© 2006 The Chemical Society of Japan

Complex Impedance and Solid-State NMR Studies on a Novel High Proton Conductor Na-RUB-18

Shin'ichi Ishimaru,*[1,2] **Maki Togawa,**[2] **Ryuichi Ikeda,**[2,3] **Tadashi Shimizu,**[3]
Emi Shinohara,[4] **and Yasushi Umemura**[4]

[1]Department of Environmental Material Sciences, School of Engineering, Tokyo Denki University,
2-1200 Muzai Gakuendai, Inzai 270-1382

[2]Department of Chemistry, University of Tsukuba, 1-1-1 Tennodai, Tsukuba 305-8571

[3]National Institute for Materials Science, 3-13 Sakura, Tsukuba 305-0003

[4]Department of Applied Chemistry, National Defense Academy, 1-10-20 Hashirimizu, Yokosuka 239-8686

Received October 26, 2005; E-mail: ishimaru@cck.dendai.ac.jp

Measurements of complex impedance and ^{2}H NMR spectra were performed on a layer silicate compound, Na-RUB-18 (sodium octosilicate, $NaSi_4O_8(OH){\cdot}nH_2O$), to investigate hydrogen dynamics in crystals. A high proton conductivity amounting to ca. 10^{-1} S m^{-1} was observed at room temperature under 100% relative humidity. Activation energies of the proton conduction were estimated to be 125 and 18 kJ mol^{-1} below and above 290 K, respectively. ^{2}H NMR spectra observed on a deuterated analog revealed 1-D proton conduction through hydrogen-bond networks formed among silanol groups on the layer surface and water molecules in the interlayer space. This material was discovered to be a new type of solid proton-conductor contributed by very weak acids in contrast to the strong-acid type ones so far reported.

Recently, much attention has been directed to proton conductors as materials for electrolytes applicable to fuel cells. Solid-state conductors are especially important for mobile fuel cells from the view point of convenience and safety, and a number of solid proton-conducting materials have been studied so far.[1] Since perfluoro sulfonic acid polymers such as Nafion®, well-known as the most popular solid proton-conductor, have several disadvantages, e.g., high price and limited working temperature range below 100 °C, development of cheap and thermal-resistant inorganic materials is desirable.

One of the layer silicates, Na-RUB-18 ($NaSi_4O_8(OH){\cdot}nH_2O$), is a material attracting attention as an inhomogeneous catalyst and a high-performance ion exchanger. This substance consists of polysilicate layers, exchangeable Na^+ ions in the interlayer space and water molecules coordinating to the cations.[2] 50% of dense silanol groups on the silicate layer exist as silanolate (SiO^-) in Na-RUB-18, and hydrogen-bond networks formed between silanol and silanolate keep a stable layer structure.[3]

Browski et al. predicted proton conduction in Na-RUB-18 based on MD simulations.[4] They also described the proton exchange between silanol groups and water molecules from the results of ^{1}H MAS NMR measurements. In this paper, we report a temperature dependence of proton conductivity measured on Na-RUB-18. The details of hydrogen dynamics in this material are also discussed from the analysis of ^{2}H NMR spectra.

Experimental

Na-RUB-18 was hydrothermally synthesized from a mixture of silicon dioxide, sodium hydroxide, and water with a molar ratio of $SiO_2{:}NaOH{:}H_2O = 4{:}1{:}25.8$.[2] The mixture was put in a Teflon-sealed stainless autoclave and kept at 100 °C for two weeks. The product was washed with an NaOH solution of pH 9.5, and dried at 40 °C for two days. The obtained colorless powder was identified by the measurement of powder X-ray diffraction with a Philips X'pert PW3040. Three kinds of samples were prepared under three different conditions: the first, in desiccators with diphosphorus pentaoxide; the second, in air; and the last, in desiccators with pure water, corresponding to relative humidities (RH) of 0, ca. 15, and 100%, respectively.

Thermal analyses were conducted on the synthesized Na-RUB-18 kept under 0 and 100% RH at room temperature with a heating rate of 5 K min^{-1} to determine the water contents using a Seiko EXTRA TG/DTA 6300 at the Chemical Analysis Center, University of Tsukuba.

Electrical conductivities (σ) on Na-RUB-18 kept under 15 and 100% RH were determined at room temperature, and the temperature dependence of σ was measured on the latter sample between 240 and 310 K by measurement of the complex impedance for pellet specimens of 2.5 mm in diameter and 0.70 mm thick by applying the pseudo four-terminal method between 40 and 4×10^{6} Hz by use of an Agilent Technologies 4294A LCR meter. The isotope effect on σ was observed with a Hioki 3532 LCR HiTESTER on an Na-RUB-18 pellet by flowing N_2 gas saturated with H_2O and D_2O vapor at room temperature.

^{2}H NMR spectra were recorded between 140 and 320 K on a Bruker MSL-300 NMR system. A sample sealed in a glass tube with saturated D_2O vapor was used for this measurement after keeping under vacuum overnight.

Results and Discussion

Thermal Analyses. Thermogravimetry (TG) and differential thermal analysis (DTA) measurements on a sample kept

Published on the web April 7, 2006; DOI: 10.1246/bcsj.79.656

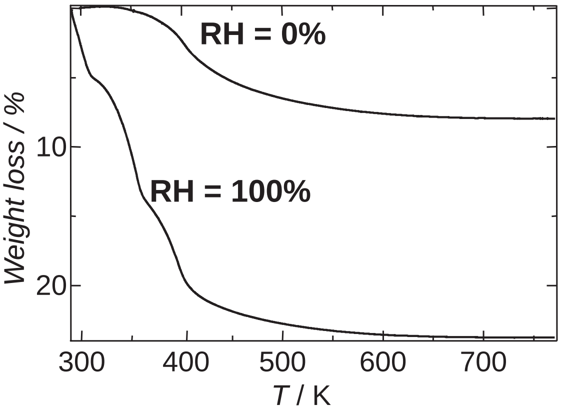

Fig. 1. Thermogravimetry curve observed in Na-RUB-18 kept under 0 and 100% relative humidity.

under 100% RH showed a small endothermic weight loss between 20 and 30 °C, an endothermic loss of ca. 20% in two steps in the range 30–150 °C, and a broad exothermic loss above 150 °C (Fig. 1). The second endothermic and the third exothermic events coincide well with reported results[5,6] and the first endothermic weight-loss is attributable to the desorption of water molecules on the surface. The TG/DTA curve measured on a sample kept under 0% RH showed an endothermic weight loss of ca. 4% in the range of 80–150 °C and an exothermic loss of ca. 4% above 150 °C. A composition of RUB-18 under 0% RH can be estimated to be $NaSi_4O_8(OH)\cdot H_2O$ from the present result.

Complex Impedance. Figure 2 shows Cole–Cole plots of the complex impedance measured on Na-RUB-18 under two different RH values at room temperature. The observed plot showed parts of two arcs under all RH. A clear arc between $Z' = 0$ and ca. $1.5 \times 10^7\,\Omega$ measured at 15% RH, and a small increase observed between 1290 and 1320 Ω at 100%. These data correspond to σ values of 8.9×10^{-6} and 1.1×10^{-1} S m^{-1}, at respective RH, by the estimation from the x-intercept of the extrapolation of the arcs.

To determine whether the conduction is governed by proton diffusion or not, we observed the isotope effect of the σ value. Figure 3 shows a time-evolution of relative σ values observed at room temperature under the flow of N_2 gas saturated with H_2O, then with D_2O. σ reached a constant value, σ_s, at ca. 60 min after starting the H_2O flow. After the gas was changed from H_2O to D_2O at the time (t_D) of ca. 130 min after the start, values almost constant were observed, then they gradually decreased, and another equilibrium value was reached 300 min after the gas exchange, where the equilibrium relative σ was reduced to ca. 0.7 compared with that in the H_2O flow. This value close to $1/\sqrt{2}$ is explainable by the mass-effect on the proton conduction.[1] From this result, we can conclude that the carriers of the conduction in Na-RUB-18 are protons.

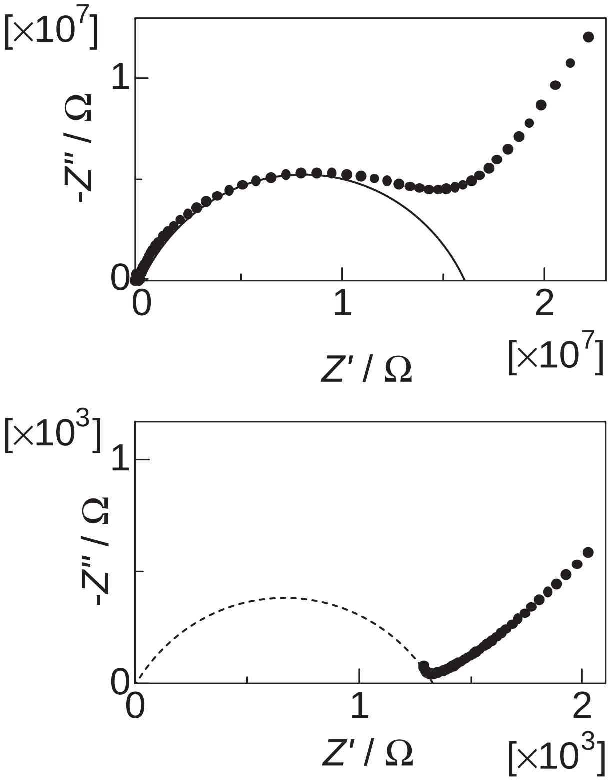

Fig. 2. Cole–Cole plots of complex impedances measured on Na-RUB-18 under 15 (upper) and 100% (lower) relative humidity at room temperature. The solid and dashed lines show the best fitted and an expected arcs.

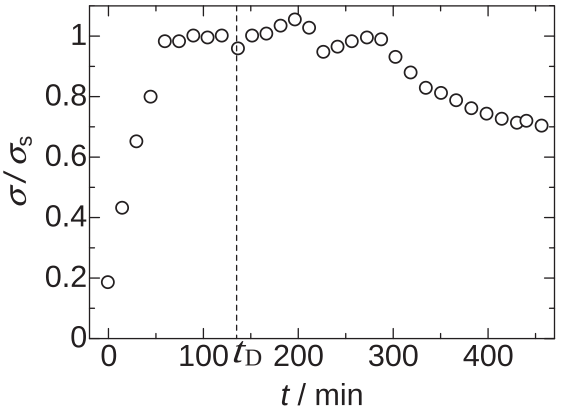

Fig. 3. A time development of electrical conductivity estimated on Na-RUB-18 under an N_2 gas flow saturated with water vapor. At $t = 0$, gas saturated with H_2O vapor was started to flow on a pellet of Na-RUB-18 kept in air and the gas was changed to that saturated with D_2O vapor at $t = t_D$ shown by a broken line. Observed conductivities (σ) were normalized by σ_s (see in text).

An Arrhenius plot of the σ observed on Na-RUB-18 under 100% RH is shown in Fig. 4. Activation energies of the proton conduction were estimated to be 125 ± 20 and 18 ± 2 kJ mol^{-1} in the ranges, 230–290 and 290–330 K, respectively, from the observed slopes of temperature dependences of σT. The activation energy obtained on the high temperature side agrees well with the reported value, ca. 20 kJ mol^{-1}, for the proton exchange between silanol groups and water molecules in this material observed in a similar temperature range.[4] In case two or more mechanisms contribute to the conductivity, the conduction with the higher activation energy should be observed in the higher temperature region. The observed data showing an opposite tendency suggests the occurrence of a phase change

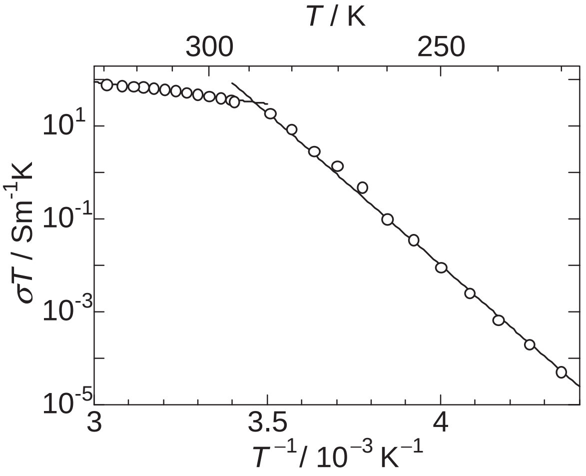

Fig. 4. An Arrhenius plot of the electrical conductivity estimated for Na-RUB-18. Solid lines represent the best fitted curves. The slope changed around 290 K.

around 290 K. The dehydration beginning around 300 K shown by the TG measurement implies this phase change. It is possible for the water molecules to reside in the interlayer space as nearly free water under high humidity as often seen in clay minerals.[7] This implies that the proton jump occurs among the oxygen atoms that fixed in crystals, in silanol and/or silanolate and water molecules in the low temperature region, but it is possible for a part of water molecules to rearrange to more advantageous positions for the proton jump as in liquid water in the high temperature region. The ^{2}H NMR results, which showed the existence of liquid-like deuterons implying free water molecules above this temperature, described below seem to support this expectation.

^{2}H NMR Line-Shape. The motional state of hydrogen can be discussed more in detail from the analysis of the ^{2}H NMR spectra shown in Fig. 5. The line-shape observed at 140 K was reproduced by a superposition of two Pake-patterns[8] with quadrupole coupling constants (e^2Qq/h) and asymmetric parameters (η) estimated to be (200 ± 10 kHz, 0.2 ± 0.05) and (55 ± 2 kHz, 0.6 ± 0.05), respectively, where e^2Qq/h and η were represented by $e^2Qq/h = eQ/h \cdot V_{zz}$ and $\eta = (V_{xx} - V_{yy})/V_{zz}$, using the principal values of an electric field gradient (EFG) tensor, V_{xx}, V_{yy}, and V_{zz}. The former component is attributable to rigid OH groups in Na-RUB-18, because both e^2Qq/h and η values coincide with those of rigid water molecules in ice.[9] The latter component implies the occurrence of some motions of hydrogen in Na-RUB-18.

Browski et al.[4] showed the proton exchange between water molecules and silanol groups in this compound by observing ^{1}H MAS NMR spectra, and proposed two kinds of models (named "Low T" and "High T" networks) of the proton delocalization among hydrogen-bond networks by applying the MD simulation. According to their report, protons delocalize in a square made by two water molecules, a silanol and a silanolate group in the Low T model, and a one-dimensional proton-conduction becomes possible in the High T model by proton exchanges between adjacent squares in addition to the Low T delocalization.

From $\eta = 0.2$ estimated for the broad component attributed to the rigid OD in Na-RUB-18 observed at 140 K, a ratio among EFG principal values, where $|V_{xx}| \leq |V_{yy}| \leq |V_{zz}|$, can be determined to be V_{xx}:V_{yy}:V_{zz} = −0.4:−0.6:1. According to this relation, the apparent e^2Qq/h value of the deuterons in the delocalization among 4-sites in a plane as assumed in the Low-T model is expected to keep at least a smallest principal value corresponding to V_{xx}, i.e., 40% with respect to the rigid state. The small e^2Qq/h value, 55 kHz (27.5% of the rigid value), of the second component is unexplainable by the Low-T model, and thus seems to support the High-T delocalization model involving a 3-dimensional average of the EFG tensor.

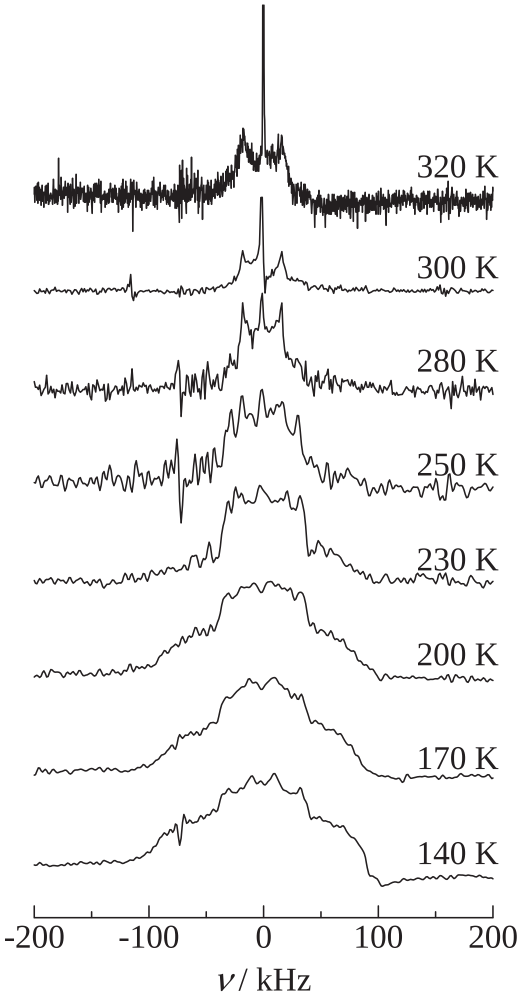

Fig. 5. A temperature dependence of ^{2}H NMR spectra observed in Na-RUB-18. The spectrum observed at 320 K is magnified its intensity 50 times to show the broad component.

The intensity of the broader component attributed to the rigid deuterons decreases gradually with the temperature increase. At 280 K, the spectrum is reproducible by the superposition of a Pake-pattern with $(e^2Qq/h, \eta) = (50 \pm 2\,\text{kHz}, \approx 0)$ and a sharp peak with no-fine structure. The sharp peak implies the existence of a small amount of free water. With further heating, the intensity of the sharp component drastically increased and became about half of the total signal in the spectrum observed at 320 K, implying the occurrence of dehydration in Na-RUB-18.

Conclusion

The proton conduction in Na-RUB-18 between 240 and 310 K could be measured for the first time. The proton conduction showed a marked humidity dependence and a high value $\approx 10^{-1}\,\mathrm{S\,m^{-1}}$ around room temperature under 100% relative humidity. The activation energies of the proton conduction were determined to be 125 and $18\,\mathrm{kJ\,mol^{-1}}$ below and above 290 K, respectively. ^{2}H NMR spectra support the "High T" hydrogen-delocalization model proposed by Browski et al.,[4] which suggests that the present system shows a 1-D proton delocalization even at 140 K. From these results, this material, possessing protons only as silanol and water, which work as very weak acids, can be concluded to be a different type of proton conductor compared to the strongly acidic compounds so far reported as good solid proton-conductors working around room temperature.[1]

This work was partly supported by "Nanotechnology Support Project" and Grant-in-Aid for scientific research No. 17036007 0247 of the Ministry of Education, Culture, Sports, Science and Technology (MEXT), Japan.

References

1 K.-D. Kreuer, *Chem. Mater.* **1996**, *8*, 610.

2 R. K. Iler, *J. Colloid Sci.* **1964**, *19*, 648.

3 G. G. Almond, R. K. Harris, K. R. Franklin, *J. Mater. Chem.* **1997**, *7*, 681.

4 M. Browski, I. Wolf, H. Gies, *Chem. Mater.* **2002**, *14*, 38.

5 S. Vortmann, J. Rius, S. Siegmann, H. Gies, *J. Phys. Chem. B* **1997**, *101*, 1292.

6 M. Browski, B. Marler, H. Gies, *Z. Kristallogr.* **2002**, *217*, 233.

7 C. Poinsignon, J. D. F. Ramsay, *J. Chem. Soc., Faraday Trans. 1* **1986**, *82*, 3447.

8 A. Abragam, *The Principle of Nuclear Magnetism*, Clarendon Press, Oxford, **1961**.

9 P. Waldstein, S. W. Rabideau, J. A. Jackson, *J. Chem. Phys.* **1964**, *41*, 3407.