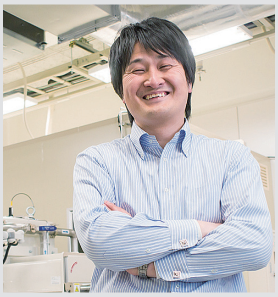
Study on Ion Conductive Materials for Novel Energy Storage/Conversion Devices

Department of Materials Molecular Science
Division of Molecular Functions



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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 Fundation
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

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Keywords Solid State Ionics, H^- Conductor, Battery

Chemical energy conversion/storage using electrochemical devices such as fuel cells and batteries will become increasingly important for future sustainable societies. As ion transport in solids is key for determining the performance of these devices, an improved understanding of the characteristics of existing electrode and electrolyte materials is required. For example, crystal structure, thermal stability, and reaction mechanisms are important to enhancing battery performance. Furthermore, the development of novel ion conduction phenomena through the synthesis of a new class of substances will be expected to lead to the creation of novel battery systems. In this context, I have concentrated my research efforts into two main areas: (i) Studies into the reaction mechanisms of cathodic materials for lithium secondary batteries; and (ii) The synthesis of new materials exhibiting hydride ion (H^-) conductivity and the development of a novel battery system utilizing both the H^- conduction phenomenon and the H^-/H_2 redox reaction.

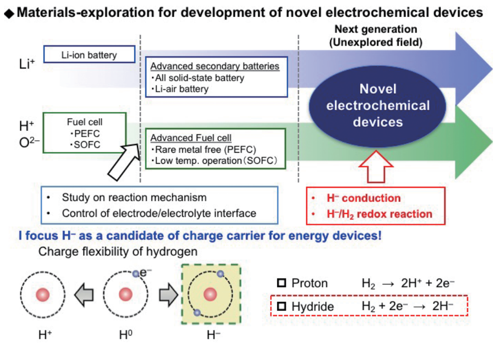

Figure 1. The concept of our research toward the realization of new energy storage/conversion devices.

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).
- G. Kobayashi, Y. Irii, F. Matsumoto, A. Ito, Y. Ohsawa, S. Yamamoto, Y. Chui, J.-Y. Son and Y. Sato, *J. Power Sources* **303**, 250–256 (2016).
- A. Watanabe, G. Kobayashi, N. Matsui, M. Yonemura, A. Kubota, K. Suzuki, M. Hirayama and R. Kanno, *Electrochemistry* **85(2)**, 88–92 (2017).
- Y. Iwasaki, N. Matsui, K. Suzuki, Y. Hinuma, M. Yonemura, G. Kobayashi, M. Hirayama, I. Tanaka and R. Kanno, *J. Mater. Chem. A* **6**, 23457–23463 (2018).
- 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).

1. Study on H^- Conductive Oxyhydrides[1–5]

Ionic charge carriers include a variety of species, such as Li^+, H^+, Ag^+, Cu^+, F^-, and O^{2-}, and their conductors have found applications in energy devices such as fuel cells and batteries. A hydride ion (H^-,) is an attractive charge carrier because it exhibits promising features for fast ionic conduction; namely, monovalence, suitable ionic size similar to that of F^- and O^{2-}, and high polarizability. Furthermore, its strong reducing properties with a standard redox potential of H^-/H_2 (–2.3 V) which is close to that of Mg/Mg^{2+} (–2.4 V) may be applied in energy storage/conversion devices with high energy densities. In 2016, we synthesized a series of K_2NiF_4-type oxyhydrides, $La_{2-x-y}Sr_{x+y}LiH_{1-x+y}O_{3-y}$, which are equipped with anion sublattices that exhibit flexibility in the storage of H^-, O^{2-}, and vacancies (Figure 2 upper) and demonstrated pure H^- conduction properties in the oxyhydrides. The Li-based oxyhydrides acted as solid electrolytes and the all-solid-state $Ti/La_{2-x-y}Sr_{x+y}LiH_{1-x+y}O_{3-y}/TiH_2$ cell showed a redox reaction based on hydrogen storage/desorption on the electrodes, which is a first battery reaction using H^- conduction phenomena.

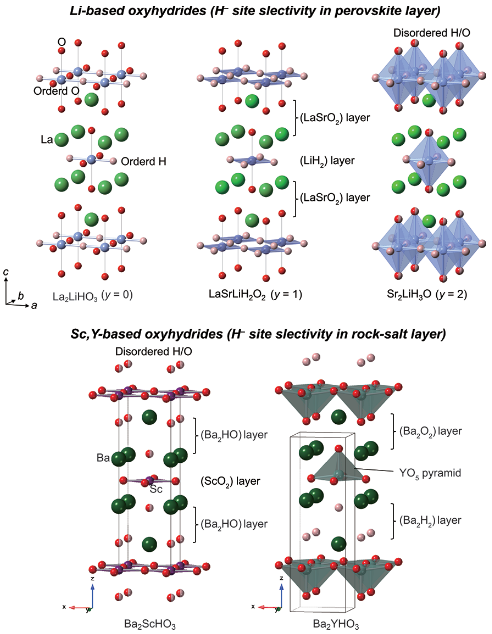

Figure 2. Crystal structures of H^- conductive oxyhydrides $La_{2-x-y}Sr_{x+y}LiH_{1-x+y}O_{3-y}$ ($x = 0$, $y = 0, 1, 2$) and Ba_2MHO_3 (M = Sc, Y).

More recently, we synthesized novel H^- conductive oxyhydrides, Ba_2MHO_3 (M = Sc, Y), with the K_2NiF_4-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 Ba_2MHO_3 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 $[Ba_2H_2]$ 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.

2. High-Performance of Li-Rich Layered Cathode Materials through A_2O_3-Surface Modification[6]

Controlling the cathode/electrolyte interface by surface modification of cathode materials with metal oxides or phosphate is being explored as a possible strategy for improving the electrochemical performance of such materials. We synthesized Al_2O_3-coated $Li[Li_{0.2}Ni_{0.18}Co_{0.03}Mn_{0.58}]O_2$ and investiated the crystal structure, the chemical bonding state from bulk to surface, and the influence of the surface modification on the electrochemical performance by X-ray diffraction, hard X-ray photoelectron spectroscopy (HAXPES), and galvanostatic charge/discharge reaction. It revealed that the surface-modification layer was composed of Li-Al oxides and Al oxides and that a $LiM_{1-x}Al_xO_2$ (M = transition metals) interlayer was formed between the modification layer and the $Li[Li_{0.2}Ni_{0.18}Co_{0.03}Mn_{0.58}]O_2$ particles (Figure 3). The cycling performance of the Li-rich layered oxide was enhanced by the surface modification with Al_2O_3. A discharge capacity of more than 310 mA h^{-1} and excellent cycling stability at 50 °C were achieved by the combination of the gradual Li-insetion/de-insertion process (stepwise precycling treatment) and the surface-modification.

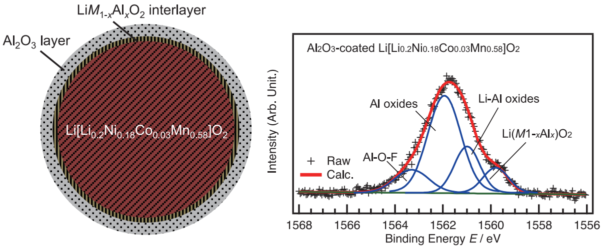

Figure 3. Schematic illustration and Al 1*s* HAXPES spectra of the 2 wt% Al_2O_3-coated $Li[Li_{0.2}Ni_{0.18}Co_{0.03}Mn_{0.58}]O_2$ particle.

References

1) H. Nawaz, G. Kobayashi* *et al.*, *Chem. Commun.* **56**, 10373–10376 (2020).
2) F. Takeiri, G. Kobayashi* *et al.*, *Inorg. Chem.* **58**, 4431–4436 (2019).
3) N. Matsui, G. Kobayashi* *et al.*, *J. Am. Ceram. Soc.* **102**, 3228–3235 (2019).
4) A. Watanabe, G. Kobayashi* *et al.*, *Electrochemistry* **85**, 88–92 (2017).
5) G. Kobayashi*, R. Kanno* *et al.*, *Science* **351**, 1314–1317 (2016).
6) G. Kobayashi* *et al.*, *J. Power Sources* **303**, 250–256 (2016).

Award

KOBAYASHI, Genki; Morino Foundation for Molecular Science (2019).

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