

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

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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.

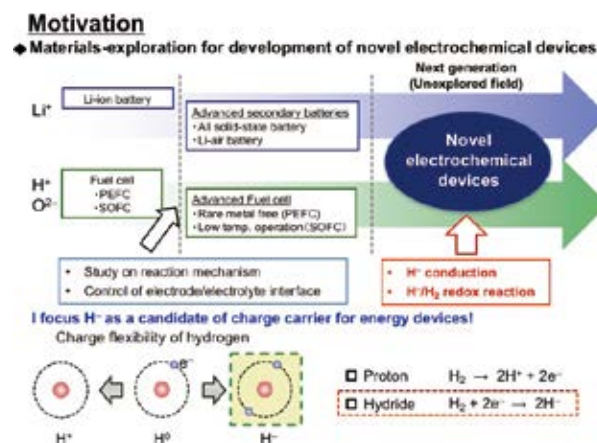


Figure 1. The concept of our research toward the realization of new energy storage/conversion devices.

Selected Publications

- G. Kobayashi, S.-I. Nishimura, M.-S. Park, R. Kanno, M. Yashima, T. Ida and A. Yamada, "Isolation of Solid Solution Phases in Size-Controlled Li_3FePO_4 at Room Temperature," *Adv. Funct. Mater.* **19**, 395–403 (2009).
- G. Kobayashi, A. Yamada, S.-I. Nishimura, R. Kanno, Y. Kobayashi, S. Seki, Y. Ohno and H. Miyashiro, *J. Power Sources* **189**, 397–401 (2009).
- 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).

1. Synthesis of H^- Conductive Oxyhydrides¹⁻⁴⁾

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, $\text{La}_{2-x-y}\text{Sr}_{x+y}\text{LiH}_{1-x+y}\text{O}_{3-y}$, which are equipped with anion sublattices that exhibit flexibility in the storage of H^- , O^{2-} , and vacancies. An all-solid-state $\text{Ti}/\text{La}_{2-x-y}\text{Sr}_{x+y}\text{LiH}_{1-x+y}\text{O}_{3-y}/\text{TiH}_2$ 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.

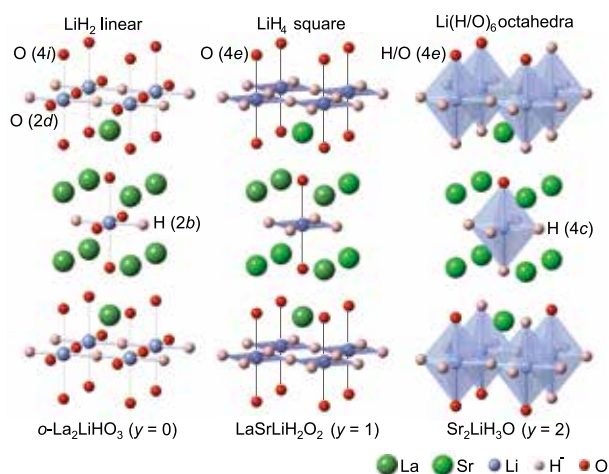


Figure 2. Crystal structures of $\text{La}_{2-x-y}\text{Sr}_{x+y}\text{LiH}_{1-x+y}\text{O}_{3-y}$ ($x = 0, y = 0, 1, 2$). Lanthanum (and strontium) ions occupy the A sites of the layered perovskite-type structure (A_2BX_4) that are 12-fold coordinated with anions. Lithium occupies the B site that are octahedrally coordinated with anions. The coordination environment around lithium ions continuously changes with a change in the O/ H^- ratio. The four axial sites of the Li-anion octahedra (anion sites in Li-anion planes perpendicular s -axis) prefer to be occupied by H^- .

2. High-Performance of Li-Rich Layered Cathode Materials through Combination of Al_2O_3 -Based Surface Modification and Stepwise Pre-Cycling⁴⁾

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 $\text{Li}[\text{Li}_{0.2}\text{Ni}_{0.18}\text{Co}_{0.03}\text{Mn}_{0.58}]\text{O}_2$ 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 $\text{LiM}_{1-x}\text{Al}_x\text{O}_2$ ($M = \text{transition metals}$) interlayer was formed between the modification layer and the $\text{Li}[\text{Li}_{0.2}\text{Ni}_{0.18}\text{Co}_{0.03}\text{Mn}_{0.58}]\text{O}_2$ 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-inset/de-insertion process (stepwise precycling treatment) and the surface-modification.

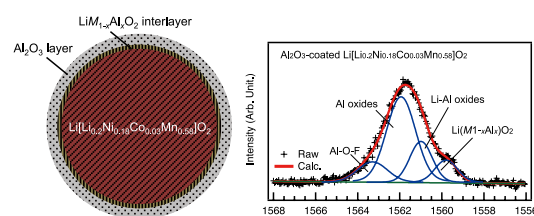


Figure 3. Schematic illustration and Al $1s$ HAXPES spectra of the 2 wt% Al_2O_3 -coated $\text{Li}[\text{Li}_{0.2}\text{Ni}_{0.18}\text{Co}_{0.03}\text{Mn}_{0.58}]\text{O}_2$ particle. The observed data, the calculated results, and the background are shown as black crosses and red, blue, and green lines, respectively.

References

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- 2) 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).
- 3) G. Kobayashi, A. Watanabe, M. Yonemura, A. Kubota and R. Kanno, under revision.
- 4) A. Watanabe, M. Yonemura, Y. Imai, K. Suzuki, M. Hirayama, R. Kanno and G. Kobayashi, under revision.
- 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).