Highlight of the ICC-IMR Integrated Project on

"Mobility and Bonding State in Complex Hydrides"

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Lithium borohydride $Li(BH_4)$ is one of the complex hydrides [1-4] showing the high-density hydrogen storage property, and also exhibits lithium fast-ion mobility (conductivity) as a novel chemical property. The lithium ion conductivity of $Li(BH_4)$ jumps by three orders of magnitude at approximately 390 K due to its structural transition from the orthorhombic room-temperature (RT) phase to the hexagonal high-temperature (HT) phase [5-6]. Although a wide variety of inorganic lithium ion conductors such as oxides and sulfides have been reported, no lithium fast-ion conductor of hydride except $Li(BH_4)$ has been found since the report of $Li_2(NH)$ in 1979. The search and development of the lithium fast-ion conductors is significantly important because they are possibly expected to be applied to solid electrolytes for all solid-state safety lithium ion batteries. From an application point of view, it is highly desired to enhance the lithium ion conductivity of $Li(BH_4)$-based materials at RT.

During the project period, we have successfully demonstrated the "enhanced conductivities in $Li(BH_4)$–Li*X* (*X* = Cl, Br and I) [7-9] and $Li(BH_4)$–$Li(NH_2)$ [10]" for the first time. In $Li(BH_4)$–LiI, for example, the HT phase of $Li(BH_4)$ can be stabilized even at RT by forming the solid-solutions in the wide composition range, resulting in the lithium ion conductivity (4×10^{-5} S/cm) more than 3 orders of magnitude higher than that of pure $LiBH_4$ (2×10^{-8} S/cm) at RT. Also in the case of $Li(BH_4)$–$Li(NH_2)$, two stoichiometric compounds $Li_2(BH_4)(NH_2)$ and $Li_4(BH_4)(NH_2)_3$, show fast-ion conductivities of 1×10^{-4} S/cm at RT due to being provided new occupation sites for lithium ions. The results have been widely announced in the web of IMR: http://www.imr.tohoku.ac.jp/jpn/result/seika/2009.html#n14

In addition to the issue on fast-ion mobility, we have intensively studied the "specific surface bonding state in aluminum hydrides AlH_3 [11-12]", mainly viewpoint from the high-density hydrogen storage property.

Selected Publication List (as References for the Highlight)

[1] S. Orimo, Y. Nakamori, J.R. Eliseo, A. Züttel, C.M. Jensen:
Chemical Reviews, 2007, Vol. 91, 4111-4132.

[2] T. Matsunaga, F. Buchter, K. Miwa, S. Towata, S. Orimo, A. Züttel:
Renewable Energy, 2008, Vol. 33, 193-196.

[3] F. Buchter, Z. Łodziana, A. Remhof, O. Friedrichs, A. Borgschulte, Ph. Mauron, A. Züttel, D. Sheptyakov, G. Barkhordarian, R. Bormann, K. Chłopek, M. Fichtner, M. Sørby, M. Riktor, B. Hauback, S. Orimo:
The Journal of Physical Chemistry B, 2008, Vol. 112, 8042-8048.

[4] T. Matsunaga, F. Buchter, P. Mauron, M. Bielmann, Y. Nakamori, S. Orimo, N. Ohba, K. Miwa, S. Towata, A. Züttel:
Journal of Alloys and Compounds, 2008, Vol. 459, 583-588.

[5] M. Matsuo, Y. Nakamori, S. Orimo, H. Maekawa, H. Takamura:
Applied Physics Letters, 2007, Vol. 91, 224103(1)-(3).

[6] M. Matsuo, H. Takamura, H. Maekawa, H.-W. Li, S. Orimo:
Applied Physics Letters, 2009, Vol. 94, 084103(1)-(3).

[7] H. Oguchi, M. Matsuo, J.S. Hummelshøj, T. Vegge, J.K. Nørskov, T. Sato, Y. Miura, H. Takamura, H. Maekawa, S. Orimo:
Applied Physics Letters, 2009, Vol. 94, 141912(1)-(3).

[8] T. Ikeshoji, E. Tsuchida, K. Ikeda, M. Matsuo, H.-W. Li, Y. Kawazoe, S. Orimo:
Applied Physics Letters, 2009, Vol. 95, 221901(1)-(3).

[9] H. Maekawa, M. Matsuo, H. Takamura, M. Ando, Y. Noda, T. Karahashi, S. Orimo:
Journal of the American Chemical Society, 2009, Vol. 131, 894-895.

[10] M. Matsuo, A. Remhof, P. Martelli, R. Capputo, M. Ernst, Y. Miura, T. Sato, H. Oguchi, H. Maekawa, H. Takamura, A. Borgschulte, A. Züttel, S. Orimo:
Journal of the American Chemical Society, 2009, Vol. 131, 16389-16391.

[11] K. Ikeda, S. Muto, K. Tatsumi, M. Menjo, S. Kato, M. Bielmann, A. Züttel, C.M. Jensen, S. Orimo:
Nanotechnology, 2009, Vol. 20, 204004(1)-(4).

[12] S. Kato, M. Bielmann, K. Ikeda, S. Orimo, A. Borgschulte, A. Züttel:
Applied Physics Letters, in press.