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Sulfur Dioxide Gas Detection Using a Na_2SO_4-$Y_2(SO_4)_3$-V_2O_5-SiO_2 Solid Electrolyte

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The title solid electrolyte was examined for the SO_2 detection. Vanadium pentoxide was mixed into the solid electrolyte for the purpose of replacement of Pt catalyst. The sulfate-based solid electrolyte contains Na_2SO_4-I phase which is effective for Na^+ ionic conduction and shows 5-9 times as high conductivity as pure Na_2SO_4. By constructing an SO_2 gas concentration cell with the use of $NiSO_4$-NiO as a reference electrode, the electrolyte can detect the SO_2 gas from 30ppm to 1% without the Pt catalyst.

Acid rain resulted from the absorption of exhausted sulfur oxides(SOx) and nitrogen oxides(NOx) has been seriously deteriorating the environment. The detection and the regulation of SOx and NOx in the exhausted gas are an urgent concern. Although instrumental analyses for SO_2, such as conductometric and absorptiometric methods, are utilized, the apparatuses are bulky and expensive. Furthermore, there are some problems in their response and selectivity. The SO_2 gas detection with a solid electrolyte such as alkali metal sulfates,[1-3] β-Alumina,[4] and NASICON[5] has been intensively investigated because of their rapid response, high selectivity, and low cost. In the electrolyte gas detection, platinum net has been applied so as to accelerate the oxidation from SO_2 in the detecting gas to SO_3. Platinum is, as is well known, considerably expensive.

In this study, vanadium pentoxide was mixed into sodium sulfate with yttrium sulfate and silicon dioxide in order to promote the SO_2 oxidation. Yttrium sulfate and silicon dioxide were mixed so as to enhance the electrical conductivi-

Table 1. The phases and thermal properties of Na_2SO_4-$Y_2(SO_4)_3$-V_2O_5-SiO_2

Na_2SO_4 mol%	$Y_2(SO_4)_3$ mol%	V_2O_5 mol%	SiO_2 mol%	Phases	DTA peaks °C
49	10	1	40	Na_2SO_4-I+Na_2SO_4-III +$Y_2Si_2O_7$+SiO_2	240 (small)
48	10	2	40	Na_2SO_4-I+Na_2SO_4-III +$Y_2Si_2O_7$+SiO_2	240 (small)

ty and to prevent the electrolyte from becoming ductile, respectively. An appropriate amount of sodium sulfate, yttrium sulfate, vanadium pentoxide, and silicon dioxide was mixed in an agate mortar. The mixture was heated at 1200 °C for 3 h in a platinum crucible and then quenched in an ice water. The product was ground and pelletized in a hydrostatic pressure at 2.65×10^8 Pa. The pellets were sintered at 750 °C for 1 h and then quenched in an ice water. The phases and thermal properties of Na_2SO_4-$Y_2(SO_4)_3$-V_2O_5-SiO_2 are tabulated in Table 1. All samples exhibit Na_2SO_4-I phase along with Na_2SO_4-III phase. This Na_2SO_4-I phase is a high temperature phase and excellent in Na^+ ionic conduction. Yttrium silicate ($Y_2Si_2O_7$) is also formed from a chemical reaction between Y_2O_3 and SiO_2. Furthermore, a starting material, SiO_2, still exists. From DTA measurements, every sample shows an endothermal peak at 240 °C. This temperature is consistent with the temperature for the III to I phase transition. The peak at 240 °C for the Na_2SO_4-Y_2-$(SO_4)_3$-V_2O_5-SiO_2 is appreciably small compared with that for pure Na_2SO_4. This is attributed to the fact that the Na_2SO_4-III phase considerably transformed to the Na_2SO_4-I

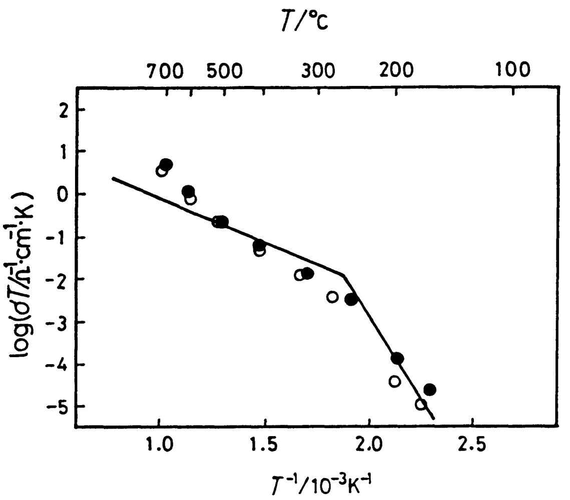

Fig. 1. Temperature dependence of electrical conductivity for Na_2SO_4-$Y_2(SO_4)_3$-V_2O_5-SiO_2 system.
Na_2SO_4-$Y_2(SO_4)_3$-V_2O_5-SiO_2
= 49 : 10 : 1 : 40 (○)
= 48 : 10 : 2 : 40 (●)
——— Na_2SO_4

phase. The result of the electrical conductivity measurements is presented in Fig. 1. The conductivity for the Na_2SO_4-$Y_2(SO_4)_3$-V_2O_5-SiO_2 system is not greatly different from that for the Na_2SO_4 system at temperatures lower than 500 °C. However, the σ value gradually increased at a higher temperature(>500 °C). At 700 °C, the conductivity for the Na_2SO_4-$Y_2(SO_4)_3$-V_2O_5-SiO_2 system is 5-9 times larger than that for Na_2SO_4. The σ of the sample mixed with 2 mol% V_2O_5 was 1.5 times as high as that with 1 mol% V_2O_5.

The electromotive force(EMF) measurements were performed with the apparatus illustrated in Fig. 2. The sulfate-based solid electrolyte was fixed between the detecting gas tube(A) and $NiSO_4$-NiO reference electrode. In our previous measurements,[1-3] platinum nets were inserted in the gas introducing tube (A) so as to improve the SO_2 gas oxidation. Platinum was also sputtered on both center surfaces of the electrolyte for the further

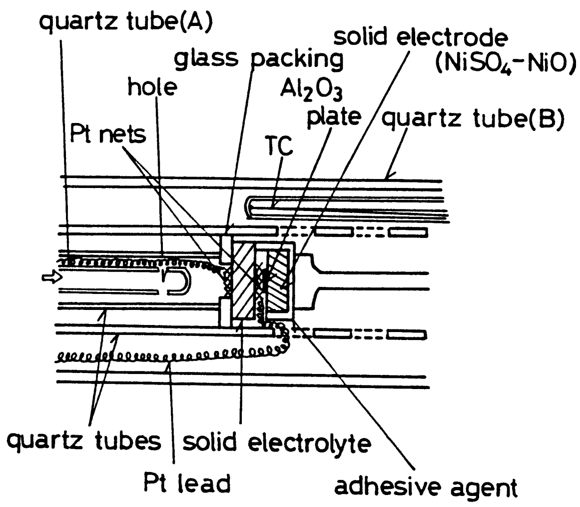

Fig. 2. The apparatus for the EMF measurement.

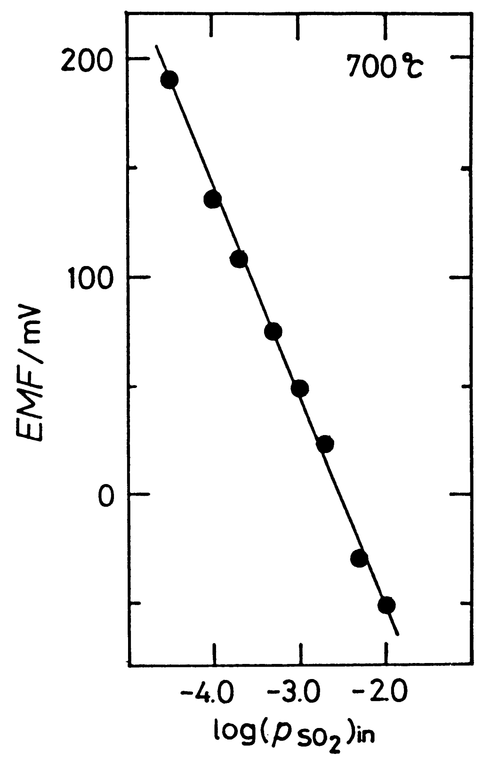

Fig. 3. The variation of the EMF for Na_2SO_4-$Y_2(SO_4)_3$-V_2O_5-SiO_2(48:10:2:40) solid electrolyte.

——— calculated EMF[3)]

oxidation. In this investigation, V_2O_5 was mixed into the solid electrolyte instead of the platinum utilization. The platinum net was eliminated from the tube(A). In addition, any platinum sputtering was not conducted. Figure 3 shows the EMF results for the Na_2SO_4-$Y_2(SO_4)_3$-V_2O_5-SiO_2. The gas concentration in the detecting gas was varied from 30ppm($\log(p_{SO_2})_{in}=-4.52$) to 1%($\log(p_{SO_2})_{in}=-2.0$). The measured EMF was in good agreement with the calculated EMF between 30ppm and 1%(the details of the EMF calculation are presented in our previous paper.[3]) This result is coincided with that for the Na_2SO_4-$Y_2(SO_4)_3$-SiO_2 system with a platinum catalyst.[1]

The sulfate-based solid electrolyte mixed with V_2O_5 but without platinum shows as good characteristics as the Na_2SO_4-$Y_2(SO_4)_3$-SiO_2 electrolyte with platinum.

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