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

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

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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.

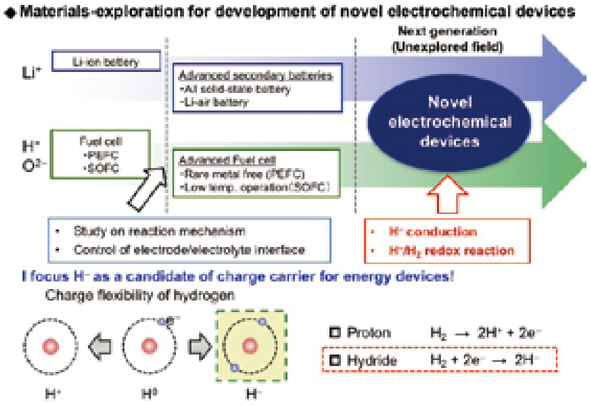

Figure 1. The concept of our research toward the realization of new energy storage/conversion devices.

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).

1. Study on H^- Conductive Oxyhydrides[1–4]

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. The conduction of hydride ions, H^-, is also attractive. These are similar in size to oxide and fluoride ions and show 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). Hydride ion conductors may therefore be applied in energy storage/conversion devices with high energy densities. Here, we prepared 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). An 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 with hydrogen storage/desorption on the electrodes. The present success in the construction of an all-solid-state electrochemical cell exhibiting H^- diffusion confirms not only the capability of the oxyhydride to act as an H^- solid electrolyte but also the possibility of developing electrochemical solid devices based on H^- conduction.

More recently, we synthesized Ba_2ScHO_3, a novel H^- conductive Sc-oxyhydride 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_2ScHO_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). This result indicated that anion arrangements in oxyhydrides could be tuned by appropriate element substitutions, which is a new insight for designing H^- conducting materials.

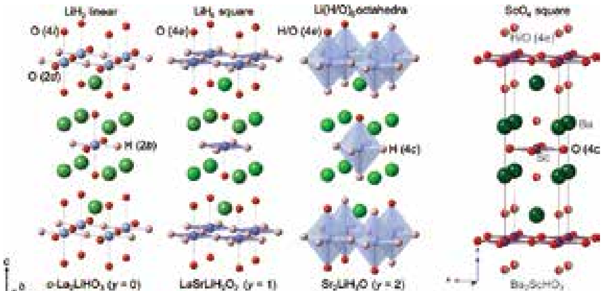

Figure 2. Crystal structures of H^- conductive oxyhydrides $La_{2-x-y}Sr_{x+y}LiH_{1-x+y}O_{3-y}$ ($x = 0$, $y = 0, 1, 2$) and Ba_2ScHO_3.

2. High-Performance of Li-Rich Layered Cathode Materials through A_2O_3-Surface Modification[5]

Controlling the cathode/electrolyte interface by modifying the surface of the cathode material with metal oxides or phosphate is being explored as a possible strategy for improving the electrochemical performance of such materials. In this study, we synthesized Al_2O_3-coated $Li[Li_{0.2}Ni_{0.18}Co_{0.03}Mn_{0.58}]O_2$ and investigated 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.

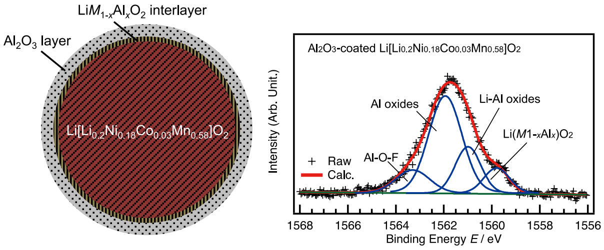

Figure 3. Schematic illustration and Al 1s HAXPES spectra of the 2 wt% Al_2O_3-coated $Li[Li_{0.2}Ni_{0.18}Co_{0.03}Mn_{0.58}]O_2$ particle.

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1) F. Takeiri, A. Watanabe, A. Kuwabara, H. Nawaz, N. Ayu, M. Yonemura, R. Kanno and G. Kobayashi*, *Inorg. Chem.* **58**, 4431–4436 (2019).

2) 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).

3) A. Watanabe, G. Kobayashi*, N. Matsui, M. Yonemura, A. Kubota, K. Suzuki, M. Hirayama and R. Kanno, *Electrochemistry* **85**, 88–92 (2017).

4) 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).

5) 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).

Awards

KOBAYASHI, Genki; Tagawa Solid State Chemistry Awards (2019).
KOBAYASHI, Genki; 7th Ishida Award (2018).

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