

Title	Proton conductivity of oligomeric poly[(1, 2-propanediamine)-alt-(oxalic acid)] thin films on Al ₂ O ₃ substrates
Author(s)	Nagao, Yuki; Naito, Nobuhiro; Iguchi, Fumitada; Sata, Noriko; Yugami, Hiroo
Citation	e-Journal of Surface Science and Nanotechnology, 7: 530-532
Issue Date	2009-04-18
Type	Journal Article
Text version	publisher
URL	http://hdl.handle.net/10119/10632
Rights	Copyright (C) 2009 日本表面科学会. Yuki Nagao, Nobuhiro Naito, Fumitada Iguchi, Noriko Sata, and Hiroo Yugami, e-Journal of Surface Science and Nanotechnology, 7, 2009, 530-532. http://dx.doi.org/10.1380/ejssnt.2009.530
Description	

Proton Conductivity of Oligomeric Poly[(1,2-Propanediamine)-*alt*-(Oxalic Acid) Thin Films on Al₂O₃ Substrates*

Yuki Nagao,[†] Nobuhiro Naito, Fumitada Iguchi, Noriko Sata, and Hiroo Yugami

*Department of Mechanical Systems and Design, Graduate School of Engineering,
Tohoku University, 6-6-01 Aoba, Aramaki, Aoba-ku, Sendai 980-8579, Japan*

(Received 7 November 2008; Accepted 22 January 2009; Published 18 April 2009)

Proton transport properties of three thin films (110, 240, and 360 nm thick films) on R-plane (1102) sapphire substrates for oligomeric poly[(1, 2-propanediamine)-*alt*-(oxalic acid)] were investigated. The maximum proton conductivity of the thin film is 1.7×10^{-3} S cm⁻¹ at the RH of 80%, which is five times higher than that of the bulk sample (3.0×10^{-4} S cm⁻¹). The activation energies of the 110, 240, and 360 nm thick films are found to 0.74, 0.67, and 0.68 eV at the RH of 80%, respectively. [DOI: 10.1380/ejsnt.2009.530]

Keywords: Electrical transport; Enhancement; Proton conduction

I. INTRODUCTION

The design of highly proton-conductive solid electrolyte is essential to many applications in the research field of solid state ionics [1, 2]. One of the fundamental methods to make highly proton-conductive material is chemical modification. The properties of chemical stability and mechanical strength are often unfavorable by using chemical modification like sulfonation, however the proton conductivity exhibits excellent value [3, 4]. Due to such a trade-off relation between the proton conductivity, mechanical strength, and chemical stability, a new method to make highly proton-conductive material has been expected for a long time.

The ionic conductivity enhancement in the 2-D system has been known for more than 20 years [5–16]. These anomalies are supposed to be attributed to interfacial effects like structural effects and/or effects of a space charge region [17]. Recently we observed the enhancement phenomenon of the proton conduction only by preparing organic thin films on SiO₂ substrates [18]. The maximum proton conductivity of the thin film exhibit 10 times higher value than that of the bulk sample. However its origin for the enhancement phenomenon of the proton conduction is still unknown, it is supposed that applying this phenomenon is a candidate for a new method to make highly proton-conductive material, which solves the trade-off relation between the proton conductivity, mechanical strength, and chemical stability.

The amide groups exhibit the proton exchange property because of the amide/imidic acid tautomerism. We have investigated a series of the proton-conductive oligomers containing amide groups [18, 19]. In this paper, we synthesized proton-conductive polyamide oligomers, oligomeric poly[(1, 2-propanediamine)-*alt*-(oxalic acid)], and investigated the proton transport properties of the thin film on another substrate (sapphire substrate) to study the enhancement of the proton conductivities.

* This paper was presented at International Symposium on Surface Science and Nanotechnology (ISSS-5), Waseda University, Japan, 9-13 November, 2008.

[†]Corresponding author: y_nagao@energy.mech.tohoku.ac.jp

II. EXPERIMENTAL

The synthesis of oligomeric poly[(1, 2-propanediamine)-*alt*-(oxalic acid)] has been reported as shown in **Scheme** (Fig. 1) in previous study [18]. The quality of the sample was checked by the X-ray diffraction, FT-IR spectra, ¹H NMR, Matrix Assisted Laser Desorption/Ionization Time of Flight (MALDI-TOF) mass spectrum [18]. The synthesized sample is amorphous, and composed of a mixture of the oligomers with the different end groups and low-molecular-weights including the macrocyclic amides. Three thin films were prepared on R-plane (1102) sapphire substrates by using a Active ACT-200 Spincoater. The thickness of the thin film was determined by using a KLA-Tencor P-10 contact stylus profiler. The obtained thin films are flat, and their thicknesses are 110, 240, and 360 nm, respectively.

Impedance measurements (1 – 10⁶ Hz) of the thin films of oligomeric poly[(1, 2-propanediamine)-*alt*-(oxalic acid)] were carried out in the relative humidity (RH) of 80% at 298 K with a Solartron 1260 Impedance/Gain-Phase analyzer and a 1296 Dielectric Interface system. The RH and temperature were controlled with an Espec Corp. SH-221 humidity- and temperature-controlled chamber. The activation energy was studied in the temperature range of 288-308 K. In the case of the impedance measurements of the thin films, the electrode configuration was selected to obtain measurements of the current flow in the plane parallel to the substrate surface. The conductivity of the R-plane (1102) sapphire substrate is negligible because its resistance is at least two orders of magnitude higher than that of the film over the film thickness range of 110-360 nm.

III. RESULTS AND DISCUSSION

In the previous study, we reported that the oligomeric poly[(1, 2-propanediamine)-*alt*-(oxalic acid)] exhibited the proton conduction [18]. The typical complex impedance plots of the bulk sample for oligomeric poly[(1, 2-propanediamine)-*alt*-(oxalic acid)] under the RH of 80% and 298 K are shown in Fig. 2. A resistance is directly given by the intersection of a depressed semicircle with the real axis. The obtained electrical conductivity at the

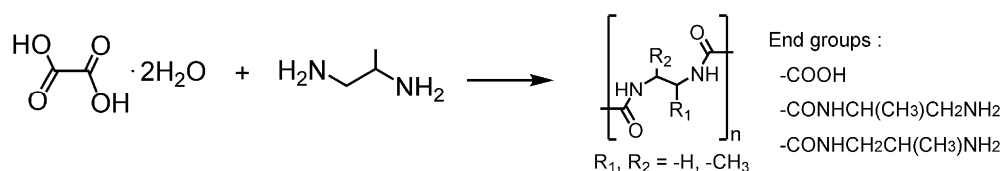


FIG. 1: Scheme: Synthesis of oligomeric poly[(1, 2-propanediamine)-*alt*-(oxalic acid)].

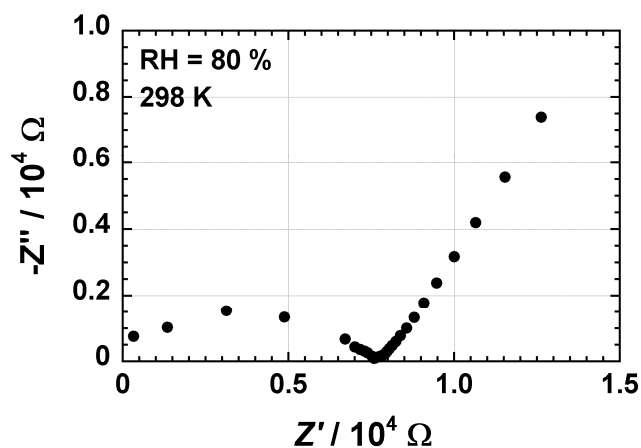


FIG. 2: Impedance plots of the bulk sample for oligomeric poly[(1, 2-propanediamine)-*alt*-(oxalic acid)] under the RH of 80% and 298 K.

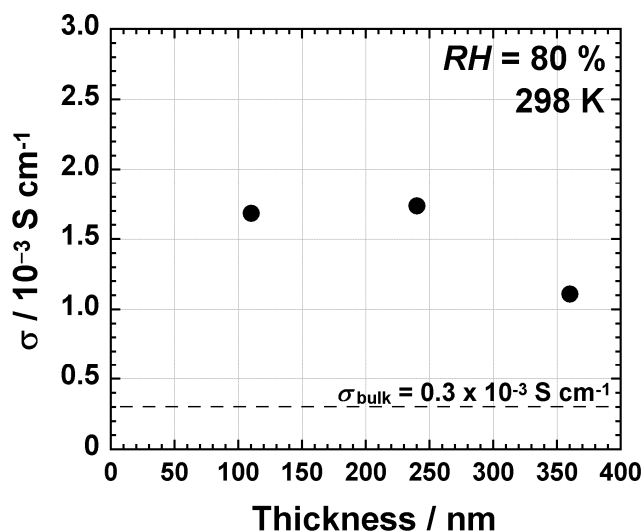


FIG. 3: Thickness dependence of the proton conductivity with bulk and thin films of oligomeric poly[(1, 2-propanediamine)-*alt*-(oxalic acid)].

RH of 80% are found to be $3.0 \times 10^{-4} \text{ S cm}^{-1}$.

Figure 3 shows thickness dependence of the proton conductivity (σ) for oligomeric poly[(1, 2-propanediamine)-*alt*-(oxalic acid)] thin films on sapphire substrates. The proton conductivity of the 110 nm thick film is found to be $1.7 \times 10^{-3} \text{ S cm}^{-1}$ at the RH of 80%. This value is found to be five times higher than that of the bulk sample of

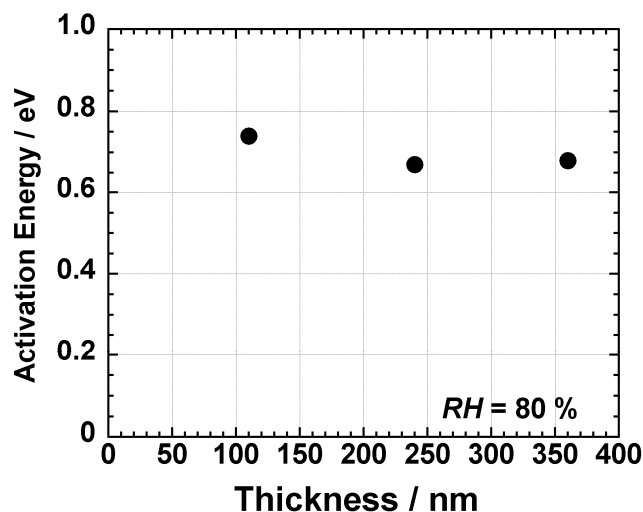


FIG. 4: Thickness dependence of the activation energy for the proton conduction with thin films of oligomeric poly[(1, 2-propanediamine)-*alt*-(oxalic acid)] on Sapphire substrates.

oligomeric poly[(1, 2-propanediamine)-*alt*-(oxalic acid)], which value is one order of magnitude lower than that of Nafion 117 membrane at the RH of 80% [20]. The proton conductivities of the 240 and 360 nm thick films exhibit 1.7×10^{-3} and $1.1 \times 10^{-3} \text{ S cm}^{-1}$ at the RH of 80%, respectively. We observed the enhancement of the proton conductivity by the synthesis of the thin films on Sapphire substrates, however the maximum proton conductivity of the thin films on Sapphire substrates is relatively lower value than that on SiO_2 substrates ($4.0 \times 10^{-3} \text{ S cm}^{-1}$).

Figure 4 shows thickness dependence of the activation energy for the proton conduction with thin films of oligomeric poly[(1, 2-propanediamine)-*alt*-(oxalic acid)] on Sapphire substrates. The activation energies of the 110, 240, and 360 nm thick films are found to be 0.74, 0.67, and 0.68 eV, respectively. The activation energy for the proton conduction of the bulk sample is $\sim 0.8 \text{ eV}$ at the RH of 80%. The activation energy of the thin films is found to be lower than that of the bulk sample of oligomeric poly[(1, 2-propanediamine)-*alt*-(oxalic acid)]. In this system, water molecules play an important role in the proton conduction from a result of relative humidity dependence of the proton conductivity [18]. The water molecules can strongly contribute to the proton conduction at the RH of 80%.

In many kinds of the inorganic ionic conductors, some theoretical models including the space charge models for understanding the enhancement phenomena of the ionic

conductivities have been discussed [17]. Considering to the contribution of the space charge model around the interface between the substrate and thin film, it is supposed that the effective length of the space charge region is much shorter than that of the thickness of the thin films in this system. However we have not yet estimated the quantitative contribution of space charge region at the interface, its degree of contribution is low in the thickness range of 110-360 nm. The obvious thickness dependence has not been observed yet. Therefore it is difficult to explain this result according to the only space charge model. In this system, these results could be originated from the structural effects like a molecular orientation by preparing of the thin film on the substrate rather than the interface effects like the space charge models. The degree of the molecular orientation by the measurements of polarized IR spectra is under investigation.

IV. CONCLUSIONS

Proton transport properties of oligomeric poly[(1, 2-propanediamine)-*alt*-(oxalic acid)] thin films on Sapphire

substrates were investigated. The maximum proton conductivity of the thin film is $1.7 \times 10^{-3} \text{ S cm}^{-1}$ at the RH of 80%, which is five times higher than that of the bulk sample ($3.0 \times 10^{-4} \text{ S cm}^{-1}$). The activation energies of the 110, 240, and 360 thick films are found to 0.74, 0.67, and 0.68 eV, respectively. The activation energy of the thin films is found to be lower than that of the bulk sample. These results could be originated from the structural effects like a molecular orientation by the synthesis of the thin film on the substrate rather than the interface effects like the space charge models in this system.

Acknowledgments

The authors thank M. Sasaki for helping the synthesis of the proton-conductive oligomers. This study was supported by Program for Improvement of Research Environment for Young Researchers from Special Coordination Funds for Promoting Science and Technology (SCF) commissioned by the Ministry of Education, Culture, Sports, Science and Technology (MEXT) of Japan.

-
- [1] P. Colomban (Ed.), *Proton Conductors* (Cambridge University Press, Cambridge, 1992).
 - [2] T. S. Zhao, K. D. Kreuer, T. V. Nguyen (Eds.), *Advances in Fuel Cells*, Volume 1 (Elsevier, Oxford, 2007).
 - [3] X. Jin, M. T. Bishop, T. S. Ellis, and F. E. Karasz, *Br. Polym. J.* **17**, 4 (1985).
 - [4] K. N. T. Do and D. Kim, *J. Appl. Polym. Sci.* **110**, 1763 (2008).
 - [5] E. Schreck, K. Laeuger, and K. Dransfeld, *Zeitschrift fuer Physik B: Condensed Matter* **62**, 331 (1986).
 - [6] S. Mühlherr, K. Läuiger, E. Schreck, K. Dransfeld, and N. Nicoloso, *Solid State Ionics* **28-30**, 1495 (1988).
 - [7] F. A. Modine, D. Lubben, and J. B. Bates, *J. Appl. Phys.* **74**, 2658 (1993).
 - [8] D. Lubben and F. A. Modine, *J. Appl. Phys.* **80**, 5150 (1996).
 - [9] I. Kosacki and H. U. Anderson, *Sensors and Actuators B* **48**, 263 (1998).
 - [10] N. Sata, K. Eberman, K. Eberl, and J. Maier, *Nature (London)* **408**, 946 (2000).
 - [11] I. Kosacki, T. Suzuki, V. Petrovsky, and H. U. Anderson, *Solid State Ionics* **136-137**, 1225 (2000).
 - [12] X. X. Guo and J. Maier, *Surf. Sci.* **549**, 211 (2004).
 - [13] S. Azad, O. A. Marina, C. M. Wang, L. Saraf, V. Shutthanandan, D. E. McCready, A. El-Azab, J. E. Jaffe, M. H. Engelhard, C. H. F. Peden, and S. Thevuthasan, *Appl. Phys. Lett.* **86**, 131906 (2005).
 - [14] I. Kosacki, C. M. Rouleau, P. F. Becher, J. Bentley, and D. H. Lowndes, *Solid State Ionics* **176**, 1319 (2005).
 - [15] S.-i. Furusawa, H. Tabuchi, and T. Tsurui, *Solid State Ionics* **178**, 1033 (2007).
 - [16] A. Peters, C. Korte, D. Hesse, N. Zakharov, and J. Janek, *Solid State Ionics* **178**, 67 (2007).
 - [17] R. C. Agrawal and R. K. Gupta, *J. Mater. Sci.* **34**, 1131 (1999).
 - [18] Y. Nagao, N. Naito, F. Iguchi, N. Sata, and H. Yugami, *Solid State Ionics*, DOI: 10.1016/j.ssi.2008.09.022 (in press).
 - [19] Y. Nagao, A. Haneda, N. Naito, F. Iguchi, N. Sata, and H. Yugami, *Solid State Ionics* **179**, 1142 (2008).
 - [20] Y. Sone, P. Ekdunge, and D. Simonsson, *J. Electrochem. Soc.* **143**, 1254 (1996).