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A new type of bromide anion conducting solid

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A new type of bromide anion conducting solid electrolyte was designed with the solid electrolyte based on oxybromide; the oxybromide lends unique characteristics of thermal stability and water insolubility (5.6 mg in 100 g of water at 25 °C) to the electrolyte which shows the highest Br^- anion conductivity reported above 500 °C.

While bromine is useful for the production of medical and photonic materials and in the dye industry, it is highly toxic. Some semiconductor sensing devices[1,2] have been proposed for bromine detection in these processes but, to date, they have shown unsatisfactory selectivity. In contrast, solid electrolytes are unique materials in which single ion species can migrate inside the solids; a feature which could be a great advantage for specific gas selective sensing. In addition, since the sensor component can be fabricated in an all-solid state, a compact, maintenance-free, and inexpensive sensing tool could be realized.

Conventional, bromide anion conductors, $PbBr_2$[3,4] and $CsPbBr_3$[5] have been reported to be excellent solid electrolytes, showing high Br^- anion conductivities of 5.6×10^{-4} (at 250 °C) and 7.8×10^{-4} S cm^{-1} (at 500 °C). However, the critical disadvantage of these reported solid electrolytes is the water-soluble nature of the bromide-based solids and this demerit greatly restricts their practical applications.

In this communication, a bromide anion conducting solid electrolyte which possesses both the characteristics of high Br^- anion conductivity and water insolubility is successfully obtained. Since most bromides are water soluble, they are not practically applicable. Whilst seeking a new type of bromide anion conductor, which has a unique water insoluble character, we focused on the oxybromide series. Among the oxybromides, rare earth oxybromides have the merit of being stable even at elevated temperature with accompanying water insolubility. Herein, we study lanthanum oxybromide† which shows the highest thermal stability (as high as around 900 °C) in the rare earth oxybromide series.[6]

Fig. 1 presents the X-ray powder diffraction results for the $(La_{1-x}Sr_x)OBr_{1-x}$ solid solution with the data for pure LaOBr. From the figure, it is found that the X-ray peaks shift to lower angles, indicating that the La site (ionic radius 0.130 nm[7]) in $(La_{1-x}Sr_x)OBr_{1-x}$ was partially substituted with the larger Sr cation (ionic radius 0.140 nm[7]). The inset depicts Sr content variation of the $(La_{1-x}Sr_x)OBr_{1-x}$ lattice volume. The lattice volume increases monotonously with the replacement of Sr ion, and the volume becomes constant at Sr concentrations higher than $x = 0.1$. The result explicitly indicates the fact that the solid solution limit estimated from Fig. 1 is at around 10 at% Sr replacement of the La site in $La_{1-x}Sr_xOBr_{1-x}$.

The x dependencies of the conductivity for the $La_{1-x}Sr_xOBr_{1-x}$ series at 600 °C are shown in Fig. 2. By substituting $x = 0.05$ in $La_{1-x}Sr_xOBr_{1-x}$, the conductivity is enhanced more than 50 times due to anion vacancy formation by the divalent Sr^{2+} ion substitution on a trivalent La^{3+} site. The highest conductivity of 1.9×10^{-3} S cm^{-1} was obtained at an Sr content of $x = 0.1$. Further La site replacement for Sr^{2+} results in a decrease in conductivity due to the formation of secondary insulating La_2O_3 as presented in Fig. 1.

The conductivity of the $La_{0.9}Sr_{0.1}OBr_{0.9}$ solid solution does not change with variation of the oxygen pressure between 10^2 and 10^5 Pa, suggesting that the migrating species in the solid is neither an electron nor a hole, but an ionic species, as demonstrated in our previous paper.[8] For the purpose of identifying the conducting ion species in the $La_{0.9}Sr_{0.1}OBr_{0.9}$ solid, two electrolysis experiments were carried out as illus-

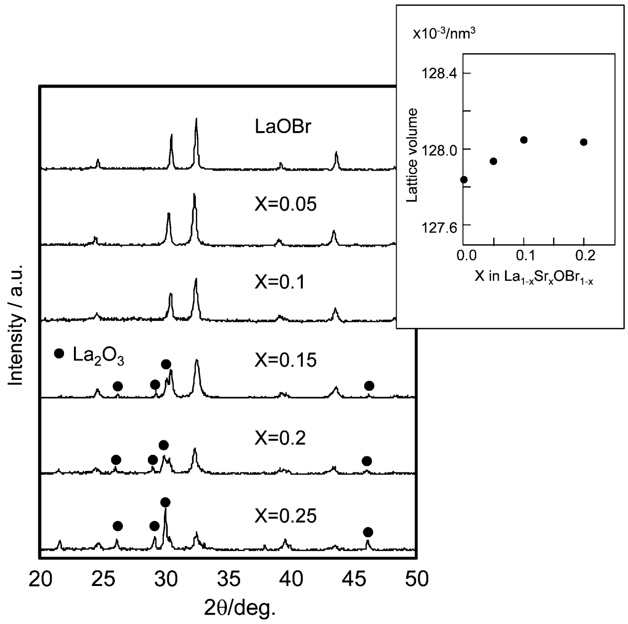

Fig. 1 X-Ray powder diffraction analysis results for the $(La_{1-x}Sr_x)OBr_{1-x}$ solid solution with the data for pure LaOBr. (Inset) Sr content variation of the $(La_{1-x}Sr_x)OBr_{1-x}$ lattice volume.

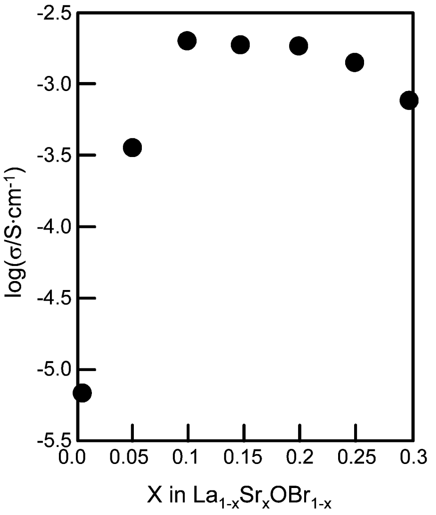

Fig. 2 The x dependencies of the conductivity for the $La_{1-x}Sr_xOBr_{1-x}$ series at 600 °C.

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trated in Fig. 3(a) and (b). In Fig. 3(a), La_2O_3 and $La_{0.9}Sr_{0.1}OBr_{0.9}$ pellets were located at the anode and cathode sides, respectively. In contrast, in Fig. 3(b), the two pellets were set in the reverse direction. After the dc electrolyses, a clear difference was observed. From the EPMA line analysis results depicted in Fig. 3(a), Br migration into the La_2O_3 pellet was clearly recognized as highlighted by a dotted circle near the cathodic surface of La_2O_3, while no such phenomenon was observed in the case of the electrolyzed La_2O_3 pellets as shown in Fig. 3(b). In the case of Fig. 3(b), the Br^- anion migrates only in the $La_{0.9}Sr_{0.1}OBr_{0.9}$ solid and a Br deficient layer was observed, depicted as a broken circle in Fig. 3(b) (the intensity of Br, except for near the cathodic side of $La_{0.9}Sr_{0.1}OBr_{0.9}$ solid, is equal to that of the solid before electrolysis). If the migrating ion species was O^{2-}, the Br^- deficient layer would not appear near the cathodic side of the $La_{0.9}Sr_{0.1}OBr_{0.9}$ pellet which suggests that O^{2-} is not the migrating ion species in $La_{0.9}Sr_{0.1}OBr_{0.9}$. In addition, the considerable high polarization behavior was observed in both oxygen and helium atmospheres, suggesting that oxide anion conduction did not occur and the predominant migrating species is only ions and not electrons in $La_{0.9}Sr_{0.1}OBr_{0.9}$ as similarly demonstrated in ref. 8. From these results, it is clear that the conducting Br^- anion reaches the interface between the two pellets and reacts with La_2O_3 to form LaOBr. Therefore, it is concluded that the conducting species is Br^- anion in the $La_{0.9}Sr_{0.1}OBr_{0.9}$ solid. Compared with the typical Br^- anion conducting bromides, the present $La_{0.9}Sr_{0.1}OBr_{0.9}$ solid electrolyte possesses an extremely low water solubility (5.6 mg in 100 g of water at 25 °C), and high thermal stability (as high as 900 °C), which appreciably exceeds the melting temperatures of representative Br^- anion conducting solids such as $CsPbBr_3$ (*ca.* 500 °C) and $PbBr_2$ (*ca.* 370 °C).

Fig. 4 depicts the temperature dependencies of the Br^- anion conductivity of the present $La_{0.9}Sr_{0.1}OBr_{0.9}$ solid solution electrolyte with the data of pure LaOBr and typical Br^- ion conducting solid electrolytes of $PbBr_2$[4] and $CsPbBr_3$.[5] The present $La_{0.9}Sr_{0.1}OBr_{0.9}$ solid electrolyte shows a high Br^- anion conductivity of 4.2×10^{-3} S cm^{-1} at 750 °C, which lies in the superionic conductor region (> 10^{-3} S cm^{-1}, shaded area in Fig. 4), while the highest Br^- anion conductivities of $CsPbBr_3$ and $PbBr_2$ are still below this region due to their low melting points.

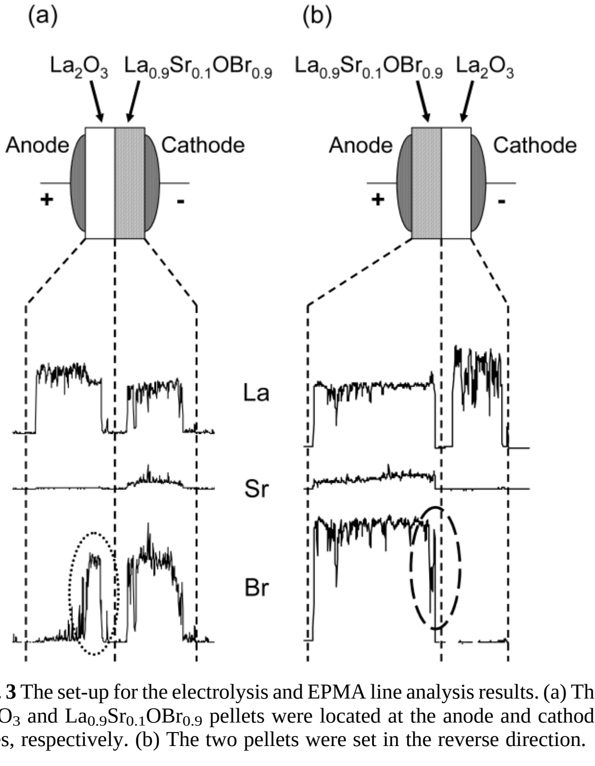

Fig. 3 The set-up for the electrolysis and EPMA line analysis results. (a) The La_2O_3 and $La_{0.9}Sr_{0.1}OBr_{0.9}$ pellets were located at the anode and cathode sides, respectively. (b) The two pellets were set in the reverse direction.

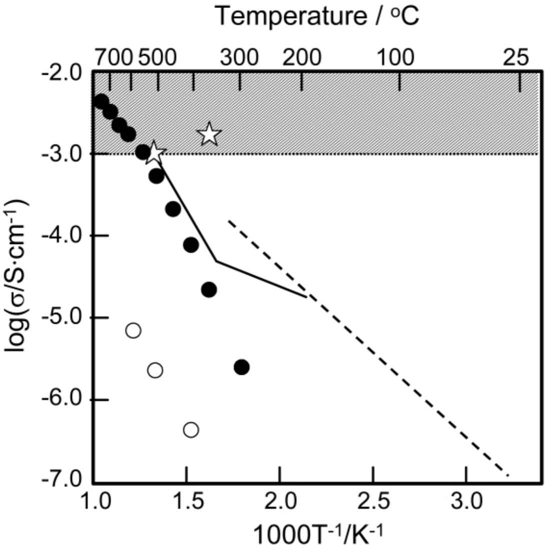

Fig. 4 Temperature dependencies of Br^- anion conductivity for $La_{0.9}Sr_{0.1}OBr_{0.9}$ solid solution electrolyte (●) compared with the data for typical Br^- ion conducting solid electrolytes such as $PbBr_2$ (---),[4] $CsPbBr_3$ (—),[5] and pure LaOBr (○). Open stars (☆) indicate individual melting points.

In conclusion, a practically applicable Br^- anion conducting solid electrolyte was successfully realized by applying the water insoluble LaOBr as the mother phase of a new type of Br^- anion conductor. The Br^- anion conductivity of the oxybromide is as high as 4.2×10^{-3} S cm^{-1} at 750 °C, which exceeds those of the representative Br^- anion conductors of $CsPbBr_3$ and $PbBr_2$. As the conventional Br^- anion conductors are all soluble in water with comparably lower melting temperatures, the present new Br^- anion conducting solid is greatly expected to be applied in many kinds of devices such as chemical sensors over wide temperature ranges and various atmospheres in the future. Further evaluation is underway.

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Notes and references

† LaOBr was prepared by heating a mixture of La_2O_3 and NH_4Br (1 : 2 molar ratio) at 800 °C for 6 h in air. Sr doped LaOBr was synthesized by heating a mixture of LaOBr and $SrCO_3$ in a suitable mixing ratio at 800 °C for 12 h in air. The $(La_{1-x}Sr_x)OBr_{1-x}$ solid solution was pelletized and sintered at 800 °C for 12 h in air. The X-ray powder diffraction analysis (Mac Science M18XHF diffractometer) was carried out using Cu-Kα radiation. XRD data were collected by a step scanning method in the 2θ range between 10 and 70° with a step scan width of 0.04°. Conductivity measurements were performed by an ac complex impedance method with a Hewlett Packard precision LCR meter (4192A) using the sample pellet with two platinum electrodes. Oxygen pressures from 10^2 to 10^5 Pa were controlled by mixing air(oxygen)–N_2 in the appropriate ratio. The dc electrolysis was carried out at 700 °C at 4 V [approximately 88 and 60 h for Fig. 3(a) and (b)] by setting La(Sr)OBr and La_2O_3 pellets between two Pt electrodes. The line analyses of the electrolyzed pellets were performed by EPMA (EPMA-1500, Shimadzu).

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