FULL PAPER

Novel Br[−] ion conducting solid electrolyte based on LaOBrMuhammad Radzi Iqbal Bin MISRAN¹, Naoyoshi NUNOTANI¹,
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Highly Br[−] ion conducting solid electrolytes were developed by replacing La³⁺ ion site in LaOBr with lower valent Sr²⁺ and Ca²⁺ ions to form Br[−] ion vacancies for Br[−] ion conduction with suppressing the sample decomposition. By doping two kinds of divalent cations simultaneously into LaOBr lattice, high amount of Br[−] ion vacancy was successfully introduced compared to the previously reported La_{0.9}Sr_{0.1}OBr_{0.9}. Among the samples prepared, the highest Br[−] ion conductivity was obtained for the La_{0.85}Sr_{0.10}Ca_{0.05}OBr_{0.85} solid, which was ca. 5 times higher than that of La_{0.9}Sr_{0.1}OBr_{0.9}.

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1. Introduction

Solids in which single ion species can migrate macroscopically are called as solid electrolytes or ion conducting solids. Ion conduction in a solid generally depends on the size of conducting ion species, and therefore, cations having relatively small ionic size is known to migrate smoothly even in a rigid crystal lattice. In contrast, for the anion conducting solids, only several anion species have been known to conduct in solids, for example O^{2−} ion [ionic size: 0.126 nm, coordination number (CN) = 6¹⁾, 2)–4) F[−] ion (0.119 nm, CN = 6¹⁾, 5)–7) and Cl[−] ion (0.167 nm, CN = 6¹⁾, 8), 9) whose ionic radii are comparatively small among anions.

For the Br[−] ion having large ionic size (0.182 nm, CN = 6¹⁾), the ionic conduction in solids has been reported for Pb_{0.99}K_{0.01}Br_{1.99}¹⁰⁾ and CsPbBr₃¹¹⁾ while these bromide compounds have some critical disadvantages that should be solved for the practical application use; i.e., low melting point (PbBr₂: 373°C,¹²⁾ CsPbBr₃: 567°C¹³⁾) and water-soluble nature (PbBr₂: 0.97 g/100 g_{water} at 25°C,¹⁴⁾ CsBr: 123 g/100 g_{water} at 25°C¹⁵⁾). In our previous study,¹⁶⁾ we have focused on lanthanum oxybromide, LaOBr, which has high thermal stability (m.p.: 850°C)¹⁷⁾ and insoluble nature in water (0.0035 g/100 g_{water}).¹⁸⁾ Although the LaOBr solid itself possessed the low electrical conductivity (ca. 10^{−5} S·cm^{−1} at 800°C), we have realized the enhancement of the conductivity by replacing the La³⁺ ion site in the LaOBr solid with lower valent Sr²⁺ ion to form

Br[−] ion vacancies as a result of charge compensation.¹⁶⁾ Especially, the La_{0.9}Sr_{0.1}OBr_{0.9} solid exhibited the highest Br[−] ion conductivity, which is ca. 300 times higher than that of LaOBr. Although further enhancement of Br[−] ion conductivity is expected by intentional increase of Br[−] vacancy, we could not obtain the single-phase solids whose Br[−] vacancy ratio was above 0.1, due to the lattice collapse caused by the high amount of large Sr²⁺ ion (0.140 nm, CN = 8¹⁾) doping into La³⁺ ion (0.130 nm, CN = 8¹⁾) site.

For further enhancement of Br[−] ion conductivity in LaOBr solid, it is essential to introduce additional Br[−] ion vacancies in the LaOBr structure without distortion of crystal lattice. Therefore, we partially substituted the La³⁺ ion (0.130 nm, CN = 8¹⁾) sites in the La_{0.9}Sr_{0.1}OBr_{0.9} solid by the lower valent and smaller ionic size of Ca²⁺ ion (0.126 nm, CN = 8¹⁾) for inhibiting the lattice expansion, and ion conducting properties of the La_{0.9−x}Sr_{0.1}Ca_xOBr_{0.9−x} solids were investigated. In addition, La_{0.95−y}Sr_yCa_{0.05}OBr_{0.95−y} was also investigated for optimization of Sr content.

2. Experimental

La_{0.9−x}Sr_{0.1}Ca_xOBr_{0.9−x} solids were synthesized by solid-state reaction method. La₂O₃ (Shin-Etsu Chemical, 99.99%), Sr(NO₃)₂ (Wako Pure Chemical Industries, 99.9%), Ca(NO₃)₂·4H₂O (Kojundo Chemical Laboratory, 99.9%), and NH₄Br (Kishida Chemical, 99.9%) were mixed in the La: Sr: Ca: Br ratio of 0.9 − x: 0.1: x: 2(0.9 − x) and the mixture was heated at 800°C for 12 h in air flow. The obtained powder was pelletized and calcined twice at 800°C for 12 h.

X-ray powder diffraction (XRD; SmartLab, Rigaku) measurement was performed with Cu-Kα radiation (40 kV,

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30 mA), where the data were collected by a step scanning method in 2θ range between 10 and 70° with a step scan width of 0.04°. The lattice volume of samples was estimated from the XRD peak angles, refined using α -Al₂O₃ as a standard material.

For the electrochemical measurements, the sample powder was pelletized and sintered at 800°C for 12 h in air flow. After polishing the sintered pellet with waterproof abrasive papers, the platinum sputtered layer was formed on both center surfaces of the sample, and platinum paste was fixed on sputtered layer. AC conductivity (σ_{AC}) of the pellet was measured by complex impedance method in the frequency range from 5 Hz to 13 MHz (1260 Impedance/Gain-Phase Analyzer, Solartron) at temperatures between 800 and 300°C in the atmospheric air. Modified Tubandt electrolysis was carried out by applying DC voltage of 0.7 V for three pellets sandwiched by platinum bulk electrodes at 700°C for 4 h in air. After the electrolysis, the elemental distribution in each pellet was examined by energy dispersion X-ray spectroscopy (EDX; SSX-550, Shimadzu).

3. Results and discussions

From the XRD patterns of the La_{0.9-x}Sr_{0.1}Ca_xOBr_{0.9-x} solids (Fig. 1), the samples with $x \leq 0.05$ was a single-phase LaOBr based solid, whereas the samples with $x > 0.05$ were two-phase mixture of the LaOBr structure and SrBr₂. This result suggests that the solid solubility limit composition is $x = 0.05$ for the La_{0.9-x}Sr_{0.1}Ca_xOBr_{0.9-x} solids.

Figure 2 shows the lattice volume for the La_{0.9-x}Sr_{0.1}Ca_xOBr_{0.9-x} solids. For the samples with $x \leq 0.05$, the lattice volume decreased with increasing Ca²⁺ ion content, indicating that the smaller Ca²⁺ ion (0.126 nm, CN = 8¹⁾) was successfully substituted into the La³⁺ ion (0.130 nm, CN = 8¹⁾) site. In general, the lattice volume for the

main phase should be constant in the multi-phase region. However, a continuous decrease of the volume was observed even for the sample with $x > 0.05$. This lattice shrinkage might be caused by the preferential substitution of the smaller Ca²⁺ ion in the La³⁺ ion site, involved with the precipitation of larger Sr²⁺ ion as SrBr₂.

Figure 2 also depicts the compositional dependence of AC conductivity at 800°C for the La_{0.9-x}Sr_{0.1}Ca_xOBr_{0.9-x} solids. An increase in conductivity was clearly observed with increasing Ca²⁺ ion amount, and the highest conductivity was obtained for the solid solubility limit composition, La_{0.85}Sr_{0.1}Ca_{0.05}OBr_{0.85} ($x = 0.05$), caused by the increase of Br⁻ ion vacancies. For the samples with $x > 0.05$, the conductivity decreased due to the appearance of impurity phase.

Since the La_{0.85}Sr_{0.1}Ca_{0.05}OBr_{0.85} solid showed the highest Br⁻ ion conductivity, the Sr²⁺ ion doping amount into La³⁺ ion site was optimized; i.e., the La_{0.95-y}Sr_yCa_{0.05}OBr_{0.95-y} solids were synthesized. From the XRD pattern (Fig. 3), the samples with $y \leq 0.1$ possessed the single-phase LaOBr structure, whereas the sample with $y = 0.15$ was a two-phase mixture of the LaOBr structure and SrBr₂.

Figure 4 shows the lattice volume for the La_{0.95-y}Sr_yCa_{0.05}OBr_{0.95-y} solids. In the single-phase region ($y \leq 0.1$), a lattice expansion was observed with increasing the Sr²⁺ ion content, supporting that the larger Sr²⁺ ion (0.140 nm, CN = 8¹⁾) was successfully substituted into the La³⁺ ion (0.130 nm, CN = 8¹⁾) site. When the Sr²⁺ ion content was over 0.1, the lattice volume had almost the same value as the sample with $y = 0.1$; therefore, the solid solubility limit composition was found to be $y = 0.1$. Figure 4 also shows the compositional dependence of AC conductivity at 800°C for the La_{0.95-y}Sr_yCa_{0.05}OBr_{0.95-y}. For the single phase samples ($y \leq 0.1$), the conductivity increased with increasing Sr²⁺ amount up to $y = 0.1$ due to the increase of Br⁻

Fig. 1. XRD patterns of the La_{0.9-x}Sr_{0.1}Ca_xOBr_{0.9-x} solids.

Fig. 2. Compositional dependence of the lattice volume and conductivity at 800°C for the La_{0.9-x}Sr_{0.1}Ca_xOBr_{0.9-x} solids.

Fig. 3. XRD patterns of the $\text{La}_{0.95-y}\text{Sr}_y\text{Ca}_{0.05}\text{OBr}_{0.95-y}$ solids.

Fig. 4. Compositional dependence of the lattice volume and conductivity at 800°C for the $\text{La}_{0.95-y}\text{Sr}_y\text{Ca}_{0.05}\text{OBr}_{0.95-y}$ solids.

ion vacancies and the expansion of the Br^- ion-conducting pathway. In the two-phase mixture region of $y > 0.1$, the conductivity decreased compared to the sample with $y = 0.1$, caused by the formation of impurity phase. Therefore, it was clear that the $\text{La}_{0.85}\text{Sr}_{0.1}\text{Ca}_{0.05}\text{OBr}_{0.85}$ solid exhibited the highest conductivity.

For demonstrating the Br^- ion conduction in the $\text{La}_{0.85}\text{Sr}_{0.1}\text{Ca}_{0.05}\text{OBr}_{0.85}$ solid, modified Tubandt electrolysis was performed by applying DC voltage of 0.7 V, which was higher than the decomposition voltage of the sample. Here, the decomposition voltage at 700°C was preliminarily determined to be ca. 0.6 V from the current–voltage relationship. As shown in Fig. 5, one La_2O_3 sample (pellet A)

Fig. 5. Set up of the modified Tubandt electrolysis using La_2O_3 and $\text{La}_{0.85}\text{Sr}_{0.1}\text{Ca}_{0.05}\text{OBr}_{0.85}$ pellets and the EDX line analysis results after the electrolysis applied at 0.7 V, 700°C for 4 h in air.

and two $\text{La}_{0.85}\text{Sr}_{0.1}\text{Ca}_{0.05}\text{OBr}_{0.85}$ samples (pellets B and C) were set up side by side and sandwiched by platinum electrodes. Assuming that Br^- ions migrate, $\text{La}_{0.85}\text{Sr}_{0.1}\text{Ca}_{0.05}\text{OBr}_{0.85}$ at the cathodic side (pellet C) should decompose according to the following reaction, with the generation of Br^- ions:

The produced Br^- anions are forced to conduct through $\text{La}_{0.85}\text{Sr}_{0.1}\text{Ca}_{0.05}\text{OBr}_{0.85}$ in the middle (pellet B), and then reach La_2O_3 (pellet A). The reached Br^- ions react with La_2O_3 to form LaOBr , as the following reaction:

From the elemental distribution inside the pellets after the electrolysis at 700°C for 4 h (Fig. 5), only clear segregation of Br was evident on and near surface of La_2O_3 pellet (A) in contact with $\text{La}_{0.85}\text{Sr}_{0.1}\text{Ca}_{0.05}\text{OBr}_{0.85}$ pellet (B), while such segregation was not recognized for the other ions. Furthermore, since it was clear that no thermal diffusion of ions or chemical reaction took place from the comparative experiment without applying DC voltage (Fig. 6), the observed Br^- ion conduction in the $\text{La}_{0.85}\text{Sr}_{0.1}\text{Ca}_{0.05}\text{OBr}_{0.85}$ solid was due to the potential gradient, that means Br^- ion conduction in the solid.

For clarifying the Br^- ion conduction quantitatively, the theoretical weight changes for each pellet were estimated from the total electric charge passed during the electrol-

Fig. 6. EDX line analysis results for the La₂O₃ and La_{0.85}Sr_{0.1}Ca_{0.05}OBr_{0.85} pellet after the heating at 700°C for 4 h in air without applying DC voltage.

Table 1. Weight changes for La₂O₃ (pellet A) and La_{0.85}Sr_{0.1}Ca_{0.05}OBr_{0.85} (pellet B and C) after the modified Tubandt electrolysis applied at 0.7 V, 700°C for 4 h in air

Pellet	Theoretical weight change /mg	Measured weight change /mg	Measured/Theoretical weight change
A	+0.303	+0.265	87%
B	0	-0.277	91%
C	-0.303		

ysis. Here, to compensate a slight vaporization of the sample, weight change of La₂O₃ and La_{0.85}Sr_{0.1}Ca_{0.05}OBr_{0.85} pellet were also investigated at the same condition. If Br⁻ ion is the conducting species, the weight of pellet A would increase and that of pellet C would decrease. In the middle pellet B, no weight change should be observed, because the ions only pass through it. Table 1 lists the theoretical and measured weight of respective pellet obtained by the modified Tubandt electrolysis performed by applying 700°C for 4 h in air. The weight increase of La₂O₃ (pellet A) was confirmed. In addition, while it was difficult to separate middle pellet B and cathodic pellet C due to adhesion, the weight decrease was clearly observed. Furthermore, the measured values were almost consistent with the theoretical values; i.e., the measured/theoretical weight changes were ca. 90%. Because the theoretical weight change estimated as Br⁻ ion conduction in the sample was successfully obtained, Br⁻ anion migration in La_{0.85}Sr_{0.1}Ca_{0.05}OBr_{0.85} was quantitatively demonstrated. In order to eliminate the possibility of O²⁻ ion conduction in the solid, polarization behavior was investigated by measuring the DC and AC conductivity in oxygen gas atmosphere. Because the DC to AC conductivity ratio (σ_{DC}/σ_{AC}) of the

Fig. 7. Temperature dependencies of the conductivity for the La_{0.85}Sr_{0.1}Ca_{0.05}OBr_{0.85}, La_{0.9}Sr_{0.1}OBr_{0.9}, and LaOBr solids.

La_{0.85}Sr_{0.1}Ca_{0.05}OBr_{0.85} solid was nearly 0 after 30 min, it was confirmed that the La_{0.85}Sr_{0.1}Ca_{0.05}OBr_{0.85} solid did not show O²⁻ ion conduction.¹⁹⁾

The temperature dependence of the Br⁻ ion conductivity in the La_{0.85}Sr_{0.1}Ca_{0.05}OBr_{0.85} solid is shown in Fig. 7, with the corresponding data for La_{0.9}Sr_{0.1}OBr_{0.9} and LaOBr. The conductivity of the La_{0.85}Sr_{0.1}Ca_{0.05}OBr_{0.85} solid was ca. 5 times higher than that of the La_{0.9}Sr_{0.1}OBr_{0.9} solid at 800°C, because additional Br⁻ ion vacancies were formed by introducing the Ca²⁺ ion simultaneously, while the activation energy (91.95 kJ mol⁻¹) for Br⁻ conduction in the La_{0.85}Sr_{0.1}Ca_{0.05}OBr_{0.85} solid was slightly increased compared with that (84.30 kJ mol⁻¹) of La_{0.9}Sr_{0.1}OBr_{0.9} solid due to the lattice shrinkage.

4. Conclusions

Novel Br⁻ ion conducting solid of La_{0.95-x-y}Sr_yCa_xOBr_{0.95-x-y} was developed by partially substituting the La³⁺ ion sites in LaOBr by the lower valent Sr²⁺ and Ca²⁺ ions in order to form a high amount of Br⁻ ion vacancies. As a result of the optimization of the Sr²⁺ and Ca²⁺ ion contents, the La_{0.85}Sr_{0.1}Ca_{0.05}OBr_{0.85} solid exhibited the highest Br⁻ ion conductivity, and the value was ca. 5 times higher than that of La_{0.9}Sr_{0.1}OBr_{0.9}.

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