



# Proton diffusion in the room-temperature phase of $[(\text{NH}_4)_{1-x}\text{Rb}_x]_3\text{H}(\text{SO}_4)_2$ as studied by $^1\text{H}$ spin-lattice relaxation in the rotating frame

Shigenobu Hayashi <sup>a,\*</sup>, Hironori Omi <sup>b</sup>

<sup>a</sup> Research Institute of Instrumentation Frontier, National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba Central 5, 1-1-1 Higashi, Tsukuba, Ibaraki 305-8565, Japan

<sup>b</sup> Faculty of Engineering, Chiba Institute of Technology, 2-1-1 Shibazono, Narashino, Chiba 275-0023, Japan

## ARTICLE INFO

### Article history:

Received 8 February 2010

Received in revised form

12 April 2010

Available online 25 May 2010

### Keywords:

Proton dynamics

Proton conduction

Proton diffusion

Inorganic solid acid salts

Nuclear magnetic resonance

Solid-state NMR

Spin-lattice relaxation

## ABSTRACT

Proton diffusion in the room-temperature phase (phase II) of  $[(\text{NH}_4)_{1-x}\text{Rb}_x]_3\text{H}(\text{SO}_4)_2$  ( $0 < x \leq 1$ ) has been studied by means of  $^1\text{H}$  spin-lattice relaxation times in the rotating frame,  $T_{1\rho}$ . The  $^1\text{H}$   $T_{1\rho}$  values were measured at 200.13 MHz in the range of 380–490 K. The ammonium protons and the acidic protons have independent  $T_{1\rho}$  values in the higher temperature range of phase II, suggesting that the spin diffusion between the two species is ineffective. The translational diffusion of the acidic protons is the most dominant mechanism to relax both the ammonium protons and the acidic protons in phase II. The  $^1\text{H}$   $T_{1\rho}$  values in phase II are analyzed theoretically and the motional parameters are obtained. The results of NMR well explain the macroscopic proton conductivity.

© 2010 Elsevier Inc. All rights reserved.

## 1. Introduction

Research and development of fuel cells are being performed intensively because  $\text{CO}_2$  evolution is expected to be suppressed. Polymer electrolyte membrane fuel cells are being developed for mobile applications. In those cells the operating temperature is limited to lower than 373 K, because the membranes require water for proton conduction. Haile et al. have demonstrated that water-soluble inorganic solid acid salts such as  $\text{CsHSO}_4$  and  $\text{CsH}_2\text{PO}_4$  are used successfully in  $\text{H}_2/\text{O}_2$  and direct methanol fuel cells at temperature ranges higher than 373 K [1,2].

Inorganic solid acid salts such as  $\text{MHXO}_4$  and  $\text{M}_3\text{H}(\text{XO}_4)_2$  ( $\text{M}=\text{Cs}, \text{NH}_4, \text{Rb}$ ;  $\text{X}=\text{S}, \text{Se}$ ) families show a high proton conductivity in a high-temperature phase, so-called “a superprotonic phase” [3–6]. In those compounds, tetrahedral  $\text{XO}_4$  anions form hydrogen bond networks, and proton diffusion takes place through the networks. We studied proton dynamics in several inorganic solid acid salts,  $\text{CsHSO}_4$  [7–9],  $\text{Rb}_3\text{H}(\text{SO}_4)_2$  [10],  $(\text{NH}_4)_3\text{H}(\text{SO}_4)_2$  [11] and so on, by means of  $^1\text{H}$  solid-state NMR. Reorientation of tetrahedral  $\text{XO}_4$  anions plays an important role in the proton diffusion, and we concluded that a motion breaking the hydrogen bonds is rate-determining in the proton diffusion.

$(\text{NH}_4)_3\text{H}(\text{SO}_4)_2$  and  $\text{Rb}_3\text{H}(\text{SO}_4)_2$  belong to the  $\text{M}_3\text{H}(\text{XO}_4)_2$  family. The structures of the two compounds are isomorphic at room temperature [12–14]. An isolated dimer,  $[\text{SO}_4\text{—H}\cdots\text{SO}_4]^{3-}$  is formed in the room-temperature phase (phase II).  $(\text{NH}_4)_3\text{H}(\text{SO}_4)_2$  shows a superprotonic phase transition at 413 K [15,16]. A dynamically disordered hydrogen bond network is formed in the (0 0 1) plane of the high-temperature phase (phase I) [17].  $\text{Rb}_3\text{H}(\text{SO}_4)_2$  shows a phase transition at 495 K and indicates a high proton conductivity in the high-temperature phase [18,19]. However, the presence of a superprotonic phase transition is controversial in  $\text{Rb}_3\text{H}(\text{SO}_4)_2$  [20], because the structure of the high-temperature phase is not established. The mixed-cation  $[(\text{NH}_4)_{1-x}\text{Rb}_x]_3\text{H}(\text{SO}_4)_2$  crystals also show a superprotonic phase transition, and the transition temperature is sensitive to  $\text{NH}_4\text{—Rb}$  substitution [18,21]. The  $x$  value can cover the whole range between 0 and 1, and thus  $[(\text{NH}_4)_{1-x}\text{Rb}_x]_3\text{H}(\text{SO}_4)_2$  is a good model system to study the role of cations in the superprotonic transition.

In the previous works, we have studied proton dynamics in  $[(\text{NH}_4)_{1-x}\text{Rb}_x]_3\text{H}(\text{SO}_4)_2$  ( $0 < x < 1$ ) by  $^1\text{H}$  solid-state NMR [22–24]. We have measured and analyzed  $^1\text{H}$  MAS NMR spectra, NMR spectra for static samples (static NMR spectra) and spin-lattice relaxation times in the laboratory frame,  $T_1$ , as well as X-ray powder diffraction and thermal analyses. We discussed the proton dynamics and the range of the superprotonic phase in the mixed-cation crystals by comparing with those in  $(\text{NH}_4)_3\text{H}(\text{SO}_4)_2$  and  $\text{Rb}_3\text{H}(\text{SO}_4)_2$ .

\* Corresponding author. Fax: +81 29 861 4515.

E-mail address: hayashi.s@aist.go.jp (S. Hayashi).

In the room-temperature phase (phase II) of  $[(\text{NH}_4)_{1-x}\text{Rb}_x]_3\text{H}(\text{SO}_4)_2$  ( $0 < x < 1$ ) as well as  $(\text{NH}_4)_3\text{H}(\text{SO}_4)_2$  and  $\text{Rb}_3\text{H}(\text{SO}_4)_2$ , the acidic protons show  $^1\text{H}$  NMR spectral line shapes characterized by chemical shift anisotropy [10,11,22,23]. This fact demonstrates that the acidic protons undergo a very fast local and anisotropic motion, and we obtained no evidences indicating isotropic translational diffusion of protons from the NMR results. On the other hand, the AC impedance measurements show a considerable electric conductivity even in phase II [16,18,21]. The acidic protons should undergo some slow translational diffusion even in phase II.

In the present work, we have studied the proton diffusion in phase II of  $[(\text{NH}_4)_{1-x}\text{Rb}_x]_3\text{H}(\text{SO}_4)_2$  ( $0 < x < 1$ ) as well as  $(\text{NH}_4)_3\text{H}(\text{SO}_4)_2$  and  $\text{Rb}_3\text{H}(\text{SO}_4)_2$  by  $^1\text{H}$  spin-lattice relaxation times in the rotating frame,  $T_{1\rho}$ . The  $T_{1\rho}$  value is sensitive to a motion of the order of 50 kHz. We have measured  $^1\text{H}$   $T_{1\rho}$  values and analyzed them theoretically. As a result, we have detected the diffusion of the acidic protons in phase II and have estimated the contribution of the acidic proton diffusion to the macroscopic electric conductivity.

## 2. Experimental

### 2.1. Materials

$[(\text{NH}_4)_{1-x}\text{Rb}_x]_3\text{H}(\text{SO}_4)_2$  ( $0 \leq x \leq 1$ ) crystals were the same as those used in the previous works [10,11,22–24]. They were grown by slow evaporation of the aqueous solution containing stoichiometric amounts of  $(\text{NH}_4)_2\text{SO}_4$ ,  $\text{Rb}_2\text{SO}_4$  and  $\text{H}_2\text{SO}_4$ . The  $x$  values in the solid were 0.00, 0.06, 0.27, 0.54, 0.76 and 1.00. The crystalline powder was dried *in vacuo* at room temperature. The samples for  $^1\text{H}$   $T_{1\rho}$  measurements were sealed in a glass tube with helium gas of about 100 Torr (13 kPa).

### 2.2. NMR measurements

$^1\text{H}$  NMR was measured with a Bruker ASX200 spectrometer at 200.13 MHz in the range of 380–490 K. A Bruker probehead with a solenoid coil was used. The  $^1\text{H}$   $T_{1\rho}$  values were measured with the ordinary spin-lock pulse sequence, which was  $90^\circ_x$ -(spin-lock pulse) $_y$ -(acquisition). The NMR signal was acquired as a function of the spin-lock pulse length. The spin-lock field was 51.0 kHz.

## 3. Results and discussion

### 3.1. $^1\text{H}$ $T_{1\rho}$ values

A spin-lattice relaxation time is a time constant with which a perturbed spin system recovers to reach an equilibrium state. Fluctuation of the environment causes the relaxation. For example, diffusing protons modulate the dipolar interaction, causing the relaxation of the surrounding protons. A spin-lattice relaxation time in the rotating frame is sensitive to a motion with a rate comparable to the spin-lock field, i.e., about 50 kHz in the present work.

$^1\text{H}$  NMR spectra of  $[(\text{NH}_4)_{1-x}\text{Rb}_x]_3\text{H}(\text{SO}_4)_2$  ( $0 < x < 1$ ) as well as  $(\text{NH}_4)_3\text{H}(\text{SO}_4)_2$  at 200.13 MHz consist of two components: acidic protons and ammonium protons [11,22,23]. Proton exchange between the acidic protons and the ammonium ions is slow. The relaxation time has been measured for each component. The ammonium protons and the acidic protons show different relaxation behavior. The relaxation curves of both species are single exponential. However, the two components have similar  $T_{1\rho}$  values below 420 K in  $[(\text{NH}_4)_{1-x}\text{Rb}_x]_3\text{H}(\text{SO}_4)_2$  ( $x=0.76$ ). This

fact indicates that spin diffusion works between the acidic protons and the ammonium protons in the above temperature range.

Fig. 1 shows the obtained  $T_{1\rho}$  values of  $[(\text{NH}_4)_{1-x}\text{Rb}_x]_3\text{H}(\text{SO}_4)_2$  ( $0 < x < 1$ ) in the temperature region around the phase transition, together with those of  $(\text{NH}_4)_3\text{H}(\text{SO}_4)_2$  [25] and  $\text{Rb}_3\text{H}(\text{SO}_4)_2$ . The  $T_{1\rho}$  values of both the ammonium protons and the acidic protons take a minimum value in phase II of the samples with  $x=0.54$  and 0.76. Only the increasing side with temperature is observed in phase II of those with  $x=0.00$ –0.27. The  $T_{1\rho}$  value of the acidic protons in  $\text{Rb}_3\text{H}(\text{SO}_4)_2$  ( $x=1.00$ ) decreases with temperature. The  $T_{1\rho}$  value of the ammonium protons starts to decrease just below the transition temperature for the samples with  $x=0.00$ –0.54, whereas such decrease is not observed for the acidic protons.

### 3.2. Consideration of relaxation mechanisms

In the previous works, dynamic behavior in  $[(\text{NH}_4)_{1-x}\text{Rb}_x]_3\text{H}(\text{SO}_4)_2$  ( $0 < x < 1$ ) was studied extensively [23] as well as those in  $(\text{NH}_4)_3\text{H}(\text{SO}_4)_2$  [11] and  $\text{Rb}_3\text{H}(\text{SO}_4)_2$  [10]. In all the phases, very fast isotropic reorientation of  $\text{NH}_4^+$  ions takes place. In phase II, the acidic protons undergo a very fast local and anisotropic motion, probably a wobbling motion of the O–H bond in one direction.  $\text{NH}_4^+$  ions start to diffuse translationally just below the transition temperature. In phase I, both  $\text{NH}_4^+$  ions and the acidic protons diffuse translationally.  $\text{Rb}^+$  ions might also diffuse similarly to  $\text{NH}_4^+$  ions.

As described above, the  $T_{1\rho}$  value is sensitive to a motion with a rate of about 50 kHz. In phase II, the isotropic reorientation of  $\text{NH}_4^+$  ions and the wobbling motion of the O–H bond are too fast to cause the relaxation in the rotating frame. In phase I, the translational diffusion of the acidic protons is too fast to cause the  $T_{1\rho}$  relaxation. On the other hand, proton exchange between  $\text{NH}_4^+$  ions and the acidic protons is too slow to relax the spins in the rotating frame. The exchange rate has been determined by two-dimensional  $^1\text{H}$  NOESY MAS NMR experiments, which is 12–25 Hz at about 420 K [26].

In  $(\text{NH}_4)_3\text{H}(\text{SO}_4)_2$ , the ammonium protons of both phases are relaxed in the rotating frame by translational diffusion of  $\text{NH}_4^+$  ions [25]. The discontinuous change in the  $T_{1\rho}$  value at the phase transition temperature suggests that the phase transition enhances the motion. The translational diffusion of  $\text{NH}_4^+$  ions also relaxes the acidic protons in phase I. However, the acidic protons in phase II of  $(\text{NH}_4)_3\text{H}(\text{SO}_4)_2$  are relaxed in the rotating frame by another motion, because the temperature dependence for the acidic protons is different from that for the ammonium protons. The  $T_{1\rho}$  value of the acidic protons in phase II is on the higher-temperature side of the minimum point. This means that the motional rate is higher than 50 kHz.

The  $T_{1\rho}$  value of the acidic protons in phase II of  $[(\text{NH}_4)_{1-x}\text{Rb}_x]_3\text{H}(\text{SO}_4)_2$  ( $0 \leq x \leq 1$ ) depends on  $x$ . Only the increasing side with temperature is observed for  $x=0.00$ –0.27. The  $T_{1\rho}$  values take a minimum value for  $x=0.54$  and 0.76. The  $T_{1\rho}$  value decreases with temperature for  $x=1$ . Conclusively, the translational diffusion of the acidic protons causes the  $T_{1\rho}$  relaxation of the acidic protons in phase II of  $[(\text{NH}_4)_{1-x}\text{Rb}_x]_3\text{H}(\text{SO}_4)_2$  ( $0 \leq x \leq 1$ ). The  $T_{1\rho}$  value of the ammonium protons shows the similar  $x$  dependence, except for the temperature range just below the transition temperature. Thus, the translational diffusion of the acidic protons causes the  $T_{1\rho}$  relaxation of the ammonium protons in phase II of  $[(\text{NH}_4)_{1-x}\text{Rb}_x]_3\text{H}(\text{SO}_4)_2$  ( $0 \leq x \leq 1$ ), except for the above temperature range. Translational diffusion of  $\text{NH}_4^+$  ions also contributes to the  $T_{1\rho}$  relaxation only just below the transition temperature in phase II.

Download English Version:

<https://daneshyari.com/en/article/5420565>

Download Persian Version:

<https://daneshyari.com/article/5420565>

[Daneshyari.com](https://daneshyari.com)