The Electrical Properties of Calcium Sulfide Doped with Lanthanum Sulfide and Zirconium Sulfide

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Calcium sulfides doped with tri- and tetravalent metal sulfides were prepared. Their electromotive forces (EMF) were measured on a galvanic cell(Fe+FeS| Solid Electrolyte| Cu+Cu_2S) where the solid electrolyte was a material in a CaS-Ln_2S_3-MS_2 system. The cell, using calcium sulfide doped with La_2S_3 and ZrS_2, exhibited an EMF value as high as the one calculated for thermodynamical equilibrium. The CaS-La_2S_3-ZrS_2 solid electrolyte showed, predominantly, an ionic conduction in the sulfur pressure range from 10^{-4} to 10^2 Pa with an activation energy of approximately 56.7 kJ·mol^{-1}, which was lower than for CaS and CaS-La_2S_3.

Galvanic cell techniques, applying CaO-stabilized zirconia[1,2] and calcium fluoride,[3–7], had been investigated to determine the chemical potentials of sulfur at elevated temperatures. When ZrO_2(CaO) was used as the electrolyte, a metal oxide was formed at the interface of the metal sulfide electrode and the electrolyte, according to the following equilibrium equation:

$$MS(s) + 3/2O_2(g) = MO(s) + SO_2(g)$$

It is necessary that the resulting metal oxide is insoluble in the metal sulfide electrode. When CaF_2 was used as the electrolyte, on the other hand, the sulfur chemical potential was first converted to a calcium chemical potential and then to a fluorine chemical potential, where F^- anions were mobile species in the CaF_2 solid electrolyte. Therefore, the electromotive force(EMF) became less accurate because of the double chemical potential conversion.

Recently, calcium sulfide[8–10] has been found to be a Ca^{2+} ionic conductor at elevated temperatures. Otowa *et al.*[9] measured the isotope tracer diffusion coefficients of sulfur and proved that the electric charge carrier in the ionic-conductive calcium sulfide is predominantly the Ca^{2+} ions. Attempts[11–16] have been concentrated on applying calcium sulfide to a solid electrolyte in order to determine the sulfur chemical potentials. However, calcium sulfide holds several disadvantages. One is its lower electrical conductivity. The other is the presence of a region where electronic conduction cannot be ignored. The doping of a tri-, or tetravalent ion into calcium sulfide[12–16] has been carried out in order to improve its electrical properties.

In this study, tri- and tetravalent metal sulfides were doped into calcium sulfide so as to increase the Ca^{2+} ion vacancies and to obtain a larger sulfur pressure independent region. EMF measurements were conducted by constructing a galvanic cell (Fe+FeS and Cu+Cu_2S as electrodes) for the purpose of examing the possibilities of the calcium sulfide doped with metal sulfides as an electrolyte. The sulfur pressure dependency on the electrical conductivity were also investigated on a sample with the most promising properties.

Experimental

Materials. Calcium sulfate dihydrate ($CaSO_4 \cdot 2H_2O$; impurity, Chloride: max. 0.003%, Nitrate: max. 0.005%, Heavy metals: 0.001%, Copper: 0.0005%, Lead: 0.0005%, Arsenic: 0.0001%, Iron: 0.001%) was purchased from Wako Pure Chemical Indusries Ltd.. Lanthanum (purity: 99.9%) and yttrium (purity: 99.9%) oxides were secured from Shinetsu Chemical Co. Ltd.. Zirconium (purity: 97%), titanium (purity: 99.5%) and neobium (purity: 99.9%), and wolfram (purity 99.9%) metals were bought from Mitsuwa's Pure Chemicals, and Wako Pure Chemical Industries Ltd., respectively. FeS (Practical Grade) and Cu_2S (purity: 99.99%) were purchased from Wako Pure Chemical Industries Ltd. and Mitsuwa's Pure Chemicals, respectively. Pure calcium sulfide was prepared by heating $CaSO_4 \cdot 2H_2O$ in a carbon boat at 973 K for 2 h and then at 1273 K for 5 h under a flowing gas atmosphere of hydrogen sulfide (purity: 99%). Lanthanum and yttrium chloride were prepared by adding a diluted hydrochloric acid aqueous solution to La_2O_3 and Y_2O_3, respectively. Ln_2S_3 (Ln=La and Y) were obtained by heating $LnCl_3$ (Ln=La and Y) in a carbon boat at 673 K for 2 h in an argon gas flowing atmosphere and then at 1273 K for 5 h in an H_2S gas flow. Metal sulfides (M=Zr, Ti, W, and Nb) were prepared by heating a mixture of the metal and sulfur in an evacuated quartz capsule at 773 K for 2 h and at 1273 K for 5 h. The CaS, Ln_2S_3 (Ln=La and Y), and MS_2 (M=Zr, Ti, W, and Nb) was thoroughly mixed in an agate mortar. The cation ratio in the CaS-Ln_2S_3-MS_2 system was 96:2:2 for Ca^{2+}, Ln^{3+}, and M^{4+}, respectively. The mixture was made into pellets with a pressure of 6.7×10^8 Pa. Sintering of the pellets was performed for 4 h at 1273 K in a flow of hydrogen sulfide gas. The samples were analysed using an X-ray diffraction apparatus (Rigaku's Rotaflex diffractometer with Cu $K\alpha$ radiation). The preparation of the electrodes (Fe+FeS and Cu+Cu_2S) was also conducted by sintering the pellets of the metal and metal sulfide (50:50 by molecular weight) for 3 h at 773 K in an argon gas-flow atmosphere.

Measurements. The apparatus for the EMF measurements (galvanic cell technique) is illustrated in Fig. 1. A good contact between the electrolyte and the electrodes was assured by pushing the quartz rod B to the quartz tube A with springs. The electrical conductivity was also measured with the apparatus shown in Fig. 1. In the conductivity measurements, a gold film was deposited on both surfaces of the sample with Shinku Kiko's vacuum-deposition apparatus (ULVAC, VP-C2A) so as to reduce the resistance between the sample and the platinum plate electrodes. The electrical conductivity was measured with a Hewlett Packard vector impedance meter 4800A (from 5 Hz to 500 kHz). The sulfur pressure was controlled by the regulation of the hy-

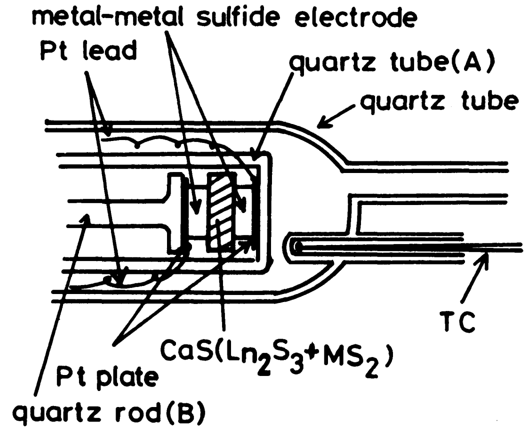

Fig. 1. The apparatus for the EMF and the electrical conductivity measurements.

Table 1. The properties of $CaS-Ln_2S_3-MS_2$ solid electrolytes

composition (Ca^{2+}:Ln^{3+}:M^{4+} =96:2:2)	EMF/mV[1)]	invasion of Cu^+	Average ionic radius of dopants[2)]/nm
$CaS-La_2S_3-ZrS_2$	40	No	0.102
$CaS-La_2S_3-TiS_2$	40	Yes	0.096
$CaS-La_2S_3-WS_2$	0	Yes	0.099
$CaS-La_2S_3-NbS_2$	0	Yes	0.100
$CaS-Y_2S_3-ZrS_2$	40	Yes	0.095
$CaS-Y_2S_3-TiS_2$	11	No	0.089

1) Measured at 973 K. 2) Ca^{2+}(0.114 nm), La^{3+} (0.117 nm), Y^{3+}(0.104 nm), Zr^{4+}(0.086 nm), Ti^{4+} (0.0745 nm), W^{4+}(0.080 nm), Nb^{4+}(0.082 nm). These ionic radii are cited from the reference.[17)]

drogen and hydrogen sulfide gas-flow volumes by flow meters. A noninductive resistance furnace was used in order to avoid any noise in both the EMF and conductivity measurements.

Results and Discussion

By X-ray diffraction analysis, samples of $CaS-Ln_2S_3$ (Ln=La and Y)-MS_2 (M=Zr, Ti, W, and Nb) were found to form solid solution. The properties of these solutions are summarized in Table 1. The invasion of the Cu^+ ion from the $Cu-Cu_2S$ electrode into the solid electrolyte occurred in samples of $CaS-La_2S_3-MS_2$ (M =Ti, W, and Nb) and $CaS-Y_2S_3-ZrS_2$. When the $CaS-Y_2S_3-TiS_2$ sample was employed as a solid electrolyte, the measured EMF was considerably lower than the calculated EMF at 973 K, which is derived from the Gibbs free energy data of Oishi *et al.*[4)] and Brooks.[18)] On the other hand, the cell with calcium sulfide doped with La_2S_3 and ZrS_2 exhibited an EMF as high as the calculated value. In addition, the Cu^+ ion invasion from the electrode disappeared. For the $CaS-La_2S_3-ZrS_2$ electrolyte, the average ionic radius of the dopants was 0.102 nm,[17)] which is the closest to the ionic radius of Ca^{2+} (0.114 nm)[17)] for the three component systems.

A good candidate for a solid electrolyte in the three component systems is considered to be the $CaS-La_2S_3-ZrS_2$ system.

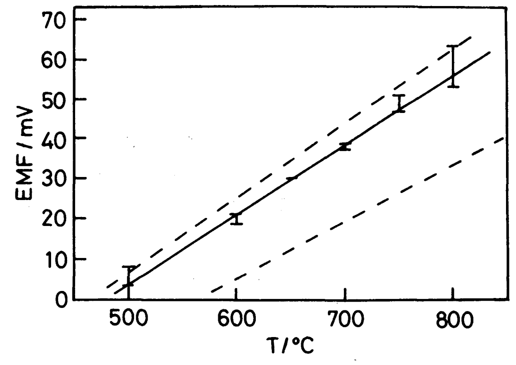

Fig. 2. The temperature dependences of the EMF for Fe+FeS|CaS(2 atom% La_2S_3 and 2 atom% ZrS_2)| $Cu+Cu_2S$ cell.
The maximum and minimum EMF (---) are calculated from the Gibbs free energy data of Oishi *et al.*[4)] and Brooks,[18)] and Alcock and Richardson[19)] and Nagamori,[20)] respectively.

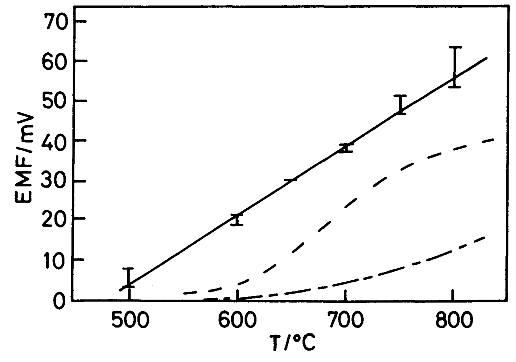

Fig. 3. The temperature dependences of the EMF for Fe+FeS|Solid electrolyte|$Cu+Cu_2S$ cell.
——: CaS(2 atom% La_2S_3 and 2 atom% ZrS_2), – – –: CaS(5 atom% La_2S_3), ––––: CaS.

The EMF results for the $CaS-La_2S_3-ZrS_2$ electrolyte are presented in Fig. 2. The maximum and minimum EMF were calculated from the Gibbs free energy data of Oishi *et al.*[4)] and Brooks,[18)] and Alcock and Richardson[19)], and Nagamori,[20)] respectively. The measured EMF shows itself in well within the calculated EMF range.

A comparison of the EMF results for cells using CaS, $CaS-La_2S_3$,[15)] and $CaS-La_2S_3-ZrS_2$ systems is shown in Fig. 3. The calcium sulfide in which La_2S_3 was held in a solid solution, exhibited a higher EMF compared with the calcium sulfide alone. This was attributed to the formation of cation vacancies during doping. In the $CaS-La_2S_3-ZrS_2$ system, the EMF properties were appreciably improved in comparison with both CaS and $CaS-La_2S_3$.

The sulfur pressure dependency of the electrical conductivity is illustrated in Fig. 4. The conductivities are independent of the sulfur pressure variation for all samples measured at 700, 800, and 900 °C. This result indicates that electrical conduction is predominantly ionic in an $CaS-La_2S_3-ZrS_2$ system. In a previous work,[11)] it was reported that calcium sulfide exhibits a

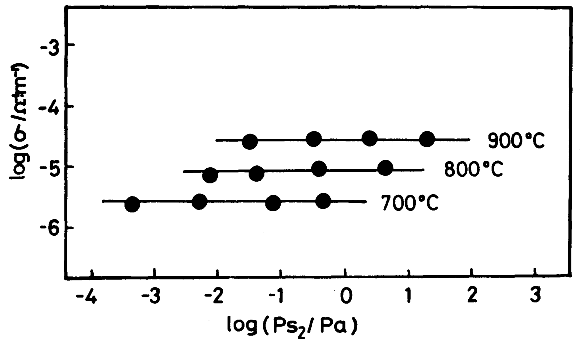

Fig. 4. The variation of the electrical conductivity of CaS(2 atom% La_2S_3 and 2 atom% ZrS_2) with sulfur pressure at 700, 800, and 900 °C.

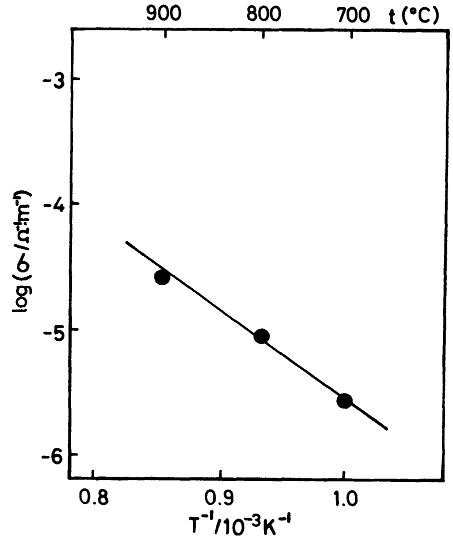

Fig 5. The temperature dependences of the electrical conductivity for CaS(2 atom% La_2S_3 and 2 atom% ZrS_2) under an atmosphere of $H_2/H_2S=1.5/1$.

P-type conduction at log P_{S_2} higher than approximately −6. In our earier paper,[15] electronic conduction was found to appear in the CaS-La_2S_3 system, at log P_{S_2} lower than about −5.5. By doping La_2S_3 and ZrS_2 simultaneously into CaS, the ionic conduction becomes dominant. The electronic conduction seems to be negligibly small compared with the ionic conduction due to the Ca^{2+} migration.

The temperature dependences of the log σ are shown in Fig. 5. From the slope of the line, the activation energy for the CaS-La_2S_3-ZrS_2 system was calculated to be 56.7 kJ·mol^{-1}. This value is smaller than both 99.6 kJ·mol^{-1}[11] for CaS, and 79.9 kJ·mol^{-1}[15] for CaS-La_2S_3.

The migration of a Ca^{2+} ion from a cation site to a cation vacancy becomes easier after increasing the number of cation vacancies.

In conclusion, the EMF characteristics of CaS with Cu+Cu_2S and Fe+FeS electrodes are remarkably improved by the doping of La_2S_3 and ZrS_2 simultaneously into the host CaS. The conduction mechanism of the CaS-La_2S_3-ZrS_2 solid solution is predominantly ionic. The CaS-La_2S_3-ZrS_2 system has the potential of being utilized as a solid electrolyte for a galvanic cell over a large range of sulfur pressures (10^{-4} to 10^2 Pa).

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