CHEMISTRY LETTERS, pp. 287-288, 1983.

PROPERTIES OF Na_2SO_4 DOPED WITH $NaVO_3$ AND $Pr_2(SO_4)_3$ AS A SOLID ELECTROLYTE

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Sodium sulfate doped with both sodium vanadate and praseodymium sulfate has been investigated as solid electrolyte for SO_2 detecting device. Na_2SO_4-$NaVO_3$-$Pr_2(SO_4)_3$(91.1:3.9:5.0) shows higher electric conductivity than pure Na_2SO_4. The measured EMF for an SO_2 concentration cell using this electrolyte is in good accord with the calculated one. $NaVO_3$ stabilizes a high temperature phase, Na_2SO_4-I.

Recently, attempts have been made to use Na_2SO_4 as solid electrolyte for an SO_2 detector concentration cell.[1-3] Especially, a high temperature phase, Na_2SO_4-I, has been considered to be a good solid electrolyte. However, the sulfate is not an effective solid electrolyte because of the lack of sufficient electric conductivity, the existence of phase transformations, and the sluggishness of the SO_2-SO_3 equilibrium on the surface.

In the present study, $NaVO_3$ was doped in order to accelerate the attainment of the SO_2-SO_3 equilibrium, and $Pr_2(SO_4)_3$ was doped so as to increase electric conductivity. The phases and thermal properties were investigated by X-ray analysis and DTA measurement. The electric properties were examined by measuring electric conductivities and EMF for the concentration cell;

$$Pt|O_2(p_1'),\ SO_2(p_2')|\ \text{electrolyte}\ |O_2(p_1''),\ SO_2(p_2'')|Pt$$

where p_i' and p_i'' stand for the initial mole fractions of the components indicated.

Anhydrous Na_2SO_4, NH_4VO_3 and Na_2CO_3 were purchased from Wako Pure Chemical Industries Ltd.. $NaVO_3$ was prepared by heating the mixture of NH_4VO_3 and Na_2CO_3 (NH_4VO_3:Na_2CO_3=2:1 by molar ratio) for 5 h at 823 K. Praseodymium sulfate was produced by adding concd. sulfuric acid to Pr_6O_{11}. Appropriate amounts of Na_2SO_4, $NaVO_3$ and $Pr_2(SO_4)_3$ were weighed and then mixed. The mixture was made into pellets and heated for 3 h at 1073 K in air. The pellets were ground, remade into pellets and then sintered for 3 h at 1073 K in air. X-ray diffraction analyses were done with a Rigaku Rotaflex diffractometer with CuKα radiation. DTA measurements were performed by using a Rigaku's Thermoflex. Electric conductivities were measured with a Hewlett Packard vector impedance meter 4800A.

Phases and thermal properties of Na_2SO_4-$NaVO_3$-$Pr_2(SO_4)_3$ are summarized in Table 1. Phases α and β are analogous to a low temperature phase, Na_2SO_4-III, and a high temperature phase, Na_2SO_4-I, respectively, which were investigated by

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Table 1 Phases and Thermal Properties of the Na_2SO_4-$NaVO_3$-$Pr_2(SO_4)_3$

Sample NO.	Na_2SO_4 (mol%)	$NaVO_3$ (mol%)	$Pr_2(SO_4)_3$ (mol%)	phase	DTA peak (K)
1	98.0	1.0	1.0	α	493
2	96.0	2.0	2.0	α	413
3	94.4	2.6	3.0	β	———
4	92.8	3.2	4.0	β	———
5	91.1	3.9	5.0	β	583(very small)

DTA measurements were done from room temperature to 973 K

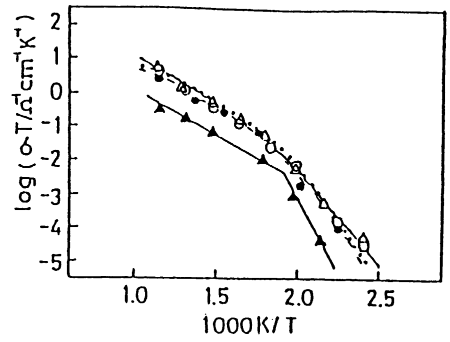

Figure 1 Temperature dependences of electric conductivities for the Na_2SO_4-$NaVO_3$-$Pr_2(SO_4)_3$

–●–●– $Na_2SO_4:NaVO_3:Pr_2(SO_4)_3$ = 94.4:2.6:3.0

·△··△· $Na_2SO_4:NaVO_3:Pr_2(SO_4)_3$ = 92.8:3.2:4.0

–○–○– $Na_2SO_4:NaVO_3:Pr_2(SO_4)_3$ = 91.1:3.9:5.0

–▲–▲– Na_2SO_4

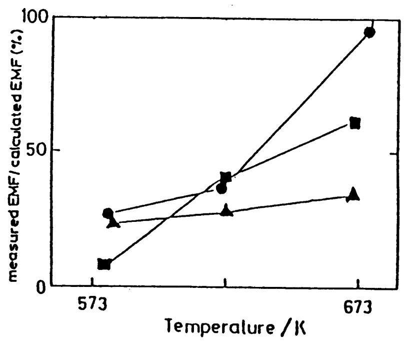

Figure 2 The ratio of measured EMF/calculated EMF for Na_2SO_4, Na_2SO_4-$Pr_2(SO_4)_3$ and Na_2SO_4-$NaVO_3$-$Pr_2(SO_4)_3$

–●–●– $Na_2SO_4:NaVO_3:Pr_2(SO_4)_3$ = 91.1:3.9:5.0

–■–■– $Na_2SO_4:Pr_2(SO_4)_3$ = 95.2:4.8

–▲–▲– Na_2SO_4

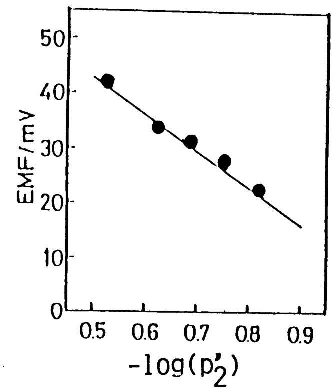

Figure 3 Variation of the EMF for the concentration cell; Pt|$O_2(p_1')$, $SO_2(p_2')$|Na_2SO_4(3.9 mol% $NaVO_3$, 5.0 mol% $Pr_2(SO_4)_3$)|$O_2(p_1'')$, $SO_2(p_2'')$|Pt with p_1''=0.93, p_2''=0.07 at 673 K

E. L. Kreidl and Ivan Simon[4] and Y. Saito et al.[5] The samples which exhibited the β phase showed no endothermal peak on their DTA curves, indicating that no phase transformation occurred. Sodium sulfate doped with 3.9 mol% $NaVO_3$ and 5.0 mol% $Pr_2(SO_4)_3$ (sample NO.5) exhibited a very small peak at 583 K. Log(σT) vs. 1/T curves of Na_2SO_4 doped with $NaVO_3$ and $Pr_2(SO_4)_3$ which exhibited the β phase are shown in Figure 1. No snap of line on these three curves means that no phase transformation has occurred. The sample NO.5 exhibited the highest electric conductivity and its log(σT) vs. 1/T plot is the most linear among the three samples. The Na_2SO_4-$NaVO_3$-$Pr_2(SO_4)_3$ of this composition is considered to be of the best performance as solid electrolyte. The ratio of the measured EMF to calculated EMF at a given gas composition for the samples of Na_2SO_4, Na_2SO_4-$Pr_2(SO_4)_3$ and Na_2SO_4-$NaVO_3$-$Pr_2(SO_4)_3$ are shown in Figure 2 as a function of temperature, the initial mole fractions of SO_2 for the higher SO_2-content side and the lower SO_2-content side in the cell being about 0.24 and 0.08, respectively. The Na_2SO_4-$NaVO_3$-$Pr_2(SO_4)_3$(91.1:3.9:5.0) at 673 K gave an EMF almost the same as the calculated one。 The EMF response to the gas compositions of the sample NO.5 is shown in Figure 3, where p_i' and p_i'' are abbreviations of the initial mole fractions. The solid line indicates the calculated EMF.[3]

The Na_2SO_4 doped with 3.9 mol% $NaVO_3$ and 5.0 mol% $Pr_2(SO_4)_3$ is proved to be a very effective solid electrolyte for an SO_2 detector concentration cell even at a temperature as low as 673 K.

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(Received November 22, 1982)