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Conductivity enhancement investigation at the interface between sodium-ion conductive $Na_4Zr_2Si_3O_{12}$ and solid superacid particles

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The contributing factors for the conductivity enhancement in $Na_4Zr_2Si_3O_{12}$ by the dispersion of $SbF_5/(SiO_2–Al_2O_3)$ have been confirmed. Theoretical estimations of the enhanced conductivity based on the space-charge formation and interfacial acid–base interaction showed lower conductivity than the observed conductivity of the composite. This means that the obtained enhancement includes the chemical and structural contributions of dispersed solid superacid particles such as change of density, crystal structure of the matrix, grain size and induced dislocation. These effects would also result in the formation of ionic defects leading to an increase in conductivity.

1. Introduction

The ionic conductivity of the sodium oxide conductor $Na_4Zr_2Si_3O_{12}$ (NZS), which is one of the end members of NASICON series, has been enhanced drastically by the dispersion of insulator particles such as ferroelectric materials and acidic materials [1–4]. In the results, the intention of using solid superacid particles was that the acidic sites could attract ions of the conductor to create defects of sodium-ion vacancies available for the ionic migration. The acidic property is composed of two dominant factors, that is, the acid strength and the number of acidic sites. When the SbF_5-adsorbed binary oxides, one of the typical solid superacids, were dispersed into the NZS particles, the conductivity increase mainly depended on the acid strength rather than on the content of the acidic sites [4]. It is inevitably predicted, however, that the quantitative relationship exists between the content of the acidic sites on the acid particles and induced defects at the surface of the ionic conductor under the same acid strength.

The mechanisms responsible for the conductivity increase have been discussed from several aspects [5]. It has now become widely accepted that the overall effect of forming the composite is to create highly conductive paths along the interfaces [6, 7]. The simple and successful investigation of the conductive paths is the estimation of space-charge effects which are identified as the defect-concentrated regions along the interface. The estimated results reasonably agree with the experimental conductivity values of $AgCl–Al_2O_3$ composite [8]. However, the model could not always satisfy the enhancement results of several kinds of composite systems. This fact simply suggests the existence of factors responsible for the increased conductivity other than space-charge effects at the interface.

The present work investigated the contributing factors for the conductivity increase in the $Na_4Zr_2Si_3O_{12}–SbF_5/(SiO_2–Al_2O_3)$ system by the quantitative estimation of enhanced conductivity, assuming models of the space-charge formation and defect formation by interfacial acid–base interaction.

2. Defect formation mechanism at the interface between NZS and $SbF_5/(SiO_2–Al_2O_3)$

SbF_5-adsorbed $SiO_2–Al_2O_3$ binary oxide shows a high acidity of $pK_a \leqslant -16$ and is called a "solid superacid". The formation mechanism of the acidic sites could be represented as in Fig. 1. The Brønsted acidic sites of the solid superacid easily disconnect the hydrogen ions when some basic species approach [9]. It is reasonable to assume that oxygen ions of NZS are primarily attracted to the hydrogen ions of the acid because the oxygens would exist outside the NZS particles. Following the rearrangement of the oxygen ions near the surface, the mobile sodium ions would shift to allow charge compensation. Otherwise, the acidic sites would directly shift the sodium ions by repulsion because the sodium ions have a high mobility in the NZS framework structure. The mobile and then easily shifted behaviour of sodium ions is demonstrated by the SEM observations in which the concentrated electron beam attracts sodium ions and reduces them to sodium metal in NZS [10]. In either process of interfacial rearrangements, the displacement of sodium ions leads to the formation of the sodium-ion vacancies which are available for the ion migration

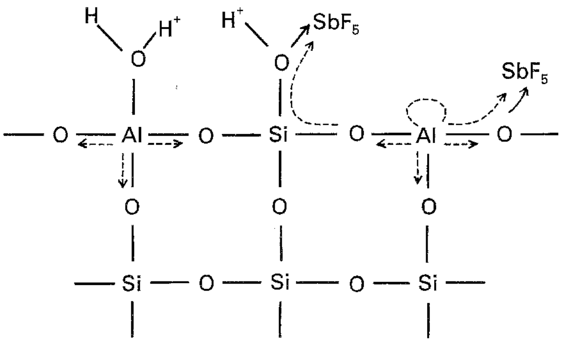

Figure 1 The appearance of the acidic sites of SbF_5-adsorbed SiO_2–Al_2O_3. SbF_5 adsorption strengthens the acidity of Lewis and Brønsted acidic sites by attracting electrons towards SbF_5.

along the interface. This process is the initial contribution to the conductivity increase in NZS dispersed with acid particles, SbF_5/SiO_2–Al_2O_3.

3. Estimation of enhanced conductivity at the interface between NZS and solid superacid

3.1. Conventional space-charge formation model

The conductivity increase after the space-charge formation could be represented as

$$\begin{aligned}\sigma_m &= \sigma_\infty + \sigma_{mL}\\ &= \sigma_\infty + \beta_A \Omega_A \varphi_A F(2\lambda)\mu_V (C_{V0} C_\infty)^{1/2} \qquad (1)\end{aligned}$$

where σ_∞ is the bulk conductivity, β_A is the correction factor which is given by the ratio of the effective phase volume to the whole phase volume, φ_A is the ratio of the surface to volume of the dispersed particle, φ_A is the volume fraction of the dispersant, λ is the Debye length, μ_V is the carrier mobility, C_{V0} is the vacancy concentration at the surface and C_∞ is the bulk concentration of the vacancy [6, 8]. An upper limit could be obtained assuming $C_{V0} \equiv$ (mole number of vacancies per NZS formula unit)/(molar volume) = $(4/V_m)$ mol cm^{-3}, therefore,

$$\sigma_{mL} \sim \beta_A \Omega_A \varphi_A \mu_V (8\varepsilon\varepsilon_0 RT/V_m)^{1/2} \qquad (2)$$

where ε is the relative dielectric constant of NZS, ε_0 is the absolute dielectric constant of a vacuum, and V_m is the molar volume. The μ_V of NZS has not been obtained because the NZS has no available vacant sites for sodium-ion migration in the fundamental crystal structure and the observed conductivity of NZS is mainly due to the grain-boundary conduction in the polycrystalline ceramics. However, the mobility is also expressed as

$$\begin{aligned}\mu &= v_D/E\\ &= a^2 q\omega_p/(kT) \qquad (3)\end{aligned}$$

where v_D is the drift velocity, E the applied electrical field, a the mean jump distance, q the charge of the ion and ω_p the hopping frequency [11]. The hopping frequency can be obtained by the frequency dispersion analyses of impedance data [4, 12]. Fig. 2 shows the obtained results for ω_p of the NZS series [4]. The ω_p of NZS ($x = 0$) is fairly low because it was estimated from the "grain-boundary" conductivity of the ceramics, because NZS has essentially no vacant sites. On the other hand, partial doping of Nb^{5+} ions for Zr^{4+} ions of NZS has increased ω_p independently of the Nb^{4+} content in the range $0 < x < 0.2$ as shown in Fig. 2 [13]. This is clearly due to the increase of the sodium-vacancies in the structure, and almost consistent with the situation where adsorbed acidic sites at the NZS surface induce the sodium-ion vacancies. Therefore, it is reasonable to use the ω_p value of niobium-doped NZS for the estimation of sodium-ion mobility. The estimated result of σ_m using Equations 1–3 is shown in Fig. 3 compared with the experimental results of the composite conductivity.

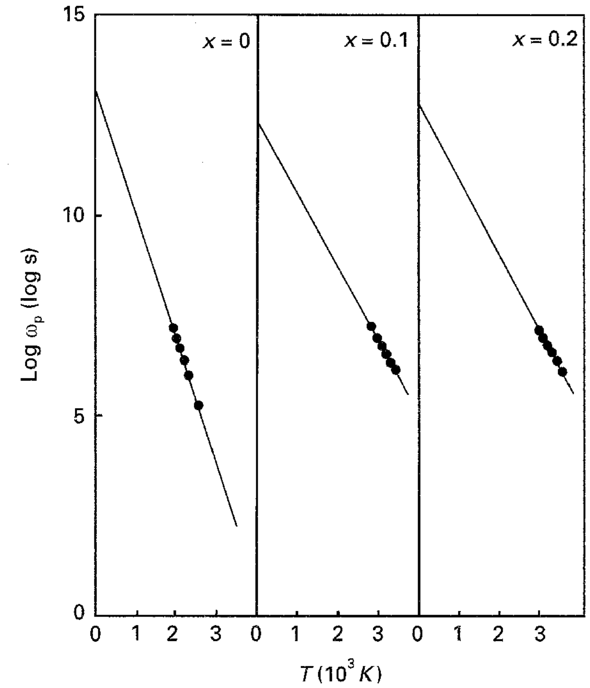

Figure 2 Temperature dependence of the hopping frequency of $Na_{4-x}Zr_{2-x}Nb_xSi_3O_{12}$. These were obtained by frequency dispersion analyses of the impedance results [4, 12].

3.2. Interfacial acid–base interaction model

When the practical acid–base interaction is considered, a reliable approach is to assume that each acidic site on the solid superacid particles attracts a sodium ion to form a sodium-ion vacancy based on the process of Section 2. In this case, the conductivity increase can simply be calculated from the content of the acidic sites. The enhanced conductivity is, therefore, expressed as

$$\begin{aligned}\Delta\sigma &= \int (C_0 - C_\infty)\mathrm{d}x\,\mu F\\ &= \frac{n_s}{\alpha}\mu F = \Gamma\mu F \qquad (4)\end{aligned}$$

where n_s is the content of adsorbed acid species at the surface, α the surface area, and Γ is the surface density of induced sodium-ion vacancies. With the several factors for the real conductivity obtained, the total

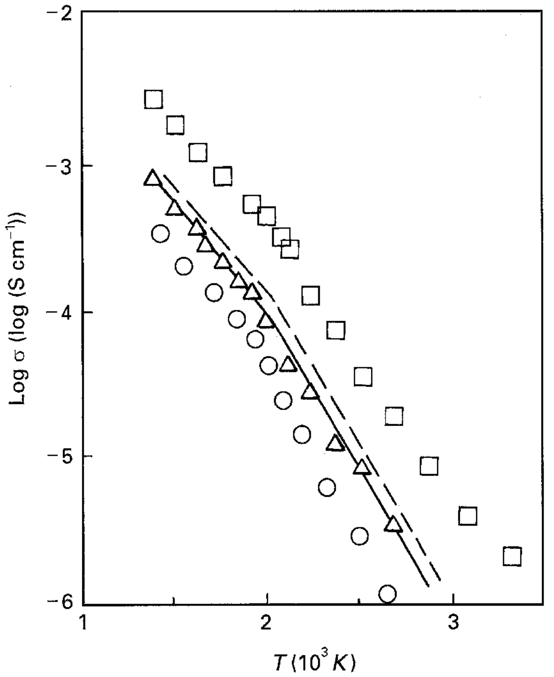

Figure 3 Temperature dependence of ionic conductivities of NZS and NZS–$SbF_5/(SiO_2–Al_2O_3)$ composites. Experimental values: (○) 0 vol %, (△) 3 vol %, (□) 20 vol %. Calculated values: (——) space charge formation model, (– –) acid–base interaction model in the case of 20 vol % dispersion.

conductivity could be expressed as

$$\sigma_L = \sigma_\infty + \beta_A \Omega_A \varphi_A F u \Gamma \qquad (5)$$

An ideal interface is estimated by assuming that the surface of the conductor is completely covered by acidic particles where each sodium-ion interacts with an acidic site. In that case, we obtain a Γ value of 4.0×10^{-10} mol cm^{-2} for NZS. The line corresponding to this estimation is shown in Fig. 3. It may appear surprising that the conductivity values calculated in this way turn out to be greater than the values estimated from the apparent maximum effect calculated from Equation 2 by using $C_{V0} = 4/V_m$. The reason is that Equation 5 assumes a continuous distribution of carriers, such that the actual number in the first defect layer, whose extension is of the order of the lattice constant, is distinctly less than C_{V0}.

The content of the acidic sites on the solid superacid particles estimated from the chemical adsorption content of NH_3 was 3.2×10^{-10} mol cm^{-2}. This reveals that about 80% of the sodium ions at the NZS surface could be affected by the solid superacid particles in the case where the contact of heterogeneous particles is ideal. Both estimated results, assuming the space-charge model and acid–base interaction, showed about three times lower conductivities than the experimental values. The main reason for this difference is that the observed enhanced conductivity would include the effect of dispersed second-phase dispersion, such as a change in the chemistry and microstructure of the matrix material to give an additional phase, alter the grain size or dislocation density, and change the crystal structure of the matrix material. They would contribute to the conductivity change, such as creating the ionic defects. However, it is, in practice, difficult unambiguously to separate all of the possible contributions to the enhanced conduction because they are correlated to each other. When the acid molecules were directly adsorbed on the particle surface of the ionic conductor CaF_2, the observed enhancement was obviously lower than the estimated value [14]. In that case, there was no additional second phase of the dispersant in the "composite conductor" except the adsorbates on the particle surface and, therefore, the situation conveniently excludes any other complicated effects of insulator particles causing the enhancement and/or reduction of the conductivity in addition to the formation of the high conduction layers at the interface. Another reason for mismatching of the conductivity is that the model does not follow the real interface phenomena. The induced surface defects (corresponding to Γ) lead to the rearrangement of ionic configuration near the surface. Therefore, consideration of the surface monolayer would not be sufficient for the estimation of the total highly conductive phase after the adsorption of acidic molecules. A region a few tens of nanometres from the surface, almost corresponding to the Debye length, could contribute to the effective high conductivity, considering the space-charge formation processes to equilibrate the interface.

4. Conclusions

By the dispersion of solid superacid particles, SbF_5-adsorbed $SiO_2–Al_2O_3$, the conductivity of NZS has been increased. The estimation of induced defects based on the space-charge model and defect-induced model by a simple acid–base interaction compensated the partial conductivity increase. The difference between the estimated results and observed values reveals the existence of other effects of dispersants, such as change of density, grain size and induced dislocations. They would also contribute to the defect formation different from the space-charge formation process. Further, the estimation process using the two models may not be sufficient for the survey of the total defects content. The formation of a defect layer at the surface should induce the rearrangement of ionic configuration near the surface to equalize the chemical potentials at the interface. Therefore, extension of the model, which is possible, to estimate several effective layers would be more reasonable.

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