Na₂SO₄-based solid electrolytes for SOₓ sensors

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Na₂SO₄-based solid electrolytes with compositions Na₂SO₄+x mol% Y₂(SO₄)₃ (x=0, 3, 5, 6, 9, 12, 15) and Na₂SO₄ + y mol% La₂(SO₄)₃ (y=0, 2, 4, 6, 8) were synthesized by solid state reaction. The crystal structure, phases, and electrical conductivity of these solid electrolytes were studied by XRD, SEM, EDX, DTA, TGA and impedance spectroscopy. Upon doping with La₂(SO₄)₃ or Y₂(SO₄)₃ the high-temperature fast-ion conducting phase Na₂SO₄-I can be stabilized down to room temperature. Doping increases the ionic conductivity as well. Of these solid electrolytes the Na₂SO₄ + 5 mol% Y₂(SO₄)₃ and Na₂SO₄ + 4 mol% La₂(SO₄)₃ solid solutions exhibit the highest ionic conductivity values at 400°C (17.6 x 10⁻² S cm⁻¹ and 2.95 x 10⁻² S cm⁻¹, respectively) and lowest activation enthalpies (0.38 eV and 0.37 eV, respectively). When x ≥ 12 or y ≥ 8, the Na₂SO₄-I structure can be completely stabilized down to room temperature. For the solid electrolytes with x=5 and y=4, Na₂WO₄ was used to further stabilize phase I, and to improve the mechanical properties. In the Na₂SO₄ + 5 mol% Y₂(SO₄)₃ + m mol% Na₂WO₄ (m=5, 10, 15, 20) and Na₂SO₄ + 4 mol% La₂(SO₄)₃ + n mol% Na₂WO₄ (n=5, 10, 15, 20) samples, XRD analysis reveals the Na₂SO₄-I structure to be stable at room temperature as is illustrated by DTA. Impedance measurements show that the stability of these solid solutions with Na₂WO₄ decreases the ionic conductivity. However, their conductivity is still higher than that of unaided Na₂SO₄. In the ionic conductivity measurements of Na₂SO₄ + 4 mol% La₂(SO₄)₃ + Na₂WO₄ system, an unusual Arrhenius behavior has been observed, i.e. the activation enthalpy at higher temperatures being larger than that at lower temperatures. This behavior is discussed based on the phases present and the structure of the specimens. From a point of view of practical application as SO₂ sensor material, the Na₂SO₄ + 5 mol% Y₂(SO₄)₃ + Na₂WO₄ and Na₂SO₄ + 4 mol% La₂(SO₄)₃ + Na₂WO₄ materials are better than unaided Na₂SO₄ because of their higher conductivity, and absence of a phase transition.

1. Introduction

Sulfur oxides (SO₂ and SO₃) are widely emitted in many industrial combustion processes and the detection of these gases has attracted a wide spread attention in recent years not only for the process control but also for the detection of air pollution. Since the early seventies, many efforts have been devoted to the development of potentiometric sensors based on SO₂-O₂-SO₃ concentration cells using alkali sulfates as solid electrolytes [1-4]. At elevated temperatures, alkali sulfates are alkali ion conductors. Gauthier et al. [1,2] first pointed out that K₂SO₄ can be used as a solid electrolyte for a SO₂ sensor. Following this study, Na₂SO₄ and Li₂SO₄ were examined by Jacob and Rao [3], and Worrell and Liu [4], respectively. In these studies, the EMF of the sensor agreed with the value calculated from the Nernst equation, if a small difference in SO₂ partial pressure between the reference and measuring electrode was applied. However, a large difference in SO₂ partial pressure yielded EMF values which were lower than the theoretical values. This deviation was due to the occurrence of a phase transition, poor sintering, and low values of the electrical conductivity [5-7].

Na₂SO₄ exhibits several phase transitions [8]. The room temperature phase V is orthorhombic in nature. When it is dried, a metastable phase III an orthorhombic structure results, and it takes some days to undergo a slow III-V phase transition. The
prominent phase transition at 241°C results in the hexagonal phase I, which cannot be quenched at room temperature. The hexagonal phase Na$_2$SO$_4$-I (241-884°C) with the lattice parameters $a=5.38$ Å and $c=7.26$ Å [12] is a sodium ion conductor, and can be used as a solid electrolyte in a SO$_2$ sensor. However, the volume change due to the III-I phase transition will cause microcracks in the Na$_2$SO$_4$ material, while the poor sinterability of this material may lead to the presence of micropores. All these microscopic defects will lead to gas permeation and hence to lowering of EMF values. In order to avoid these problems, several dopants [8-11] such as La$_2$(SO$_4$)$_3$ (Ln=rare earth elements), Na$_2$WO$_4$ and NaVO$_3$ were employed not only to increase the ionic conductivity of Na$_2$SO$_4$, but also to stabilize phase I down to room temperature, and to improve the sinterability. In addition to these dopants, inert oxides have been dispersed into these solid electrolytes, in order to improve the properties. Usually, the rare earth sulfates act both as a stabilizer and as a conductivity increasing dopant. As a stabilizer, it reacts with sodium sulfate to form a solid solution, which is more stable than the pure Na$_2$SO$_4$-I phase, while as a doping element, the rare earth ion replaces the sodium ion in the lattice under the formation of sodium ion vacancies for charge compensation, which will obviously increase the ionic conductivity. More recently, Dekker [12] has described the behaviour of a solid phase mixture, comprising Na$_2$SO$_4$, Y$_2$(SO$_4$)$_3$+PSZ. When partially stabilized zirconia (PSZ) is dispersed into the solid solution Na$_2$SO$_4$-Y$_2$(SO$_4$)$_3$, the phase transition III-I is suppressed completely by a transformation toughening mechanism.

In the present work, Y$_2$(SO$_4$)$_3$, La$_2$(SO$_4$)$_3$ and Na$_2$WO$_4$ were applied to improve the phase stability, electrical conductivity, and mechanical properties of Na$_2$SO$_4$.

2. Experimental aspects

2.1. Materials

Y$_2$(SO$_4$)$_3$ and La$_2$(SO$_4$)$_3$ were prepared from Y$_2$O$_3$ and La$_2$O$_3$ by a wet chemical method. Y$_2$O$_3$ (or La$_2$O$_3$) of 4N purity was dissolved in hot HNO$_3$ to yield a Y(NO$_3$)$_3$ (or La(NO$_3$)$_3$) solution. Y$_2$(SO$_4$)$_3$ (or La$_2$(SO$_4$)$_3$) was synthesized by adding concentrated H$_2$SO$_4$ to the rare earth nitrate solution and heating. Na$_2$SO$_4$ and Na$_2$WO$_4$·2H$_2$O (Shanghai Yueyong Chemicals Co. Ltd., AR) were dried at 200°C for three hours in order to eliminate any water content and to obtain pure Na$_2$SO and Na$_2$WO$_4$. Mixtures of appropriate amounts of Na$_2$SO$_4$, Y$_2$(SO$_4$)$_3$ (or La$_2$(SO$_4$)$_3$), and Na$_2$SO$_4$, Y$_2$(SO$_4$)$_3$ (or La$_2$(SO$_4$)$_3$) and Na$_2$WO$_4$ were ground and calcined at 650°C for three hours. The calcined samples were reground and pelletized (100 kg/cm²) and subsequently sintered at 700°C for six hours in air. The specimens were ground, pelletized and sintered in air 3 times in order to obtain dense pellets. The pellets typically have a diameter of 1.3 cm and a thickness of 0.2 cm. It was observed that for some high concentrations Y$_2$(SO$_4$)$_3$ or La$_2$(SO$_4$)$_3$ doped Na$_2$SO$_4$ samples partially melted during sintering, while doping of Na$_2$WO$_4$ results in the absence of this partial melting. Furthermore, the mechanical properties of the pellets were substantially improved, while densities of 95.5% were obtained.

2.2. Measurements

The XRD patterns of the specimens were recorded on a D/max 12 kW diffractometer (Rikadenki, Japan). An X-650 SEM equipped with EDX (Hitachi, Japan) was used to observe the morphology of the polished surfaces of the specimens. DTA and TG were employed to investigate the phase transitions and thermal stability of the sample materials using a DF-30 Thermoanalyzer (Shimadzu, Japan) and a Simultan Thermoanalyzer (Model 429). The ionic conductivity of the specimens was measured by the impedance spectroscopy technique using a GenRad 1689 Precise RLC Digibridge computer system with a frequency range of 12 Hz to 100 kHz in the temperature range of 100 to 700°C.

3. Results and discussion

3.1. Na$_2$SO$_4$+x mol% Y$_2$(SO$_4$)$_3$ (x=0, 3, 6, 9, 12, 15)

After sintering, the polished surface of the undoped Na$_2$SO$_4$ specimen (x=0) revealed a dense
microstructure as is shown in fig. 1a. The grain size is not uniform. When $Y_2(SO_4)_3$ is added to Na$_2$SO$_4$, the surface microstructure changes substantially. Fig. 1b presents an example for a specimen with $x=15$.

Fig. 2a presents the DTA curve for the sample Na$_2$SO$_4$+$12$ mol% $Y_2(SO_4)_3$ before sintering and fig. 2b presents the DTA curve for the same sample after sintering 3 times at 700°C for six hours in air.

Before sintering the DTA pattern of the Na$_2$SO$_4$+$12$ mol% $Y_2(SO_4)_3$ mixture resembles the pattern for undoped Na$_2$SO$_4$. There are three peaks at 135°C, 240°C and 880°C, indicating the release of adsorbed water vapour, the III–I phase transition and the melting point of Na$_2$SO$_4$, respectively. After sintering the Na$_2$SO$_4$–$Y_2(SO_4)_3$ solid solution is formed, and yields a different DTA curve with only one peak at 833°C, being its melting point. The III–I phase transition is absent in this solid solution. The Na$_2$SO$_4$–I phase has been fully stabilized down to room temperature, and the solid solution does not adsorb water vapour anymore. Na$_2$SO$_4$+$15$ mol% $Y_2(SO_4)_3$ exhibits a DTA pattern similar to that in fig. 2b, but the melting point is 820°C. For the specimens with $x\leq9$ mol% in the Na$_2$SO$_4$+$x$ mol% $Y_2(SO_4)_3$ system, the III–I phase transition still exists at 240°C. However, with increasing doping amount a weaker peak results concordant to the partial stabilization of the Na$_2$SO$_4$–I phase by $Y_2(SO_4)_3$.

The XRD analysis gives results which are in agreement with the DTA results as mentioned below. The undoped Na$_2$SO$_4$ exhibits a phase III structure at room temperature. For $x\leq9$ mol%, the XRD pattern reveals a mixture of phases I and III, the amount of phase I being larger with increasing amount of dopant. When $x\geq12$ mol%, the XRD pattern is a pure phase-I pattern, the only difference being a larger $d$ value compared to that of an undoped Na$_2$SO$_4$–I phase, indicating the slight expansion of the unit cell for the Na$_2$SO$_4$–$Y_2(SO_4)_3$ solid solution.

Fig. 3 shows the ionic conductivity of the Na$_2$SO$_4$+$x$ mol% $Y_2(SO_4)_3$ ($x=0, 3, 5, 6, 12$) solid solutions as a function of temperature. Table 1 presents the conductivity activation enthalpies as calculated from the Arrhenius curves. Fig. 4 gives the relation of the isothermal conductivities and the amount of $Y_2(SO_4)_3$ doping.

As can be seen from fig. 3 the curves of solid solutions with $x<12$ mol% exhibit two different slopes in the low and high temperature range, the slope at higher temperatures being smaller than that at lower temperatures. This result is due to the different ion conducting pathways because of the I–III phase transition. At higher temperatures, Na$_2$SO$_4$–I constitutes the stable phase, and this phase exhibits a high ionic conductivity, and a low activation enthalpy. However, at lower temperatures, the material comprises a mixture of phases I and III. Both phases exhibit sodium ion conductivity via sodium ion vacancies. The ionic conductivity of phase III material is smaller than that of phase I material. Moreover the conductivity activation enthalpy of phase III is larger than that of phase I. Therefore, the conductivity activation enthalpy increases below the phase transition. For $x=12$ mol% phase-I is completely stabilized down to room temperature, therefore, a straight line of $\ln(\sigma T)$ versus $1/T$ was observed.
It is seen from the conductivity isotherms in fig. 4 that doping with $Y_2(\text{SO}_4)_3$ increases the ionic conductivity of $\text{Na}_2\text{SO}_4$. The highest conductivity ($\sigma=1.76 \times 10^{-2}$ S cm$^{-1}$) and lowest activation enthalpy (0.38 eV) are obtained at 400°C with $\text{Na}_2\text{SO}_4+5$ mol% $Y_2(\text{SO}_4)_3$. This result can be explained if we consider that the dopant ion $Y^{3+}$ ion will occupy a $\text{Na}^+$ ion in the lattice of $\text{Na}_2\text{SO}_4$ to produce one $Y_{\text{Na}}$ and two sodium ion vacancies $V_{\text{Na}}$ (Kröger–Vink notation). At low doping levels, a linear increase of the isothermal conductivity with increasing amount of doping is observed due to the linear increase of the concentration of sodium ion vacancy, $V_{\text{Na}}$. With increasing $Y_2(\text{SO}_4)_3$ doping level, the sodium ion vacancies may interact with the dopant ions to form an associate. In case that an equilibrium is reached, the concentration of $V_{\text{Na}}$ is proportional to the cubic root of the doping amount.
Fig. 3. Arrhenius plots of the ionic conductivity of the Na$_2$SO$_4$–Y$_2$(SO$_4$)$_3$ solid solutions as a function of temperature.

Fig. 4. Isothermal conductivities of the Na$_2$SO$_4$–Y$_2$(SO$_4$)$_3$ solid solutions as a function of the dopant concentrations.

Table 1
Ionic conductivity and activation enthalpies of the Na$_2$SO$_4$+x mol% Y$_2$(SO$_4$)$_3$ solid solutions: log($\sigma$T)=$A/T$+$B$, $\Delta$H=$-2.303$ $A/R$ (eV).

<table>
<thead>
<tr>
<th>$x$</th>
<th>Temperature range (°C)</th>
<th>$A$</th>
<th>$B$</th>
<th>$\Delta$H (eV)</th>
<th>$\sigma$(400°C) (S·cm$^{-1}$)</th>
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</thead>
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<tr>
<td>0</td>
<td>100–320</td>
<td>−5061</td>
<td>6.50</td>
<td>1.01</td>
<td>$7.24\times10^{-5}$</td>
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<td>3</td>
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<td>−2994</td>
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<td>0.80</td>
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<td>6</td>
<td>315–650</td>
<td>−2516</td>
<td>3.53</td>
<td>0.50</td>
<td>$1.67\times10^{-3}$</td>
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<tr>
<td>12</td>
<td>356–650</td>
<td>−4017</td>
<td>7.28</td>
<td>0.80</td>
<td>$1.58\times10^{-3}$</td>
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<tr>
<td></td>
<td>394–650</td>
<td>−1911</td>
<td>3.73</td>
<td>0.38</td>
<td>$1.74\times10^{-3}$</td>
</tr>
</tbody>
</table>

[12]. At high doping levels, extended clustering of defects will block the conduction pathways, thereby decreasing the overall mobility of $V_{Na}^{+}$, and hence reducing the ionic conductivity. The doping amount of Y$_2$(SO$_4$)$_3$, for which no defect–defect interactions occur is about 5 mol% as can be seen in Fig. 4.

A more extended discussion of the defect chemistry of doped Na$_2$SO$_4$ has been given by Dekker [12] and Schoonman [13]. The present results are fully in line with the reported defect chemistry.

3.2. Na$_2$SO$_4$+y mol% La$_2$(SO$_4$)$_3$ ($y=2, 4, 6, 8$)

The DTA curves and XRD patterns for these solid solutions are almost the same as those with the Y$_2$(SO$_4$)$_3$ dopant. Fig. 5 shows the relation between the ionic conductivity and the temperature for the specimens with $y=2, 4, 6, 8$, respectively. Table 2 presents the conductivity activation enthalpies as calculated from these Arrhenius plots. Fig. 6 shows the isothermal ionic conductivity as a function of the La$_2$(SO$_4$)$_3$ doping amount. It is apparent that the conductivity plots for $y<8$ mol% also exhibit two different slopes at high and low temperatures. When $y=8$ mol%, phase I is completely stabilized, and the conductivity plot displays a straight line. La$_2$(SO$_4$)$_3$ has the same function of increasing the conductivity of Na$_2$SO$_4$ as Y$_2$(SO$_4$)$_3$.

In Fig. 6 the maximum conductivity and the minimum activation enthalpy are achieved for Na$_2$SO$_4$+4 mol% La$_2$(SO$_4$)$_3$. At 400°C, the conductivity is as high as $2.95\times10^{-2}$ S·cm$^{-1}$, and at
290°C the ionic conductivity is $3.87 \times 10^{-3}$ S·cm⁻¹ with $\Delta H = 0.37$ eV. This result is better than the reported result in the literature [8], i.e., at 290°C, $\sigma = 1.08 \times 10^{-3}$ S·cm⁻¹ with $\Delta H = 0.50$ eV. It is noted that the highest ionic conductivity of Na$_2$SO$_4$–Y$_2$(SO$_4$)$_3$ solid solutions is achieved with 5 mol% Y$_2$(SO$_4$)$_3$, and for Na$_2$SO$_4$–La$_2$(SO$_4$)$_3$ solid solutions with 4 mol% La$_2$(SO$_4$)$_3$. This may be due to the difference in the radii of sodium, yttrium and lanthanum ions. The radius of an yttrium ion is smaller than that of a lanthanum ion, but larger than that of a sodium ion. Because the radius difference between Na$^+$ and Y$^{3+}$ ions is smaller than that between Na$^+$ and La$^{3+}$, higher concentrations of Y$_2$(SO$_4$)$_3$ can be dissolved in Na$_2$SO$_4$ compared to La$_2$(SO$_4$)$_3$.

### Table 2

<table>
<thead>
<tr>
<th>$y$</th>
<th>Temperature range (°C)</th>
<th>$A$</th>
<th>$B$ (eV)</th>
<th>$\Delta H$ (eV)</th>
<th>$\sigma$ 400°C (S·cm⁻¹)</th>
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<td>2</td>
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<td>5.51</td>
<td>0.62</td>
<td>$5.22 \times 10^{-2}$</td>
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<td>4</td>
<td>398–650</td>
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<td>6</td>
<td>100–250</td>
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<td>0.81</td>
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<tr>
<td>8</td>
<td>250–650</td>
<td>$-1861$</td>
<td>4.23</td>
<td>0.37</td>
<td></td>
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<tr>
<td></td>
<td>100–650</td>
<td>$-4961$</td>
<td>9.83</td>
<td>0.99</td>
<td></td>
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<tr>
<td></td>
<td>250–650</td>
<td>$-1997$</td>
<td>3.98</td>
<td>0.40</td>
<td>$1.95 \times 10^{-2}$</td>
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<tr>
<td></td>
<td>100–650</td>
<td>$-2304$</td>
<td>3.78</td>
<td>0.46</td>
<td>$4.57 \times 10^{-3}$</td>
</tr>
</tbody>
</table>

### 3.3. Na$_2$SO$_4$ + 5 mol%Y$_2$(SO$_4$)$_3$ + m mol% Na$_2$WO$_4$ ($m=0, 5, 10, 15, 20$)

A literature survey [8] reveals that Na$_2$WO$_4$ has three phases from room temperature to its melting point of 697°C. The cubic spinel type phase $\gamma$ is stable up to 588°C, where it undergoes a phase transition. The $\beta$-phase is stable only over a degree or so and then a $\beta \rightarrow \alpha$ transition occurs. The $\beta$-phase is the best conducting phase, a conductivity of the order of $10^{-2}$ S·cm⁻¹ at 589°C being reported. The conductivity of Na$_2$WO$_4$ is less than Na$_2$SO$_4$ at lower temperatures suggesting higher activation enthalpy of formation and of migration of Na$^+$ ions in Na$_2$WO$_4$ than in Na$_2$SO$_4$. Na$_2$SO$_4$–Na$_2$WO$_4$ composites can be solid solutions or two phase mixtures, depending on the composition selected.

In the present study of the properties and conductivity behaviour of the Na$_2$SO$_4$ + 5 mol%
Y₂(SO₄)₃ + m mol% Na₂WO₄ (m = 0, 5, 10, 15, 20) system. XRD analysis yields similar diffraction pattern for different amounts of Na₂WO₄. The d values of the strong peaks reveal a small change compared to those of Na₂SO₄ + 5 mol% Y₂(SO₄)₃. This XRD pattern refers to a solid solution with Na₂SO₄-I structure, indicating that as few as 5 mol% Na₂WO₄ together with 5 mol% Y₂(SO₄)₃ can stabilize Na₂SO₄-I. However, there are one or two additional peaks which cannot be assigned to the structure I, but are related to the Na₂WO₄ pattern although surprisingly do not represent the strongest peaks of Na₂WO₄. These additional peaks suggest the presence of a minor amount of second phase of Na₂WO₄ in addition to the solid solution. However, DTA did not indicate any phase transition or melting peaks from the second phase. For instance, DTA indicated that the specimen with 5 mol% Na₂WO₄ is stable in the temperature range of 20°C to 875°C at which it melts. In addition, no inhomogeneous distribution of elements was observed by EDX, indicating a very small size of the second phase particles. Fig. 7a and b show the surface microstructure of the m = 10 specimen after calcining and after three times of sintering, respectively. It can be seen from fig. 7a that solid state reaction takes place during calcining.

Fig. 8 presents the Arrhenius plots of the temperature dependence of the ionic conductivity of these specimens. Table 3 lists the AH values as calculated form fig. 8, and fig. 9 gives the ionic conductivity isotherms. It can be seen that doping with Na₂WO₄ decreases the ionic conductivity of Na₂SO₄ + 5 mol% Y₂(SO₄)₃. However, the conductivity decrease is not very sensitive to the Na₂WO₄ concentration.

If we assume the presence of Na₂WO₄ as a second phase in addition to the Na₂SO₄ + 5 mol% Y₂(SO₄)₃-Na₂WO₄ solid solutions, and consider that the sodium ion conductivity of Na₂WO₄ is lower than that of Na₂SO₄, the conductivity decrease with Na₂WO₄ doping is reasonable. Another possible reason is that the dispersion of Na₂WO₄ in the Na₂SO₄ + 5 mol% Y₂(SO₄)₃ solid solution leads to the association of the point defects, thereby blocking the conduction pathways and decreasing the conductivity. However, the conductivities of the Na₂SO₄ + 5 mol% Y₂(SO₄)₃-Na₂WO₄ solid electrolytes are still higher than that of undoped Na₂SO₄ (compare tables 1 and 3).

From the point of view of practical application as a SO₃ sensor material, this Na₂SO₄ + 5 mol% Y₂(SO₄)₃ + Na₂WO₄ system is better than undoped Na₂SO₄ material because of the higher conductivity and better mechanical properties. Compared to Y₂(SO₄)₃ doped Na₂SO₄, the conductivities of the Na₂SO₄ + 5 mol% Y₂(SO₄)₃ + Na₂WO₄ solid electrolytes are lower, but the good mechanical properties make these materials practically applicable.

3.4. Na₂SO₄ + 4 mol% La₂(SO₄)₃ + n mol% Na₂WO₄ (n = 5, 10, 15, 20)

The Na₂SO₄ + 4 mol% La₂(SO₄)₃ + Na₂WO₄ system reveals the phases and structures which are similar to those of the Na₂SO₄ + 5 mol% Y₂(SO₄)₃ + Na₂WO₄ specimens as indicated by DTA and XRD analysis.
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Fig. 8. Temperature dependence of the ionic conductivity of the Na$_2$SO$_4$+5 mol% Y$_2$(SO$_4$)$_3$+m mol% Na$_2$WO$_4$ solid electrolytes.

Fig. 10. Temperature dependence of the ionic conductivity of the Na$_2$SO$_4$+4 mol% La$_2$(SO$_4$)$_3$+Na$_2$WO$_4$ solid electrolytes.

Table 3
Ionic conductivity and activation enthalpies of the Na$_2$SO$_4$+5 mol% Y$_2$(SO$_4$)$_3$+m mol% Na$_2$WO$_4$ solid electrolytes: log(\(\sigma T\)) = A/T + B, \(\Delta H = -2.303\ A\cdot R\) (eV)

<table>
<thead>
<tr>
<th>(m)</th>
<th>Temperature range (°C)</th>
<th>(A)</th>
<th>(B)</th>
<th>(\Delta H) (eV)</th>
<th>(\sigma(400°C)) (S/cm)</th>
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<td>20</td>
<td>100-700</td>
<td>-2902</td>
<td>3.67</td>
<td>0.57</td>
<td>2.19×10(^{-4})</td>
</tr>
</tbody>
</table>

Fig. 9. Ionic conductivity isotherms of the Na$_2$SO$_4$+5 mol% Y$_2$(SO$_4$)$_3$-Na$_2$WO$_4$ solid electrolytes as a function of the amount of Na$_2$WO$_4$.

Fig. 11. Ionic conductivity isotherms of the Na$_2$SO$_4$+4 mol% La$_2$(SO$_4$)$_3$-Na$_2$WO$_4$ specimens as a function of Na$_2$WO$_4$ concentrations.

Fig. 10 presents the Arrhenius plots of the temperature dependence of the ionic conductivity for the Na$_2$SO$_4$+4 mol% La$_2$(SO$_4$)$_3$+Na$_2$WO$_4$ specimens. Table 4 lists the \(\Delta H\) values as calculated from Fig. 10. Fig. 11 presents the ionic conductivity isotherms.

Although the ionic conductivity isotherms of the solid electrolytes Na$_2$SO$_4$+4 mol% La$_2$(SO$_4$)$_3$+Na$_2$WO$_4$ are similar to those in the Na$_2$SO$_4$+5 mol% Y$_2$(SO$_4$)$_3$+Na$_2$WO$_4$ system (compare Figs. 9 and 11), the Arrhenius plots of the two systems are quite
Table 4
Ionic conductivity and activation enthalpies of the Na$_2$SO$_4$ + 4 mol% La$_2$(SO$_4$)$_3$ + n mol% Na$_2$WO$_4$ solid electrolytes: log(σT) = A/T + B, ΔH = -2.3034·R (eV).

<table>
<thead>
<tr>
<th>n</th>
<th>Temperature range (°C)</th>
<th>A</th>
<th>B</th>
<th>ΔH</th>
<th>σ(400°C) (S·cm$^{-1}$)</th>
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Different (compare figs. 8 and 10, tables 3 and 4, respectively). In the Na$_2$SO$_4$ + 5 mol% Y$_2$(SO$_4$)$_3$ + Na$_2$WO$_4$ system, the Arrhenius plots reveal the same conductivity activation enthalpies in the temperature range of 300 to 670°C, while in the Na$_2$SO$_4$ + 4 mol% La$_2$(SO$_4$)$_3$ + Na$_2$WO$_4$ system, the conductivity activation enthalpies at higher temperatures are surprisingly higher than those at lower temperatures. XRD analysis indicated that doping Na$_2$SO$_4$–Ln$_2$(SO$_4$)$_3$ (Ln = Y, La) with Na$_2$WO$_4$ yields two phases, one being a Na$_2$SO$_4$–Ln$_2$(SO$_4$)$_3$–Na$_2$WO$_4$ solid solution with a Na$_2$SO$_4$–I-like structure, another being a minor amount of a second phase of Na$_2$WO$_4$. In the Na$_2$SO$_4$ + 5 mol% La$_2$(SO$_4$)$_3$ + Na$_2$WO$_4$ system, this second phase plays an important role in ionic conductivity. If we take into account the different ion conducting behaviour of the β- and γ-phases of Na$_2$WO$_4$, the unusual Arrhenius behaviour of the Na$_2$SO$_4$ + 4 mol% La$_2$(SO$_4$)$_3$ + Na$_2$WO$_4$ composites can be explained.

4. Conclusions

1. Y$_2$(SO$_4$)$_3$ and La$_2$(SO$_4$)$_3$ were prepared by a wet chemical method and used as dopants in Na$_2$SO$_4$ solid electrolyte. In the Na$_2$SO$_4$–Y$_2$(SO$_4$)$_3$ system, 12 mol% Y$_2$(SO$_4$)$_3$ can stabilize the Na$_2$SO$_4$–I phase down to room temperature, while the solid solution Na$_2$SO$_4$ + 5 mol% Y$_2$(SO$_4$)$_3$ exhibits the highest ionic conductivity (at 400°C, σ = 1.76×10$^{-2}$ S·cm$^{-1}$) and lowest activation enthalpy (0.38 eV).

2. In the Na$_2$SO$_4$–La$_2$(SO$_4$)$_3$ system 8 mol% La$_2$(SO$_4$)$_3$ can stabilize phase-I down to room temperature, while the Na$_2$SO$_4$ + 4 mol% La$_2$(SO$_4$)$_3$ solid solution has the highest ionic conductivity (at 400°C, σ = 2.95×10$^{-2}$ S·cm$^{-1}$) and lowest activation enthalpy (0.37 eV).

3. 5 to 20 mol% Na$_2$WO$_4$ with 5 mol% Y$_2$(SO$_4$)$_3$ or 4 mol% La$_2$(SO$_4$)$_3$ can stabilize the Na$_2$SO$_4$–I phase down to room temperature. The solid electrolytes contain a minor amount of a second phase of Na$_2$WO$_4$. Na$_2$WO$_4$ decreases the ionic conductivity of the Na$_2$SO$_4$–Ln$_2$(SO$_4$)$_3$ (Ln = Y, La) solid solutions, but the ionic conductivities of the Na$_2$SO$_4$–Ln$_2$(SO$_4$)$_3$–Na$_2$WO$_4$ solid electrolytes are still higher than that of undoped Na$_2$SO$_4$. The Na$_2$SO$_4$ + 5 mol% Y$_2$(SO$_4$)$_3$ (4 mol% La$_2$(SO$_4$)$_3$) + Na$_2$WO$_4$ specimens are more suitable for practical applications than undoped and Y$_2$(SO$_4$)$_3$/La$_2$(SO$_4$)$_3$ doped Na$_2$SO$_4$ materials because of their better mechanical properties.

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References