Novel $\text{Br}^-$ ion conducting solid electrolyte based on LaOBr

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Highly $\text{Br}^-$ ion conducting solid electrolytes were developed by replacing $\text{La}^{3+}$ ion site in LaOBr with lower valent $\text{Sr}^{2+}$ and $\text{Ca}^{2+}$ ions to form $\text{Br}^-$ ion vacancies for $\text{Br}^-$ ion conduction with suppressing the sample decomposition. By doping two kinds of divalent cations simultaneously into LaOBr lattice, high amount of $\text{Br}^-$ ion vacancy was successfully introduced compared to the previously reported $\text{La}_{0.9}\text{Sr}_{0.1}\text{OBr}_{0.9}$. Among the samples prepared, the highest $\text{Br}^-$ ion conductivity was obtained for the $\text{La}_{0.85}\text{Sr}_{0.10}\text{Ca}_{0.05}\text{OBr}_{0.85}$ solid, which was ca. 5 times higher than that of $\text{La}_{0.80}\text{Sr}_{0.11}\text{Ca}_{0.05}\text{OBr}_{0.85}$ solid.

Key-words : Solid electrolyte, Bromide ion, Lanthanum oxybromide, Ion conductivity

[Received April 14, 2018; Accepted May 25, 2018]

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 $\text{O}^{2-}$-ion (0.126 nm, coordination number (CN) = 6¹), ²⁻ $\text{F}^-$ ion (0.119 nm, CN = 6⁵), ³⁻ $\text{Cl}^-$ ion (0.167 nm, CN = 6⁸)¹⁰ whose ionic radii are comparatively small among anions.

For the $\text{Br}^-$ ion having large ionic size (0.182 nm, CN = 6¹), the ionic conduction in solids has been reported for $\text{Pb}_{0.99}\text{K}_{0.01}\text{Br}_{1.99}$ and $\text{CsPbBr}_3$,⁶ 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°C¹⁷) and insoluble nature in water (0.0035 g/100 g water).⁶ Although the LaOBr solid itself possessed the low electrical conductivity (ca. 10⁻⁸ S·cm⁻¹ at 800°C), we have realized the enhancement of the conductivity by replacing the $\text{La}^{3+}$ ion site in the LaOBr solid with lower valent $\text{Sr}^{2+}$ ion to form $\text{Br}^-$ ion vacancies as a result of charge compensation.¹⁶ Especially, the $\text{La}_{0.9}\text{Sr}_{0.1}\text{OBr}_{0.9}$ solid exhibited the highest $\text{Br}^-$ ion conductivity, which is ca. 300 times higher than that of LaOBr. Although further enhancement of $\text{Br}^-$ ion conductivity is expected by intentional increase of $\text{Br}^-$ vacancy, we could not obtain the single-phase solids whose $\text{Br}^-$ vacancy ratio was above 0.1, due to the lattice collapse caused by the high amount of large $\text{Sr}^{2+}$ ion (0.140 nm, CN = 8¹¹) doping into $\text{La}^{2+}$ ion (0.130 nm, CN = 8¹⁷) site.

For further enhancement of $\text{Br}^-$ ion conductivity in LaOBr solid, it is essential to introduce additional $\text{Br}^-$ ion vacancies in the LaOBr structure without distortion of crystal lattice. Therefore, we partially substituted the $\text{La}^{3+}$ ion (0.110 nm, CN = 8¹⁷) sites in the $\text{La}_{0.9}\text{Sr}_{0.1}\text{OBr}_{0.9}$ solid by the lower valent and smaller ionic size of $\text{Ca}^{2+}$ ion (0.126 nm, CN = 8¹⁷) for inhibiting the lattice expansion, and ion conducting properties of the $\text{La}_{0.9-x}\text{Sr}_{0.1}\text{Ca}_{x}\text{OBr}_{0.9-x}$ solids were investigated. In addition, $\text{La}_{0.9-x}\text{Sr}_{0.1}\text{Ca}_{y}\text{OBr}_{0.95-y}$ was also investigated for optimization of Sr content.

2. Experimental

$\text{La}_{0.9-x}\text{Sr}_{0.1}\text{Ca}_{y}\text{OBr}_{0.95-y}$ solids were synthesized by solid-state reaction method. $\text{La}_2\text{O}_3$ (Shin-Etsu Chemical, 99.99%), $\text{Sr(NO}_3)_2$ (Wako Pure Chemical Industries, 99.9%), $\text{Ca(NO}_3)_2$·4H₂O (Kojundo Chemical Laboratory, 99.9%), and $\text{NH}_4\text{Br}$ (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,
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 (σAC) 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 La0.9−xSr0.1Ca0.05OBr0.9−x solids (Fig. 1), the samples with x ≤ 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 La0.9−xSr0.1Ca0.05OBr0.9−x solids.

Figure 2 shows the lattice volume for the La0.9−xSr0.1Ca0.05OBr0.9−x solids. For the samples with x ≤ 0.05, the lattice volume decreased with increasing Ca2+ ion content, indicating that the smaller Ca2+ ion (0.126 nm, CN = 8[1]) was successfully substituted into the La3+ ion (0.130 nm, CN = 8[1]) 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 La0.9−xSr0.1Ca0.05OBr0.9−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, La0.85Sr0.1Ca0.05OBr0.85 (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 La0.85Sr0.1Ca0.05OBr0.85 solid showed the highest Br− ion conductivity, the Sr2+ ion doping amount into La3+ ion site was optimized, i.e., the La0.95−ySr0.1Ca0.05OBr0.95−y solids were synthesized. From the XRD pattern (Fig. 3), the samples with y ≤ 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 La0.95−ySr0.1Ca0.05OBr0.95−y solids. In the single-phase region (y ≤ 0.1), a lattice expansion was observed with increasing the Sr2+ ion content, supporting that the larger Sr2+ ion (0.140 nm, CN = 8[1]) was successfully substituted into the La3+ (0.130 nm, CN = 8[1]) 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 La0.95−ySr0.1Ca0.05OBr0.95−y. For the single phase samples (y ≤ 0.1), the conductivity increased with increasing Sr2+ amount up to y = 0.1 due to the increase of Br−.
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 La\(_{0.85}\)Sr\(_{0.1}\)Ca\(_{0.05}\)OBr\(_{0.85}\) solid exhibited the highest conductivity.

For demonstrating the Br\(^{-}\) ion conduction in the La\(_{0.85}\)-Sr\(_{0.1}\)Ca\(_{0.05}\)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. Assuming that Br\(^{-}\) ions migrate, La\(_{0.85}\)Sr\(_{0.1}\)Ca\(_{0.05}\)OBr\(_{0.85}\) at the cathodic side (pellet C) should decompose according to the following reaction, with the generation of Br\(^{-}\) ions:

\[
\begin{align*}
20 & \text{La}_{0.85}\text{Sr}_{0.1}\text{Ca}_{0.05}\text{OBr}_{0.85}^+ + \frac{1}{2} \text{O}_2 + e^- \\
\rightarrow & \frac{1}{2} \text{La}_2\text{O}_3 + \frac{2}{17} \text{SrO} + \frac{1}{17} \text{CaO} + \text{Br}^{-}
\end{align*}
\]

The produced Br\(^{-}\) anions are forced to conduct through La\(_{0.85}\)Sr\(_{0.1}\)Ca\(_{0.05}\)OBr\(_{0.85}\) in the middle (pellet B), and then reach La\(_2\)O\(_3\) (pellet A). The reached Br\(^{-}\) ions react with La\(_2\)O\(_3\) to form LaOBr, as the following reaction:

\[
\frac{1}{2} \text{La}_2\text{O}_3 + \text{Br}^{-} \rightarrow \text{LaOBr} + \frac{1}{4} \text{O}_2 + e^{-}
\]

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\(_2\)O\(_3\) pellet (A) in contact with La\(_{0.85}\)Sr\(_{0.1}\)Ca\(_{0.05}\)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 La\(_{0.85}\)-Sr\(_{0.1}\)Ca\(_{0.05}\)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-
Here, to compensate a slight vaporization of the sample, weight changes of La$_2$O$_3$ and La$_{0.85}$Sr$_{0.1}$Ca$_{0.05}$O$_{Br0.85}$ pellet were also investigated at the same condition. If Br$^{-}$ 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 changes obtained by the modified Tubandt electrolysis performed at 0.7 V, 700°C for 4 h in air.

![EDX line analysis results for the La$_2$O$_3$ and La$_{0.85}$Sr$_{0.1}$Ca$_{0.05}$O$_{Br0.85}$ pellet after the heating at 700°C for 4 h in air without applying DC voltage.](image)

<table>
<thead>
<tr>
<th>Pellet</th>
<th>Theoretical weight change /mg</th>
<th>Measured weight change /mg</th>
<th>Measured/Theoretical weight change</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>+0.303</td>
<td>+0.265</td>
<td>87%</td>
</tr>
<tr>
<td>B</td>
<td>0</td>
<td>-0.277</td>
<td>91%</td>
</tr>
<tr>
<td>C</td>
<td>-0.303</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

La$_{0.85}$Sr$_{0.1}$Ca$_{0.05}$O$_{Br0.85}$ solid was nearly 0 after 30 min, it was confirmed that the La$_{0.85}$Sr$_{0.1}$Ca$_{0.05}$O$_{Br0.85}$ solid did not show O$^{2-}$ ion conduction.

The temperature dependence of the Br$^{-}$ ion conductivity in the La$_{0.85}$Sr$_{0.1}$Ca$_{0.05}$O$_{Br0.85}$ solid is shown in Fig. 7, with the corresponding data for La$_{0.9}$Sr$_{0.1}$O$_{Br0.9}$ and LaOBr. The conductivity of the La$_{0.85}$Sr$_{0.1}$Ca$_{0.05}$O$_{Br0.85}$ solid was ca. 5 times higher than that of the La$_{0.9}$Sr$_{0.1}$O$_{Br0.9}$ solid at 800°C, because additional Br$^{-}$ ion vacancies were formed by introducing the Ca$^{2+}$ ion simultaneously, while the activation energy (91.95 kJ mol$^{-1}$) for Br$^{-}$ conduction in the La$_{0.85}$Sr$_{0.1}$Ca$_{0.05}$O$_{Br0.85}$ solid was slightly increased compared with that (84.30 kJ mol$^{-1}$) of La$_{0.9}$Sr$_{0.1}$O$_{Br0.9}$ solid due to the lattice shrinkage.

4. Conclusions

Novel Br$^{-}$ ion conducting solid of La$_{0.95-x-y}$Sr$_{x}$Ca$_{y}$O$_{Br0.95-x-y}$ was developed by partially substituting the La$^{3+}$ ion sites in LaOBr by the lower valent Sr$^{2+}$ and Ca$^{2+}$ ions in order to form a high amount of Br$^{-}$ ion vacancies. As a result of the optimization of the Sr$^{2+}$ and Ca$^{2+}$ ion contents, the La$_{0.85}$Sr$_{0.1}$Ca$_{0.05}$O$_{Br0.85}$ solid exhibited the highest Br$^{-}$ ion conductivity, and the value was ca. 5 times higher than that of La$_{0.9}$Sr$_{0.1}$O$_{Br0.9}$. 

Acknowledgment This work was partially supported by JSPS KAKENHI, Grant Number JP17H05482, from the Ministry of Education, Science, Sports and Culture.

References