Evidence for enormous iodide anion migration in lanthanum oxyiodide–based solid

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The I⁻ ion conduction was demonstrated and quantified in the La₀.₇₀Sr₀.₂₅Zn₀.₀₅O₁.₇₀ solid. The I⁻ ion is considered to be an inferior conductor because of its large ionic size compared to the previously reported conducting ion species. Using modified Tubandt electrolysis, a weight increase at the anodic pellet and a corresponding weight decrease at the cathodic pellet were observed. The weight changes were in good agreement with the theoretical values estimated by considering pure I⁻ ion migration. Furthermore, the iodine element appeared at the anode, and the iodine concentration at the cathode decreased after electrolysis, indicating that the migrating species was only I⁻. This is the first study to elucidate the conduction of iodide ions in solids.

INTRODUCTION

Solid electrolytes are functional materials that have received significant attention owing to their unique property of single ionic conduction inside the solid lattice as a charge carrier. In solid electrolytes, it is considered that the ionic conductivity is correlated to the size of the conducting ion species, implying that a small ionic size enables smooth ionic conduction. Examples include alkali metal ions, such as the Li⁺ ion [0.106 nm, [coordination number (CN) = 8] [1]) (2–8) and Na⁺ ion [0.132 nm (CN = 8)] (1) (9–13), and anions, such as the O²⁻ ion [0.126 nm (CN = 6)] (1) (14–17). Li⁺ and Na⁺ ions are applied in various electrical devices, for example, in all-solid-state and sodium-sulfur batteries (18, 19), owing to their excellent conducting properties. Similarly, O²⁻ ions have already been commercialized as components of oxygen gas sensors, for example, in automotive oxygen gas sensors (20). However, conducting anionic species have a relatively small ionic size. Except for the F⁻ ion, other halide ions are considered weak migrant anions because of their large ionic size.

In the halide series, the bromide anion (Br⁻) has the largest ionic size [0.182 nm, (CN = 6)] among all the ion species whose conduction was quantified (21, 22). Br⁻ is also larger than the cesium cation [Cs⁺, 0.181 nm (CN = 6)] (1), which is the largest cation among all nonradioactive elements. The I⁻ ion is larger than Br⁻ and is too large [0.206 nm (CN = 6)] to migrate in solids. Such an ion generally acts as a rigid framework maintaining the crystal lattice rather than as the conducting ion species, such as α-Agl of Ag⁺ ion-conducting solids (23, 24). Previously, I⁻ ion conductors have been explored, such as lead iodide (PbI₂) (25–27), pervoskite-type iodides (CuPbI₃, CH₃NH₃PbI₃, etc.) (28–30), having low thermal and chemical stability, and iodide-based glasses (PbI₂-PbO, etc.) (31–33). These have been reported to be a type of I⁻ ion-conducting solids. However, I⁻ ion migration in the lattice has not been quantified. It is still unclear whether the I⁻ ions with a large ionic size can migrate inside the lattice. This study aims to develop a previously unidentified I⁻ ion conductor whose migrating species is I⁻ ion and demonstrate macroscopic-only I⁻ ion migration.

RESULTS AND DISCUSSION

La₀.₇₀Sr₀.₂₅Zn₀.₀₅O₁.₇₀ was synthesized by the conventional solid-state reaction method, where the composition was optimized to show the highest conductivity (fig. S1). Figure 1B shows the x-ray powder diffraction (XRD) pattern of La₀.₇₀Sr₀.₂₅Zn₀.₀₅O₁.₇₀ along with the data of LaOI. The pattern was identified to be a single-phase matlockite-type structure. The replacement of the La⁺³ sites for Sr⁺² and Zn⁺² was confirmed by the change in the lattice volume (fig S1B), where the lattice volume of La₀.₇₀Sr₀.₂₅Zn₀.₀₅O₁.₇₀ (0.1591 nm³) was larger than that of LaOI (0.1567 nm³). To investigate the formation of the I⁻ ion vacancies in La₀.₇₀Sr₀.₂₅Zn₀.₀₅O₁.₇₀, x-ray fluorescence (XRF) analysis was performed. The measured composition was estimated to be La₀.₇₃Sr₀.₂₃Zn₀.₀₅O₀.₉₉I₁₋ₓ, where x(vacancy) = 0.26, similar...
using one La$_{2}$O$_3$ (pellet A) and two La$_{0.70}$Sr$_{0.25}$Zn$_{0.05}$OI$_{0.70}$ pellets (pellets B and C) sandwiched between two Pt electrodes. This electrolysis was performed 38 times higher than that of LaOI. This improvement in the conductivity considerably improved by introducing Sr$^{2+}$ and Zn$^{2+}$ compared to La$^{3+}$ was compensated by the formation of the I$^-$ and not the O$^{2-}$ vacancies.

Figure 1C shows the temperature dependence of the conductivity for the LaOBr-based materials (22). a.u., arbitrary units. These reactions will lead to the mass increase of pellet A and the mass decrease of pellet C. Considering other species such as O$^{2-}$, e$^-$, h$^+$, proton, and cations (La$^{3+}$, Sr$^{2+}$, and Zn$^{2+}$), if the conducting species is O$^{2-}$, no mass change should be observed due to the continuous supply of O$^{2-}$ by atmospheric O$_2$. Similarly, the electron (e$^-$ or h$^+$) or proton migration would cause no weight change for each pellet. For the cation (La$^{3+}$, Sr$^{2+}$, or Zn$^{2+}$) conduction, La$_{0.70}$Sr$_{0.25}$Zn$_{0.05}$IO$_{0.70}$ decomposes at the middle pellet (pellet B), and the generated cation may be forced to migrate toward the cathodic surface (pellet C), resulting in the reduction of the cation to the metal state followed by immediate oxidation due to atmospheric oxygen gas. As an example, the possible reactions in the case of La$^{3+}$ conduction are described below

**Middle pellet:**

\[
\frac{10}{21} \text{La}_{0.70}\text{Sr}_{0.25}\text{Zn}_{0.05}\text{O}_{0.70} \rightarrow \frac{1}{2} \text{La}_3^+ + \frac{5}{14} \text{SrO} + \frac{1}{14} \text{ZnO} + I^- + e^- \tag{3}
\]

**Cathode:**

\[
\frac{1}{3} \text{La}^3^+ + e^- \rightarrow \frac{1}{3} \text{La} \tag{4}
\]

**Anode:**

\[
\frac{1}{3} \text{La}_2^3^+ + \frac{1}{4} \text{O}_2 \rightarrow \frac{1}{6} \text{La}_2^3\text{O}_3 \tag{5}
\]

These chemical equations imply that the weight of pellet B would decrease and that of pellet C would increase. The theoretical values ($\Delta m_{\text{calc}}$) for each of the conducting species can be estimated from the total electric charge (Q) corresponding to the electrolysis. The detailed theory is explained in the Supplementary Materials.

Before and after electrolysis, each pellet was weighed to obtain the mass change ($\Delta m_{\text{obs}}$). To exclude the change during the electrolysis at the elevated operating temperature, the mass change in each pellet was compensated by using reference pellets of La$_2$O$_3$ and La$_{0.70}$Sr$_{0.25}$Zn$_{0.05}$IO$_{0.70}$, which were embedded without electrolysis near the electrolytic cell. The calculation method is described in the
The obtained sample powder was pelletized by uniaxial pressing at ca. 70 kN with diameter and thickness of 10 and 1 mm, respectively, followed by sintering at 400°C for 12 hours under Ar flow (10 ml min⁻¹). The resulting powder was pressed into a pellet by uniaxial pressing at ca. 70 kN with diameter and thickness of 13 and 2 mm, respectively. The obtained samples were identified using XRD (SmartLab, Rigaku) measurement using Cu Kα2 radiation (40 kV, 30 mA) in the 2θ range from 10° to 70°. The lattice volume was calculated from the XRD peak angles, refined by using α-Al2O3 as an internal standard. XRF (EDX-800, Shimadzu) analysis was performed to confirm the composition. To investigate the electrochemical properties, the sample powder was pelletized by uniaxial pressing at ca. 70 kN with diameter and thickness of 13 and 2 mm, respectively. The pellet was calcined at 400°C for 12 hours under Ar flow (10 ml min⁻¹) several times until a single phase was obtained.

### Characterization

The obtained samples were identified using XRD (SmartLab, Rigaku) measurement using Cu Kα radiation (40 kV, 30 mA) in the 2θ range from 10° to 70°. The lattice volume was calculated from the XRD peak angles, refined by using α-Al2O3 as an internal standard. XRF (EDX-800, Shimadzu) analysis was performed to confirm the composition. To investigate the electrochemical properties, the sample powder was pelletized by uniaxial pressing at ca. 70 kN with diameter and thickness of 13 and 2 mm, respectively, followed by firing at 400°C for 12 hours under Ar flow (10 ml min⁻¹). The obtained pellet was polished with waterproof abrasive papers, so no significant mass change was observed in the middle pellet (pellet B). These reproducible mass changes clearly indicate that the conducting species are I⁻ ions and not O²⁻, e⁻, h⁺, La³⁺, Sr²⁺, or Zn²⁺. Furthermore, the observed mass changes were in agreement with the calculated values, where the ratio of the observed mass change to the theoretical value was estimated to be approximately 90%. For the pellet A (La₂O₃) surface in contact with the iodine solution, the LaOI phase was additionally detected using the XRD measurement (fig. S2), supporting the I⁻ conduction (Eq. 2).

To obtain further evidence on the I⁻ conduction, each pellet, after the modified Tubandt electrolysis, was homogeneously pulverized, and the change in the elemental ratio was determined using XRF analysis (Table 2). Although La₂O₃ is composed of La and O, the iodine element was detected in the anodic pellet A [0.48 mole percent (mol %)]. On the other hand, the iodine ratio in cathodically molded pellet C (26.41 mol %) was appreciably lower than that in the middle pellet B (26.99 mol %) and the corresponding reference (27.04 mol %). These results indicate that the source of the mass changes for pellets A and C is the I⁻ ion migration from pellet C toward pellet B. Therefore, from the mass and elemental changes, the quantitative I⁻ ion conduction was demonstrated in La₀.₇₀Sr₀.₂₅Zn₀.₀₅O₁₀.₇₀.

In summary, we have successfully identified and quantified I⁻ ion conduction in La₀.₇₀Sr₀.₂₅Zn₀.₀₅O₁₀.₇₀. However, the I⁻ ion, owing to its large ionic size, is generally considered to be a constituent component of the lattice and not the conducting ion species. To the best of our knowledge, this is the first report that demonstrates a quantitative pure I⁻ ion conduction inside the solid lattice.

### MATERIALS AND METHODS

#### Sample preparation

La₁₋ₓSrₓZn₁₋ₓO₁−ₓ-y samples were prepared using the conventional solid-state reaction method. Powders of La₂O₃ (99.99%; Shin-Etsu Chemical), Sr(NO₃)₂ (99.9%; Wako Pure Chemical), Zn(NO₃)₂·6H₂O (≥99.0%; Kishida Chemical), and NH₄I (99.5%; Kanto Chemical) in a molar ratio of (1−x−y):2x:2y:4(1−x−y) were mixed using an agate mortar and preheated at 400°C for 12 hours under Ar flow (10 ml min⁻¹). The resulting powder was pressed into a pellet by uniaxial pressing at ca. 70 kN with diameter and thickness of 13 and 2 mm, respectively. The pellet was calcined at 400°C for 12 hours under Ar flow (10 ml min⁻¹) several times until a single phase was obtained.

#### Characterization

The obtained samples identified using XRD (SmartLab, Rigaku) measurement using Cu Kα radiation (40 kV, 30 mA) in the 2θ range from 10° to 70°. The lattice volume was calculated from the XRD peak angles, refined by using α-Al₂O₃ as an internal standard. XRF (EDX-800, Shimadzu) analysis was performed to confirm the composition. To investigate the electrochemical properties, the sample powder was pelletized by uniaxial pressing at ca. 70 kN with diameter and thickness of 10 and 1 mm, respectively, followed by firing at 400°C for 12 hours under Ar flow (10 ml min⁻¹). The obtained pellet was polished with waterproof abrasive papers.

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**Table 1.** Observed and calculated mass changes for two La₀.₇₀Sr₀.₂₅Zn₀.₀₅O₁₀.₇₀ pellets and one La₂O₃ pellet after the modified Tubandt electrolysis performed under two different conditions.

| Condition | Q/mC   | Sample         | ∆m(obs)/mg | ∆m(cal)/mg (Δm(cal)/Δm(obs)) |
|-----------|--------|----------------|------------|-------------------------------|
| 400°C, 15 V, 5 days | 149.2  | A (La₂O₃)      | +0.167     | +0.184 (91%)                  |
|           |        | B (La₀.₇₀Sr₀.₂₅Zn₀.₀₅O₁₀.₇₀) | −0.0004   | 0                            |
|           |        | C (La₀.₇₀Sr₀.₂₅Zn₀.₀₅O₁₀.₇₀) | −0.174     | −0.184 (95%)                  |
| 400°C, 15 V, 7 days | 201.4  | A (La₂O₃)      | +0.220     | +0.248 (89%)                  |
|           |        | B (La₀.₇₀Sr₀.₂₅Zn₀.₀₅O₁₀.₇₀) | +0.048     | 0                            |
|           |        | C (La₀.₇₀Sr₀.₂₅Zn₀.₀₅O₁₀.₇₀) | −0.239     | −0.248 (96%)                  |

**Table 2.** Measured molar ratios for each pellet after the electrolysis was performed by applying 15 V at 400°C for 5 days.

| Sample         | I   | O   | La | Sr | Zn |
|----------------|-----|-----|----|----|----|
| A (La₂O₃)      | 0.48| 59.62| 39.90| 0% | 0% |
| B (La₀.₇₀Sr₀.₂₅Zn₀.₀₅O₁₀.₇₀) | 26.99| 36.39| 26.56| 8.25%| 1.81%|
| C (La₀.₇₀Sr₀.₂₅Zn₀.₀₅O₁₀.₇₀) | 26.41| 36.88| 26.74| 8.17%| 1.80%|
| Ref (La₂O₃)    | 0%  | 60.00| 40.00| 0%  | 0% |
| Ref (La₀.₇₀Sr₀.₂₅Zn₀.₀₅O₁₀.₇₀) | 27.04| 36.36| 26.55| 8.24%| 1.81%|
and then, platinum–sputtered layers were formed on the centers of opposite surfaces using an ion coater (IB-3, Eiko). The AC conductivity (σ) of the pellets was measured using the complex impedance method (1260 impedance per gain analyzer, Solartron) in the frequency range between 5 Hz and 13 MHz at temperatures between 400° and 300°C.

SUPPLEMENTARY MATERIALS
Supplementary material for this article is available at https://science.org/doi/10.1126/sciadv.abh0812

REFERENCES AND NOTES
1. R. D. Shannon, Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. Acta Crystallogr. Sect. A 32, 751–767 (1976).
2. H. Y.-P. Hong. Crystal structure and ionic conductivity of Li4ZnGeO4 and other new Li+ superionic conductors. Mater. Res. Bull. 13, 117–124 (1978).
3. G. Adachi, N. Imanaka, H. Aono, Fast Li+ conducting ceramic electrolytes. Adv. Mater. 8, 127–135 (1996).
4. S. Marrauere, V. Thangadurai, W. Weppner, Lithium lanthanum titanates: A review. Chem. Mater. 15, 3974–3990 (2003).
5. R. Murugan, V. Thangadurai, W. Weppner, Fast lithium ion conduction in garnet-type Li7La3Zr2O12. Angew. Chem. Int. Ed. 46, 7778–7781 (2007).
6. G. Gao, T. Brux, S. Fujii, C. Tassel, K. Yamamoto, H. Takamura, H. Ubukata, Y. Watanabe, K. Fujii, M. Yashima, A. Kuwabara, Y. Uchimoto, H. Kageyama, Hydride-based antiperovskites with soft anionic sublattices as fast alkali ionic conductors. Nat. Commun. 12, 201 (2021).
7. N. Flores-González, N. Minafra, G. Devi, R. Reardon, S. J. Smith, W. P. Adams, W. G. Zeier, D. H. Gregory, Mechanosynthesis and synthesis of lithium tetrahaloaluminate(s), LiAlX4 (X = Cl, Br, I): A family of Li-ion conducting ternary halides. ACS Lett. 3, 652–657 (2021).
8. H. Mawaka, M. Matsu, H. Takamura, M. Ando, Y. Noda, T. Karahashi, S. Orimo, Halide-stabilized LiBH4, a room-temperature lithium fast-ion conductor. J. Am. Chem. Soc. 131, 894–895 (2009).
9. Y.-F. Y. Yao, J. T. Kummer, Ion exchange properties of and rates of ionic diffusion in beta-alumina. J. Inorg. Nucl. Chem. 29, 2453–2475 (1967).
10. J. B. Goodenough, H. Y.-P. Hong, J. A. Kafalas, Fast Na+ ion transport in skeleton structures. Mater. Res. Bull. 11, 203–220 (1976).
11. A. Hayashi, K. Noi, A. Sakuda, M. Tatsumisago, Superionic glass-ceramic electrolytes for room-temperature rechargeable sodium batteries. Nat. Commun. 3, 856 (2012).
12. Y. Qie, S. Wang, S. Fu, H. Xie, J. Pena, Y. Zhuan, Y. Chakraborty, S. Banerjee, Halide replacement with complete preservation of crystal lattice in mixed-anion lanthanide oxohalides. Angew. Chem. Int. Ed. 60, 15582–15589 (2021).
13. O. Heinö, M. Leskelä, L. Niinistö, Structural and thermal properties of rare earth triiodide hydrates. Acta Cryst. Sect. A 34A, 207–211 (1980).
14. A. L. Allred, Electronegativity values from thermochemical data. J. Inorg. Nucl. Chem. 17, 215–221 (1961).
15. N. Imanaka, N. Nunotani, K. Araki, M. Yamane, Exact identification of migrating ion species in scandium tungstate solid electrolyte. J. Am. Ceram. Soc. 101, 1025–1028 (2018).
16. K. Momma, F. Izuami, VESTA: A three-dimensional visualization system for electronic and structural analysis. J. Appl. Crystallogr. 41, 653–658 (2008).
17. H. Iwahara, Proton conducting ceramics and their applications. Solid State Ionics 86-88, 9–15 (1996).
18. C. W. Struck, J. A. Baglio, Estimates for the enthalpy of formation of rare-earth oxohalides with the P4/nmm structure. Thermochim. Acta 216, 45–79 (1993).

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