Performance of SrCeO₃-Type Hydrogen and Steam Sensors Using AlPO₄·xH₂O as a Solid Standard

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Galvanic cell type high temperature steam and/or hydrogen sensors were constructed using SrCe_{0.05}Yb_{0.95}O_{3-α} ceramic as a solid electrolyte and AlPO₄·xH₂O-LaCoO₃ mixture as a solid standard material. These sensors showed stable and reproducible emfs corresponding to partial pressure of steam and hydrogen. The relation between emf and logarithm of steam or hydrogen was linear.

1 INTRODUCTION

As reported earlier, some sintered oxides based on SrCeO₃ and BaCeO₃ exhibit appreciably high proton conduction in hydrogen containing atmosphere at high temperature^{1,2)}. Using this class of proton conductor as a solid electrolyte, it is possible to construct galvanic cell type hydrogen or steam sensors which work at high temperature³⁻⁵⁾. These sensors are based on the principle of an electrochemical gas concentration cell (hydrogen or steam concentration cell) and, in general, the sensor needs a standard gas in which the partial pressure of hydrogen or steam is known and constant at a given temperature.

It is practically inconvenient to use a standard gas for this type of sensors. In stead of gaseous standard, it is desirable to use solid one which keeps an appreciable amount of water and shows constant equilibrium pressure of water vapor at high temperature. Although molecular sieve⁶⁾, hydroxyapatite⁷⁾ and other hydrated inorganic salts⁸⁾ have been tried as such materials and they acted as a solid standard, long time

stability and reproducibility were somewhat insufficient for practical use.

In this study, we found that AlPO₄·xH₂O-LaCoO₃ mixture showed better performance as a solid standard material. Using this, two types of steam and hydrogen sensors were constructed and their sensing performances were examined. These sensors exhibited a stable and very fast response.

2 EXPERIMENTAL

Solid electrolytes for the sensor, crucible-shaped or one-end-closed tube-shaped ceramics of SrCe_{0.95}Yb_{0.05}O_{3-α} were used. The relative densities of the ceramics were more than 96%. AlPO₄·xH₂O made by Yoneyama Kagaku Corporation was used as a standard material. The ignition loss of this material was 4.5% in weight, which corresponded to x=0.34. It was necessary for good sensor performance to add some electronic conductor to the standard material. As such as additive, La_{0.4}Sr_{0.6}CoO_{3-δ} was the most effective. This oxide was prepared by calcining the mixture of La₂O₃, SrCO₃ and Co₂O₃ at 1200°C in air.

Two types of sensing cells as shown in Fig. 1 were fabricated. A-type sensor has a crucible shaped ceramic electrolyte in which a standard material is packed. B-type sensor has an one-end-closed tube shaped ceramic electrolyte which is

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covered with an alumina sleeve, and a standard material was packed between the electrolyte and the alumina sleeve. The sensing performances of these sensors were examined in various condition at elevated temperatures. In case of steam sensor, the partial pressure of water vapor in the sample gas was controlled by saturating the water vapor at a given temperature in an accuracy of $\pm 1^\circ\text{C}$. Hydrogen partial pressure was controlled by mixing hydrogen gas with

Fig. 1 Schematic illustration of A type and B type sensors for steam and hydrogen.

Fig. 2 The performance of A type steam sensor using $\text{AlPO}_4 \cdot x\text{H}_2\text{O}$ as a solid standard at 700°C .

argon gas in an appropriate ratio. The concentration of hydrogen in the mixed gas was determined by gas chromatograph.

3 RESULTS AND DISCUSSION

3.1 Performance of A-type sensor

A-type sensor with pure $\text{AlPO}_4 \cdot x\text{H}_2\text{O}$ as a solid standard showed unstable electromotive force (emf). As shown in Fig. 2, the dependence of emf on $\log P_{\text{H}_2\text{O}}$ is not linear and the sensitivity expressed as the slope of emf vs. $\log P_{\text{H}_2\text{O}}$ curve is considerably low. The internal resistance of this sensor was quite high. In order to lower the internal resistance, the powder of $\text{La}_{0.4}\text{Sr}_{0.6}\text{CoO}_{3-\delta}$ which was good electronic conductor was added to $\text{AlPO}_4 \cdot x\text{H}_2\text{O}$. For the good stability a considerably large amount of electronic conductor was required; the optimum ratio of $\text{AlPO}_4 \cdot x\text{H}_2\text{O}$ to $\text{La}_{0.4}\text{Sr}_{0.6}\text{CoO}_{3-\delta}$ was 1:9 in weight. The performance of A-type humidity sensor thus fabricated was shown in Fig. 3. The sensor showed a good and linear response against the logarithm of steam partial pressure. The sensitivity (i.e. the slope of emf vs. $\log P_{\text{H}_2\text{O}}$ curve) was higher than that of Fig. 2, although it was somewhat smaller than the theoretical value ($= 2.303RT/2F$) probably because of the contribution of p-type electronic conduction which appeared in $\text{SrCe}_{0.95}\text{Yb}_{0.05}\text{O}_{3-\alpha}$ at high partial pressure of oxygen^{1,9}. The performance and stability of A-type sensor could be considerably improved by adding $\text{La}_{0.4}\text{Sr}_{0.6}\text{CoO}_{3-\delta}$ to $\text{AlPO}_4 \cdot x\text{H}_2\text{O}$.

Fig. 3 Characteristics of A type steam sensor using a solid state standard material at 700°C .

Solid state standard material; $\text{AlPO}_4 \cdot x\text{H}_2\text{O}$: $\text{La}_{0.4}\text{Sr}_{0.6}\text{CoO}_{3-\delta}$ = 1:9 in weight.

The solid standard materials for a galvanic cell type hydrogen and/or steam sensor are required to have water molecules which can be released or absorbed reversibly with the change of vapor pressure in gas phase at high temperature. In order to clarify the phenomena of water absorption and evolution, the change in sample weight was measured by thermobalance at 700°C when the gas around the specimen was changed from wet to dry and from dry to wet. Figure 4 showed the mass change of $\text{AlPO}_4 \cdot x\text{H}_2\text{O}$ - LaCoO_3 mixture. The weight of this mixture decreased on making gas dry and increased on making gas wet. From these results it is clear that $\text{AlPO}_4 \cdot x\text{H}_2\text{O}$ - LaCoO_3 mixture can absorb and release water vapor depending on the change in partial pressure of water vapor in the atmosphere.

In order to examine the constancy of $P_{\text{H}_2\text{O}}$ of standard electrode, electrode potential at the standard material was measured by using reference electrode attached to the brim of the ceramic crucible as shown in Fig. 1 A. Figure 5 shows the result. The potential of standard electrode was almost independent of $P_{\text{H}_2\text{O}}$ in the test gas, whereas the emf of the sensor (i.e. potential difference between standard electrode and test electrode) changed linearly with logarithm of $P_{\text{H}_2\text{O}}$ in the test gas. This result means that the $\text{AlPO}_4 \cdot x\text{H}_2\text{O}$ - LaCoO_3 mixture keeps the steam partial pressure constant in the cathode compartment and the $\text{AlPO}_4 \cdot x\text{H}_2\text{O}$ - LaCoO_3 mixture works as a

Fig. 4 The changing in weight of $\text{AlPO}_4 \cdot x\text{H}_2\text{O}$ - LaCoO_3 (=1:9) mixture on changing water vapor pressure in the atmosphere at 700°C.

Dry air: dried with silica gel.

Wet air: saturated the water vapor at 23°C.

Fig. 5 The steam pressure dependence of emfs between anode and cathode and potentials between cathode and reference electrode at 700°C.

standard material.

3.2 Performance of B-type sensor

Figure 6 represents the performance of B-type steam sensor at 700°C. The emf observed was stable and linearly increased with increase in the logarithm of steam partial pressure. The emf of B-type sensor was 10 mV lower than that of A-type sensor. This phenomenon can be explained by considering the temperature gradient in the electrode compartment which contains the standard material. As shown Fig. 1 B, this compartment is rather long in its size, and has temperature gradient of about 400°C across the both ends of the compartment. Therefore the average temperature in the compartment is considerably low compared with that of A-type sensor. In this case, the steam partial pressure in the standard compartment of B-type sensor was higher than that of A-type sensor.

Fig. 6 Performance of B type steam sensor at 700°C.

We examined the response speed of B-type sensor by measuring the variation of emf with time on changing steam partial pressure in the sample gas abruptly from 25.4 to 4.6 Torr or in reverse direction. Results are shown in Fig. 7. The time required to reach 90% of final value was within 10sec in the case of moistening (from 4.6 to 25.4 Torr.), and it took about 30sec in the case of reverse direction (from 25.4 to 4.6 Torr.). In the latter case, a considerable period might be necessary to dry inner wall of gas line and the response time of cell itself was considered to be as rapid as in the case of moistening.

Fig. 7 Response speed of B type steam sensor at 700°C. Flow rate = 60 ml min⁻¹.

Fig. 8 Characteristics of B type hydrogen sensor at 700°C.

3.4 Hydrogen sensing performance of B-type sensor

We tried to use B-type sensor as a hydrogen gas sensor at high temperature. In this case, hydrogen partial pressure in the standard compartment is determined by a small but constant hydrogen partial pressure equilibrated with H₂O and O₂ in the standard electrode compartment at elevated temperature. Results

are shown in Fig. 8. The sensor worked very stably and the relation between emf and log P_{H₂} was linear over the three orders of hydrogen pressure. Their reproducibilities was reasonably good. From these results it is clear that AlPO₄·xH₂O-LaCoO₃ mixture functions as a standard material for hydrogen sensor as well as steam sensor at elevated temperatures.

Based on the present study, we are now developing the portable type hydrogen and steam sensor for commercialization.

4 CONCLUSION

AlPO₄·xH₂O-LaCoO₃ mixture works as a solid standard material for galvanic cell type steam sensor and hydrogen sensor at high temperatures. Using this solid standard material, the sensor device became simple in its structure and small in its size.

High temperature type steam sensor which has AlPO₄·xH₂O-LaCoO₃ mixture as a solid standard material could be constructed. This type of sensors exhibit fast response, good reproducibility, and linear response against logarithm of steam partial pressure.

This device can also be used as a high temperature hydrogen sensor. This type of sensor has wide dynamic range and good sensitivity compared with these of steam sensor.

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