

# Study of Ion Conductive Materials for Novel Energy Storage/Conversion Devices

## Research Center of Integrative Molecular Systems Division of Trans-Hierarchical Molecular Systems



**KOBAYASHI, Genki**  
Research 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 Accosiate Professor, Institute for Molecular Science

### Awards

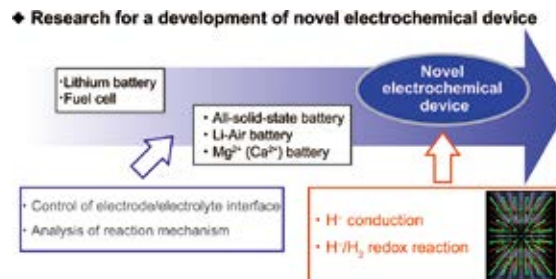
2010 ACerS Spriggs Phase Equilibria Award, American Ceramics Society  
2011 Tejima Doctoral Dissertation Award, Tokyo Institute of Technology

### Member

Graduate Student  
WATANABE, Akihiro\*  
Technical Fellow  
IMAI, Yumiko  
KUBOTA, Akiko  
Secretary  
KAWAI, Shigeko

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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. Ion conductive materials are used as electrodes or solid electrolytes, and are key for determining the performance of these devices. Therefore, much better understanding characteristics of existing electrodes/electrolytes materials such as crystal structure, thermal stability and their reaction mechanism is important for achieving enhancement of battery performances. On the other hand, finding novel ion conduction phenomena through synthesis of a new class of substances leads to a creation of new battery systems. Our group focuses mainly on two research topics; (i) Control of an electrode/electrolyte interface in lithium secondary batteries for enhancement of battery performance (ii) Synthesis of new materials possessing a hydride ion ( $H^-$ ) conductivity and development of a novel battery system utilizing the  $H^-$  conduction phenomenon and  $H^-/H_2$  redox reaction.



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

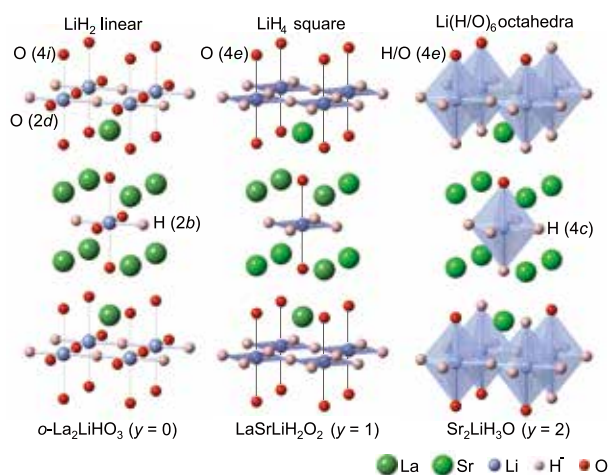
### Selected Publications

- 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  $Li_xFePO_4$  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, I. Tanaka and R. Kanno, under revision (2015).
- 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 $\text{H}^-$ Conductive Oxyhydrides<sup>1)</sup>

Indeed,  $\text{H}^-$  conduction is particularly attractive for electrochemical devices such as fuel cells and batteries, because  $\text{H}^-$  has an ionic radius suitable for fast ion conduction and a strong reducing ability. The standard redox potential of  $\text{H}^-/\text{H}_2$  ( $-2.3$  V) is comparable with that of  $\text{Mg}/\text{Mg}^{2+}$  ( $-2.4$  V); thus, effective utilization of the  $\text{H}^-$  conduction phenomenon and the  $\text{H}^-/\text{H}_2$  redox reaction may be promising for application in new energy storage/conversion devices with high energy densities.

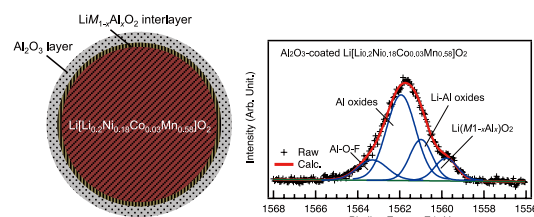
Here, we succeeded in the synthesis of a novel oxyhydride ( $\text{La}_{2-x-y}\text{Sr}_{x+y}\text{LiH}_{1-x+y}\text{O}_{3-y}$ ) with a wide composition range and provide the first conclusive evidence of a pure  $\text{H}^-$  conduction phenomenon in oxide-based materials (Figure 2). Furthermore, the capability of this oxyhydride as a solid electrolyte was confirmed by discharging reaction of the all-solid-state  $\text{H}^-$  cell.  $\text{H}^-$  conductors are the new frontier materials in the research field of solid-state ionics and electrochemistry. We anticipate that our results provide a completely novel approach for the effective use of hydrogen in a range of devices.



**Figure 2.** Crystal structures of  $\text{La}_{2-x-y}\text{Sr}_{x+y}\text{LiH}_{1-x+y}\text{O}_{3-y}$  ( $x, y = 0, 1, 2$ ). Lanthanum (and strontium) ions occupy the A sites of the layered perovskite-type structure ( $\text{A}_2\text{BX}_4$ ) 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/ $\text{H}^-$  ratio. The four axial sites of the Li-anion octahedra (anion sites in Li-anion planes perpendicular  $s$ -axis) prefer to be occupied by  $\text{H}^-$ .

## 2. High-Performance of Li-Rich Layered Cathode Materials through Combination of $\text{Al}_2\text{O}_3$ -Based Surface Modification and Stepwise Pre-Cycling<sup>2)</sup>

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  $\text{Al}_2\text{O}_3$ -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  $\text{Al}_2\text{O}_3$ . A discharge capacity of more than  $310 \text{ mA h}^{-1}$  and excellent cycling stability at  $50^\circ\text{C}$  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%  $\text{Al}_2\text{O}_3$ -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

- 1) G. Kobayashi, Y. Hinuma, S. Matsuoka, A. Watanabe, M. Iqbal, M. Hirayama, M. Yonemura, I. Tanaka and R. Kanno, under revision.
- 2) 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).

\* carrying out graduate research on Cooperative Education Program of IMS with Tokyo Institute of Technology