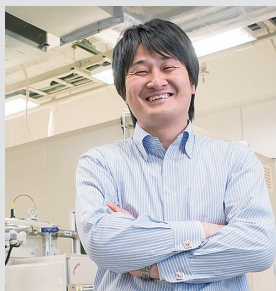


Study on Hydride Ion Conductive Materials for Novel Electrochemical Devices

Department of Materials Molecular Science
Division of Molecular Functions



KOBAYASHI, Genki
Associate Professor
[gkobayashi@ims.ac.jp]

Education

2006 B.E. Kanazawa University
2008 M.E. Tokyo Institute of Technology
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

Awards

2010 ACerS Spriggs Phase Equilibria Award, American Ceramics Society
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

Member

Assistant Professor
TAKEIRI, Fumitaka
Graduate Student
OKAMOTO, Kei
UCHIMURA, Tasuku
AYU, Nur Ika Puji*
IZUMI, Yoshiki
Technical Fellow
IMAI, Yumiko
KUBOTA, Akiko
Secretary
KAMIYA, Miho

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.

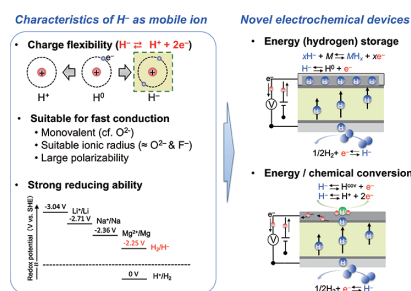


Figure 1. Our research concept toward realization of electrochemical devices utilizing hydrogen charge flexibility.

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).
- N. Matsui, G. Kobayashi, K. Suzuki, A. Watanabe, A. Kubota, Y. Iwasaki, M. Yonemura, M. Hirayama and R. Kanno, *J. Am. Ceram. Soc.* **102**, 3228–3235 (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).

1. Study on H⁻ Conductive Oxyhydrides¹⁻³⁾

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.

More recently, we synthesized novel H⁻ conductive oxyhydrides, Ba₂MHO₃ (M = Sc, Y),^{2,3)} with the K₂NiF₄-type structure and confirmed its unique site selectivity for H⁻. In accordance with the electrostatic valence rule, it was found that the hydride ions in Ba₂MHO₃ selectively occupied the rock-salt layer, in contrast to those of the observed isostructural Li-based oxyhydrides that preferentially occupy the perovskite layer (Figure 2). The cation size at the octahedral center influences the anion arrangement within the rock salt layer, and in the Y-oxyhydride, the complete ordering of H/O led to the formation of the [Ba₂H₂] layers. These results indicate that anion ordering in oxyhydrides could be tuned by appropriate element substitutions, which is a new insight for designing H⁻ conducting materials.

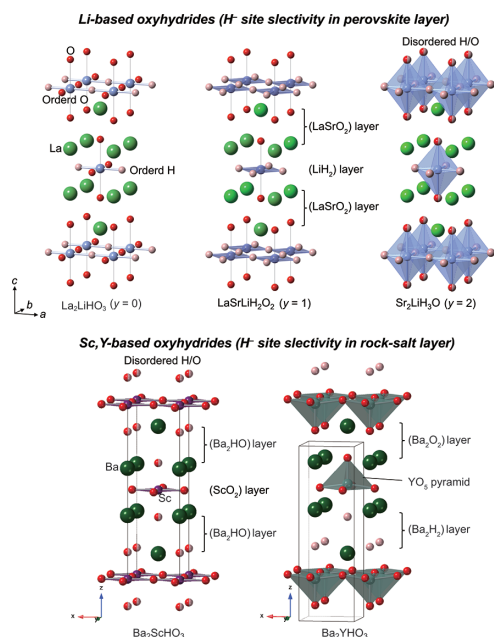


Figure 2. Crystal structures of H⁻ conductive oxyhydrides La_{2-x-y}Sr_{x+y}LiH_{1-x+y}O_{3-y} ($x = 0, y = 0, 1, 2$) and Ba₂MHO₃ ($M = \text{Sc}, \text{Y}$).

2. Materials Processing of Oxyhydrides for Electrochemical Applications⁴⁻⁶⁾

Synthesizing oxyhydrides usually requires unique methods such as solid-state reactions at high-pressure 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 using oxides as precursors and is useful for preparing metastable phases that the conventional sintering process cannot obtain. However, the low synthesis volume in the high-pressure method and less reproducibility of composition due to complicated multi-step processes such as washing in CaH₂ reduction have prevented expanding the study on oxyhydrides to applicable research for electrochemical devices. To resolve the above problems, we have been trying to establish a suitable synthesis method for oxyhydrides.

For Li-based oxyhydrides (LSLHO) with the K₂NiF₄-type structure, we have successfully established the solid-state reaction method under ambient-pressure.^{4,5)} Electromotive force measurements using hydrogen concentration cells became possible by preparing the LSLHO sintered pellets with sufficient size.

We have also 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 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 3).⁶⁾

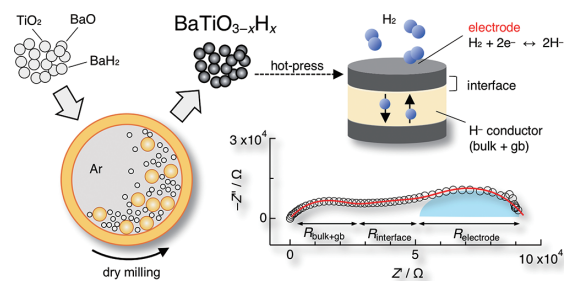


Figure 3. BaTiO_{3-x}H_x synthesized by a mechanochemical method and its performance as hydrogen permeable electrodes.

References

- 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) A. Watanabe, G. Kobayashi* *et al.*, *Electrochemistry* **85**, 88–92 (2017).
- 5) N. Matsui, G. Kobayashi* *et al.*, *J. Am. Ceram. Soc.* **102**, 3228–3235 (2019).
- 6) T. Uchimura, G. Kobayashi* *et al.*, *J. Mater. Chem. A* **9**, 20371–20374 (2021).

* carrying out graduate research on Cooperative Education Program of IMS with High Energy Accelerator Research Organization