heated the pectin/Ti/Im composite material at 180°C for 3 h to evaporate the water and Im molecules without the interaction with pectin. In contrast, pectin with the heat treatment at 180°C for 3 h showed similar TG–DTA curves to pectin without the heat treatment.

Figure 6(a,b) shows the TG and DTA of (1) pectin/Ti composite ($R = 0$), (2) pectin/Ti/Im composite ($R = 5$), (3) $R = 10$, (4) $R = 15$ composite materials after the heat treatment at 180°C for 3 h, respectively. The pectin/Ti composite material (line (1) in Figure 6) showed the TG weight loss of approximately 7% at 250°C and this TG weight loss was lower than those of the pectin without the composite and pectin with the heat treatment. In addition, the endothermic peak at 250°C decreased using the composite of tetraethyl titanate. These results suggested that the pectin material was stabilized by the addition of inorganic components, such as tetraethyl titanate. Similar stabilizations by the addition of inorganic components have been reported for various organic–inorganic composite materials.[40,41] The pectin/Ti/Im composite material (line (2)–(4) in Figure 6) showed the TG weight loss of approximately 5% at 250°C. This is due to the evaporation of water when in contact with air. Additionally, the endothermic peaks at approximately 90 and 130°C, attributed to the non-interacted Im molecule with pectin, disappeared. These results suggested that the pectin/Ti/Im composite material does not produce a diffusible ion by the melting of the samples and is stable at an intermediate temperature (<180°C). In contrast, the TG weight loss at >250°C is related to the pyrolysis of pectin.

Anhydrous Proton Conduction of Pectin/Ti/Im Composite Material

The proton conductive measurements of the pectin/Ti/Im composite material were demonstrated by the a.c. impedance method over the frequency range from 4 Hz to 1 MHz under dry-nitrogen flow. The features of the typical impedance response (Cole–Cole plots) for the pectin/Ti/Im composite material are similar to that of a highly anhydrous proton conductor.[30,42] In our research, the composite material was dried at 180°C under dry-nitrogen flow in a stainless-steel vessel for 3 h to evaporate the water and volatile components from the pectin/Ti/Im composite material. Additionally, the diffusible ions other than the protons did not exist in these materials (see the TG–DTA in Figure 6). Therefore, the impedance responses of the pectin/Ti/Im composite material are based on the anhydrous proton transfer in the membrane.

Figure 7 shows the proton conduction of ($\triangle$) $R = 1$, ($\blacktriangle$) $R = 4$, ($\bigcirc$) $R = 8$, ($\bullet$) $R = 10$, and ($\square$) $R = 12$ pectin/Ti/Im composite materials in the temperatures range from RT to 180°C under the dry-nitrogen flow conditions. The proton conductions of the pectin/Ti/Im composite materials increased with the temperature and reached a maximum value at 180°C. Additionally, the proton conductivity increased with an increase in the R value. Figure 8 shows the proton conductivity at 180°C as a function of the R values. The proton conductivity increased with the R values and reached a maximum proton conductivity of 5.6×10^{-4} S cm^{-1} at $R = 10$. Additionally, at $R > 10$, the pectin/Ti/Im composite materials showed a constant proton conductivity on the order of 10^{-4} S cm^{-1}. On the other hand, the pectin and pectin/Ti composite material without the addition of Im did not show a measurable proton conductivity ($<10^{-8}$ S cm^{-1}) at 180°C. Furthermore, since the Im molecules without the composite melted and evaporated at 89.7 and 134.3°C,
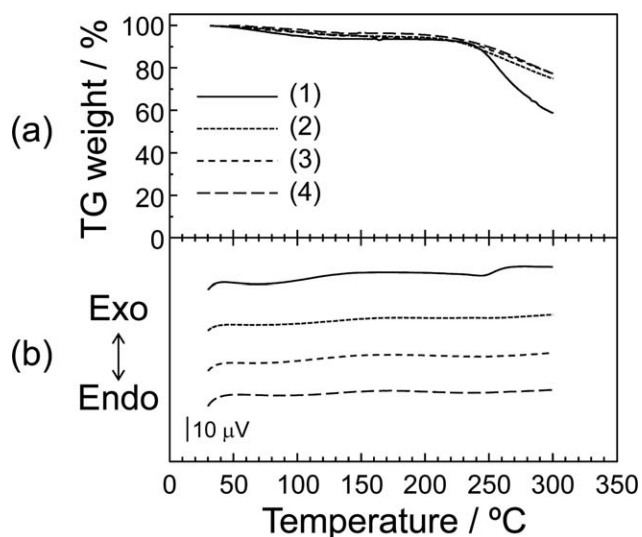

Figure 6. TG (a) and DTA (b) curves of (1) pectin/Ti composite ($R = 0$), (2) pectin/Ti/Im composite ($R = 5$), (3) $R = 10$, and (4) $R = 15$ composite materials at the heating rate of 10°C min^{-1} under dry-nitrogen flow, respectively. Before the analysis, these materials were treated at 180°C for 3 h. Triplicate experiments gave similar results.
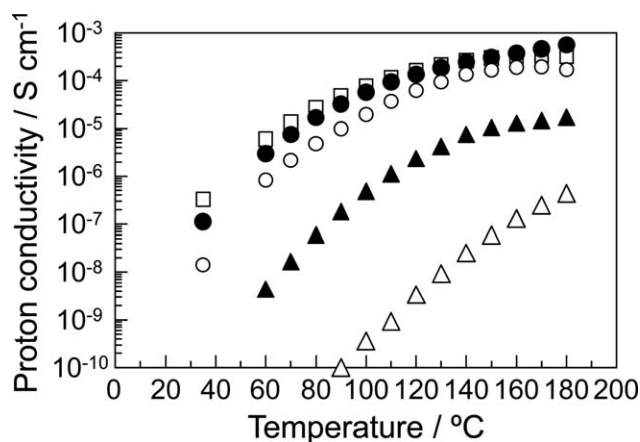
Figure 7. Proton conductivities of pectin/Ti/Im composite materials. These samples were dried at 180°C for 3 h under dry-nitrogen flow. Proton conductivity measurement was performed by the a.c. impedance method. ($\triangle$) $R = 1$, ($\blacktriangle$) $R = 4$, ($\bigcirc$) $R = 8$, ($\bullet$) $R = 10$, and ($\square$) $R = 12$.

Figure 9. Arrhenius plots of the proton conductivity of pectin/Ti/Im composite materials. The solid lines are the results of a least-squares fitting. ($\triangle$) $R = 1$, ($\blacktriangle$) $R = 4$, ($\bigcirc$) $R = 8$, ($\bullet$) $R = 10$, and ($\square$) $R = 12$.

respectively, the Im molecules dried up by the heat treatment process at 180°C for 3 h and did not show proton conductivity.

Figure 9 shows the Arrhenius plots of the proton conduction of ($\triangle$) $R = 1$, ($\blacktriangle$) $R = 4$, ($\bigcirc$) $R = 8$, ($\bullet$) $R = 10$, and ($\square$) $R = 12$ pectin/Ti/Im composite materials. Since the conductions of the pectin/Ti/Im composite materials show a straight line at 110–180°C, the proton conduction of each composite material in this temperature region is related to single proton transfer mechanism. We calculated the activation energy (E_a) of the proton conduction in the pectin/Ti/Im composite material from the slope of the straight line. Although the E_a at $R = 1$ was *ca* 1.3 eV, E_a decreased with an increase in the R value. As a result, at $R \geq 8$, E_a reached a constant value and these values were 0.32–0.22 eV. These E_a values are one order of magnitude higher than that of the typical humidified Nafion® membranes[18] and the H_3PO_4 soaked organic–inorganic membranes,[43] in which the proton in the membrane can be moved by vehicle molecules, such as water molecules. In addition, similar E_a values have been reported for DNA–heterocycle[30] and poly(vinylphos-

phonic acid)–heterocycle[44] composite materials. Therefore, the proton conduction in the pectin/Ti/Im composite materials is considered to be based on the anhydrous proton transfer from site to site without the assistance of diffusible vehicle molecules. Generally, the Im molecule is known to behave as a proton donor and acceptor in an acid–Im composite material.[30,44,45] Similar phenomena have occurred in the pectin/Ti/Im composite material. Namely, the free proton in the protonated Im molecule transferred to the nonprotonated Im molecule.

On the other hand, the anhydrous proton conductivity of the pectin/Ti/Im composite materials was lower than that of reported materials ($>1 \times 10^{-3}$ S cm^{-1} at 160°C), such as poly(vinylphosphonic acid)–heterocycle[44] and chitin phosphate–heterocycle[46] composite materials. This is due to the degree of freedom of the Im molecule in the pectin/Ti/Im composite material. In our research, the pectin/Ti composite materials have formed a three-dimensional structure with the cross-linking and Im molecule has existed in these three-dimensional networks. Therefore, the mobility of the Im molecules is disturbed by the network and the degree of freedom of Im molecules decreased. In addition, the distance between the protonated Im molecule and neighboring nonprotonated Im molecule becomes longer. As a result, at $R < 8$, the pectin/Ti/Im composite material showed a low proton conductivity and high activation energy of proton conduction.

CONCLUSION

We prepared the pectin/Ti/Im composite materials by mixing pectin, tetraethyl titanate, and imidazole molecules. This pectin/Ti/Im composite material indicated not only a water insolubility but also a thermal stability. Additionally, the pectin/Ti/Im composite material showed the anhydrous proton conductivity of 5.6×10^{-4} S cm^{-1} at 180°C. The activation energy of the proton conduction was 0.32–0.22 eV and these values were one order of magnitude higher than that of the typical humidified Nafion®. Therefore, the proton conduction of the pectin/Ti/Im composite material was based on the mechanism without the assistance of diffusible vehicle molecules, such as water molecules. These proton conductive pectin–inorganic composite
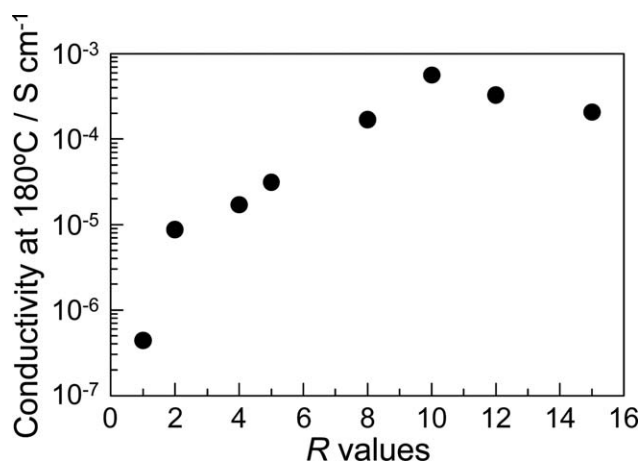

Figure 8. Change in the proton conductivities at 180°C as a function of the R values. The proton conductive measurements were done under a dry-nitrogen flow.
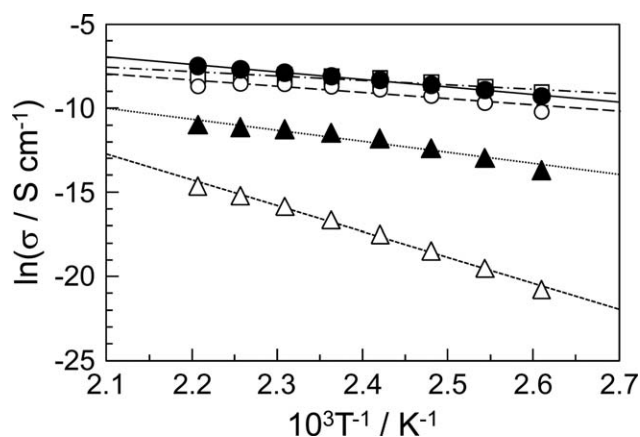
materials have the potential not only as a PEFC membrane but also for application in an implantable battery, biosensors, etc.

REFERENCES

1. Hoagland, P. D. *ACS Symp. Ser.* **1996**, *650*, 145.

2. Liu, L.; Tunick, M.; Fishman, M. L.; Hicks, K. B.; Cooke, P. H.; Coffin, D. R. *ACS Symp. Ser.* **2006**, *935*, 272.

3. Thakur, B. R.; Singh, R. K.; Handa, A. K. *Crit. Rev. Food Sci. Nutr.* **1997**, *37*, 47.

4. Paudyal, H.; Pangeni, B.; Ghimire, K. N.; Inoue, K.; Ohto, K.; Kawakita, H.; Alam, S. *Chem. Eng. J.* **2012**, *195–196*, 289.

5. Yamada, M.; Shiiba, S. *J. Appl. Polym. Sci.* **2015**, *132*, 42056.

6. Giri, T. K.; Thaku, D.; Alexander, A.; Ajazuddin; Badwaik, H.; Tripathi, D. K. *J. Mater. Sci. Mater. Med.* **2013**, *24*, 1179.

7. Liu, L. S.; Fishman, M. L.; Hicks, K. B. *Cellulose* **2007**, *14*, 15.

8. Agoudjil, N.; Sicard, C.; Jaouen, V.; Garnier, C.; Bonnin, E.; Steunou, N.; Coradin, T. *Pure Appl. Chem.* **2012**, *84*, 2521.

9. Mishra, R. K.; Anis, A.; Mondal, S.; Dutt, M.; Banthia, A. K. *Chin. J. Polym. Sci.* **2009**, *27*, 639.

10. Mishra, R. K.; Datt, M.; Banthia, A. K.; Majeed, A. B. A. *Int. J. Plast. Technol.* **2012**, *16*, 80.

11. Abramovič, H.; Klofutar, C. *Eur. Polym. J.* **1997**, *33*, 1295.

12. Andrade, J. R.; Raphael, E.; Pawlicka, A. *Electrochim. Acta* **2009**, *54*, 6479.

13. Çelik, S. Ü.; Bozkurt, A.; Hosseinib, S. S. *Prog. Polym. Sci.* **2012**, *37*, 1265.

14. Wang, Y.; Chen, K. S.; Mishler, J.; Cho, S. C.; Adroher, X. C. *Appl. Energ.* **2011**, *88*, 981.

15. Dupuis, A. C. *Prog. Mater. Sci.* **2011**, *56*, 289.

16. Rikukawa, M.; Sanui, K. *Prog. Polym. Sci.* **2000**, *25*, 1463.

17. Honma, I.; Yamada, M. *Bull. Chem. Soc. Jpn.* **2007**, *80*, 2110.

18. Sone, Y.; Ekdunge, P.; Simonsson, D. *J. Electrochem. Soc.* **1996**, *143*, 1254.

19. Kawahara, M.; Morta, J.; Rikukawa, M.; Sanui, K.; Ogata, N. *Electrochim. Acta* **2000**, *45*, 1395.

20. Bouchet, R.; Siebert, E. *Solid State Ionics* **1999**, *118*, 287.

21. Kreuer, K. D.; Fuchs, A.; Ise, M.; Spaeth, M.; Maier, J. *Electrochim. Acta* **1998**, *43*, 1281.

22. Sun, J.; MacFarlane, D. R.; Forsyth, M. *Electrochim. Acta* **2001**, *46*, 1673.

23. Hinokuma, K.; Ata, M. *Chem. Phys. Lett.* **2001**, *341*, 442.

24. Yamada, M.; Honma, I. *Electrochim. Acta* **2003**, *48*, 2411.

25. Ma, J.; Sahai, Y. *Carbohyd. Polym.* **2013**, *92*, 955.

26. Finkenstadt, V. L. *Appl. Microbiol. Biotechnol.* **2005**, *67*, 735.

27. Yamada, M.; Honma, I. *Polymer* **2004**, *45*, 8349.

28. Fujishima, M.; Matsuo, Y.; Takatori, H.; Uchida, K. *Electrochem. Commun.* **2008**, *10*, 1482.

29. Khiar, A. S. A.; Arof, A. K. *Ionics* **2010**, *16*, 123.

30. Yamada, M.; Goto, A. *Polym. J.* **2012**, *44*, 415.

31. Kandimalla, V. B.; Ju, H. *Chem. Eur. J.* **2006**, *12*, 1074.

32. Novak, B. M. *Adv. Mater.* **1993**, *5*, 422.

33. Uragami, T.; Katayama, T.; Miyata, T.; Tamura, H.; Shiraiwa, T.; Higuchi, A. *Biomacromolecules* **2005**, *6*, 368.

34. Bradley, D. C.; Mehrotra, R. C.; Gaur, D. P. Metal Alkoxides; Academic press: London, **1978**.

35. Silverstein, R. M.; Webster, F. X. Spectrometric Identification of Organic Compounds; John Wiley & Sons: New York, **1998**.

36. Yoshinaga, I.; Katayama, S. *J. Sol-Gel Sci. Technol.* **1996**, *6*, 151.

37. Shi, L.; Gunasekaran, S. *Nanoscale Res. Lett.* **2008**, *3*, 491.

38. Filippov, M. P. *J. Appl. Spectrosc.* **1972**, *17*, 1052.

39. Yamada, M.; Aono, H. *Polymer* **2008**, *49*, 4658.

40. Kim, J. D.; Honma, I. *Electrochim. Acta* **2004**, *49*, 3179.

41. Alberti, G.; Costantino, U.; Casciola, M.; Ferroni, S.; Massinelli, L.; Staiti, P. *Solid State Ionics* **2001**, *145*, 249.

42. Vargas, M. A.; Vargas, R. A.; Mellander, B. E. *Electrochim. Acta* **1999**, *44*, 4227.

43. Kim, J. D.; Honma, I. *J. Electrochem. Soc.* **2004**, *151*, A1396.

44. Yamada, M.; Honma, I. *Polymer* **2005**, *46*, 2986.

45. Kreuer, K. D. *Chem. Mater.* **1996**, *8*, 610.

46. Yamada, M.; Honma, I. *Angew. Chem. Int. Ed.* **2004**, *43*, 3688.