"Complex hydrides" as a new class of solid electrolytes
—Fast cationic conduction studies and next-generation battery device applications—

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Complex Hydrides are characterized by complex anions with high hydrogen density (such as $[BH_4]^-$, $[AlH_4]^-$, and $[FeH_6]^{4-}$), which are formed by covalent bonding between hydrogen and its nearest neighboring atoms. The complex anions form stable crystal structures by ionically bonding with cations (such as Li^+, Na^+, and Mg^{2+}). In addition to the conventional property as reducing agents, complex hydrides have exhibited ***diverse energy-related functionalities*** such as high-density hydrogen storage, highly efficient microwave absorption, and fast cationic conduction. The last property has especially attracted great attention [1].

In 2007, we found the fast lithium conduction in complex hydrides, whose mechanism is now known to be very specific as follows: When heated to above 100°C, ***complex anions freely rotate*** (reorient) and then form lithium metastable sites that incorporate lithium carriers, leading to conductivities exceeding 1×10^{-3} S/cm (Fig. 1). Accordingly, by ***optimizing size, valence, structural symmetry, and the other properties of complex anions***, we drastically increased the sodium conductivity in *closo*-type complex hydrides with "cage-type" complex anions to approximately 2×10^{-2} S/cm [2,3]. These ***unprecedented material designs will increase the conductivity of various types of cations at room temperature***.

Regarding complex hydrides as the third class of solid electrolytes after oxides and sulfides, we have eagerly carried out industry-university collaborations on the material synthesis and device implementation (refer to the websites shown below). For example, Hitachi, Ltd. and our group succeeded in developing a ***high-thermally-durable all-solid-state lithium ion battery***. Furthermore, battery operations based on the *closo*-type complex hydrides, showing both higher conductivity and higher electrochemical stability, were recently demonstrated (Fig. 2). These Japan-led achievements have increased interest in ***on-board next-generation battery devices***, and highlighted the significance of academic research and social implementation of the complex hydrides.

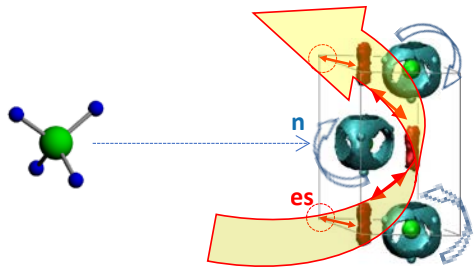

Fig. 1 Schematic of mechanism of fast lithium conduction in $LiBH_4$.

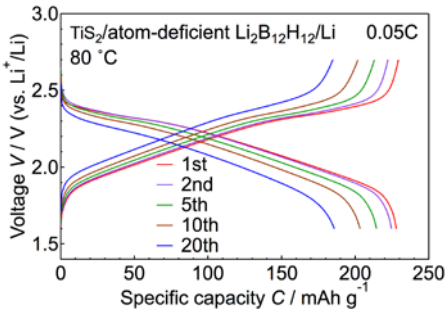

Fig. 2 Operation of an all-solid-state lithium ion battery based on a new *closo*-type complex hydride (Chem. Mater., in press).

[1] "The renaissance of hydrides as energy materials", R. Mohtadi, S. Orimo, Nature Rev. Mater. (2016).
Intense studies about hydrides reflecting recent hot topics including discovery of fast cationic conduction and superconductivity are broadly introduced. (Highly Cited Paper)

[2] "Exceptional superionic conductivity in disordered sodium decahydro-closo-decaborate",
T.J. Udovic, S. Orimo *et al*, Adv. Mater. (2014). (IF: 19.8)
Discovery of fast sodium conduction in complex hydrides with $[B_{10}H_{10}]^{2-}$ complex anion is reported.

[3] "Unparalleled lithium and sodium superionic conduction in solid electrolytes with large monovalent cage-like anions", W.S. Tang, A. Unemoto, S. Orimo *et al*, Energy Environ. Sci. (2015). (IF: 29.5)
Developments of a complex hydride lithium/sodium conductors with $[CB_{11}H_{12}]^-$ complex anion are discussed.

[Websites]
http://www.tohoku.ac.jp/japanese/2016/01/press20160120-01.html (Mitsubishi Gas Chemical - Tohoku Univ.)
http://www.hitachi.co.jp/New/cnews/month/2015/11/1112.html (Hitachi - Tohoku Univ.)