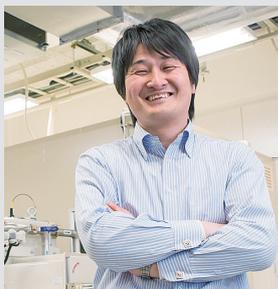


Study on Hydride Ion Conductive Materials for Novel Electrochemical Devices

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Education

2006 B.E. Kanazawa University
2010 D.S. Tokyo Institute of Technology

Professional Employment

2010 Postdoctoral Fellow, Tokyo Institute of Technology
2011 Assistant Professor, Kanagawa University
2012 JST-PRESTO Researcher (Additional post)
2013 Research Associate Professor, Institute for Molecular Science
2018 Associate Professor, Institute for Molecular Science
Associate Professor, The Graduate University for Advanced Studies
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Awards

2011 Tejima Doctoral Dissertation Award, Tokyo Institute of Technology
2018 The 39th Honda Memorial Young Researcher Award, The Honda Memorial Foundation
2018 The 7th Ishida Award, Nagoya University
2019 Tagawa Solid State Chemistry Awards, Division of Solid State Chemistry, The Electrochemical Society of Japan
2019 Morino Foundation for Molecular Science
2022 Academic Award, The NAGAI Foundation for Science & Technology

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Keywords Solid State Ionics, H⁻ Conductor, Battery

Hydrogen has a charge flexibility and can take various charge states such as proton (H⁺), atomic hydrogen (H⁰), and hydride (H⁻) depending on the different bonding states in materials. Due to this feature, whereas hydrogen diffusing in metals behaves a state close to H⁰, H⁺ becomes the charge carrier in many types of chemical compounds, including polymer, solid acid, MOF, and ceramics. In the former case, hydrogen absorbing alloys and hydrogen embrittlement of metals have been studied, and in the latter case, materials research for fuel cell applications has been actively carried out over the past few decades. In contrast, H⁻ is a relatively rare state that can only be taken when hydrogen is coordinated to metals with low electronegativity such as alkali metals and was not well recognized as a charge carrier. Therefore, even though H⁻ has attractive features such as suitability for fast ionic conduction in terms of size, valence, and polarization and strong reduction properties ($E^{\circ}(\text{H}^{-}/\text{H}_2) = -2.35 \text{ V vs. SHE}$), its electrochemical applications have not been considered. Against this back-

ground, we developed a series of H⁻ conductive oxyhydrides, $\text{La}_{2-x-y}\text{Sr}_{x+y}\text{LiH}_{1-x+y}\text{O}_{3-y}$, in 2016 and found its function as an H⁻ solid electrolyte for the first time. Based on the results, our group is challenging the progress of materials science on H⁻ conductors and the development of novel electrochemical devices utilizing H⁻ conduction phenomena.

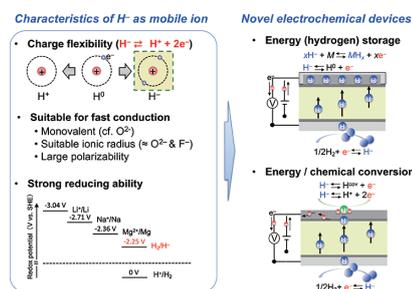


Figure 1. Our research concept toward realization of electrochemical devices utilizing hydrogen charge flexibility.

Selected Publications

- G. Kobayashi, Y. Hinuma, S. Matsuoka, A. Watanabe, M. Iqbal, M. Hirayama, M. Yonemura, T. Kamiyama, I. Tanaka and R. Kanno, *Science* **351**, 1314–1317 (2016).
- A. Watanabe, G. Kobayashi, N. Matsui, M. Yonemura, A. Kubota, K. Suzuki, M. Hirayama and R. Kanno, *Electrochemistry* **85**(2), 88–92 (2017).
- F. Takeiri, A. Watanabe, A. Kuwabara, H. Nawaz, N. Ayu, M. Yonemura, R. Kanno and G. Kobayashi, *Inorg. Chem.* **58**, 4431–4436 (2019).
- H. Nawaz, F. Takeiri, A. Kuwabara and M. Yonemura and G. Kobayashi, *Chem. Commun.* **56**, 10373–10376 (2020).
- T. Uchimura, F. Takeiri, K. Okamoto, T. Saito, T. Kamiyama and G. Kobayashi, *J. Mater. Chem. A* **9**, 20371–20374 (2021).
- F. Takeiri, A. Watanabe, K. Okamoto, D. Bresser, S. Lyonard, B. Frick, M. Yonemura, T. Saito, K. Ikeda, T. Otomo, T. Kamiyama, R. Kanno and G. Kobayashi, *Nat. Mater.* **21**, 325–330 (2022).

1. Study on H⁻ Conductive Oxyhydrides¹⁻⁴⁾

In 2016, we synthesized a series of K₂NiF₄-type oxyhydrides, La_{2-x-y}Sr_{x+y}LiH_{1-x+y}O_{3-y} (LSLHO), which are equipped with anion sublattices that exhibit flexibility in the storage of H⁻, O²⁻, and vacancies (Figure 2 upper) and demonstrated pure H⁻ conduction properties in the oxyhydrides.¹⁾ The Li-based oxyhydrides acted as solid electrolytes and the all-solid-state Ti/LSLHO/TiH₂ cell showed a redox reaction based on hydrogen storage/desorption on the electrodes, which is a first battery reaction using H⁻ conduction phenomena.

Based on elemental substitutions to LSLHO, we have been exploring hydride ion conducting oxyhydrides. As shown in Figure 2, we have found that the H⁻ and O²⁻ arrangement in the K₂NiF₄-type structure can be controlled by tuning the valence (electrostatic valence rule) and size balance of the cation species (tolerance factor). More recently, we reported a new H⁻ conductive oxyhydride, Ba_{1.75}LiH_{2.7}O_{0.9} (BLHO), containing a high amount of barium and hydrogen vacancies and exhibiting long-range ordering at room temperature. Increasing the temperature above 315 °C disorders the long-range ordering, triggering superionic conduction with a high H⁻ conductivity of over 0.01 S·cm⁻¹ nearly independent of the temperature. The finding of the H⁻ superionic conductor operating intermediate temperature range, which might open up possibilities for new electrochemical device.

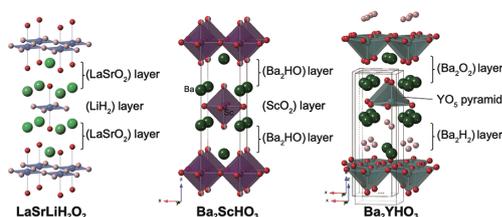


Figure 2. Comparison of the crystal structures of H⁻ conductive oxyhydrides La_{2-x-y}Sr_{x+y}LiH_{1-x+y}O_{3-y} ($x = 0, y = 0, 1, 2$) and Ba₂MHO₃ ($M = \text{Sc}, \text{Y}$).

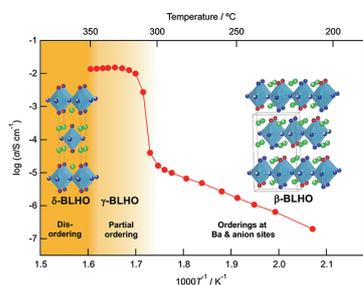


Figure 3. The temperature dependence of H⁻ conductivity for BLHO. After the β-γ transition, the conductivity drastically enhances, and its value is nearly independent of temperature.

2. Materials Processing of Oxyhydrides for Electrochemical Applications⁵⁻⁷⁾

Awards

KOBAYASHI, Genki; The NAGAI Foundation for Science & Technology Academic Award (2022).
OKAMOTO, KEI; Student Presentation Award, The Electrochemical Society of Japan (2021).

Synthesizing oxyhydrides usually requires unique methods such as high-pressure reactions, and topochemical reactions using CaH₂ reductant. Since the former method is a sealed reaction system, loss of light elements, such as hydrogen, can be prevented, making it a suitable synthesis method for composition control and, ultimately, exploration for new materials. On the other hand, the latter is an O²⁻/H⁻ exchange reaction and is useful for preparing metastable phases. However, the high-pressure method and the topochemical reaction have each problem of low synthesis volume and low reproducibility, respectively. To expand the research on hydride ionic conductors to the development of electrochemical devices, it is necessary to establish a simple and large volume synthesis process for the constituent materials. We have been trying to establish a suitable synthesis method for oxyhydrides to resolve the above problems.

For the K₂NiF₄-type oxyhydrides, we have successfully established the solid-state reaction method under ambient-pressure.^{4,5)} Furthermore, we have succeeded in direct synthesis of barium titanium oxyhydride BaTiO_{3-x}H_x by mechanochemical reaction, allowing gram-scale and speedy preparation of the functional material. Its unique reaction condition without external heating might be suitable for materials exploration of transition metal oxyhydrides. We also confirmed that the prepared polycrystalline BaTiO_{3-x}H_x worked as a hydrogen-permeable electrode. This result suggests that H⁻/e⁻ mixed conducting oxyhydrides are promising for electrode use in electrochemical chemical/energy conversion devices (Figure 4).

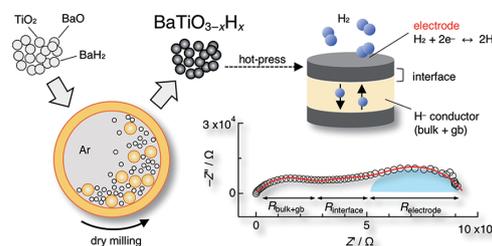


Figure 4. BaTiO_{3-x}H_x synthesized by a mechanochemical method and its performance as hydrogen permeable electrodes.

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- 1) G. Kobayashi* *et al.*, *Science* **351**, 1314–1317 (2016).
- 2) F. Takeiri, G. Kobayashi* *et al.*, *Inorg. Chem.* **58**, 4431–4436 (2019).
- 3) H. Nawaz, G. Kobayashi* *et al.*, *Chem. Commun.* **56**, 10373–10376 (2020).
- 4) F. Takeiri, G. Kobayashi* *et al.*, *Nat. Mater.* **21**, 325–330 (2022).
- 5) A. Watanabe, G. Kobayashi* *et al.*, *Electrochemistry* **85**(2), 88–92 (2017).
- 6) N. Matsui, G. Kobayashi* *et al.*, *J. Am. Ceram. Soc.* **102**, 3228–3235 (2019).
- 7) T. Uchimura, G. Kobayashi* *et al.*, *J. Mater. Chem. A* **9**, 20371–20374 (2021).