Closo-type complex hydrides with cage-type complex anions for all solid-state battery electrolytes

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Complex hydrides have recently attracted particular attention as a new class of solid electrolytes owing to their superior chemical/electrochemical stability against lithium metal, which results from their high reducing ability, as well as their high ionic conductivity [1]. Complex hydrides are generally denoted by $M(M'_xH_y)$, where M is a metal cation and M'_xH_y is a complex anion. Initial interest in complex hydride solid electrolytes has mainly focused on lithium borohydride ($LiBH_4$) and related derivative materials [2]. Recently, a series of *closo*-type complex hydrides containing cage-type complex anions such as $[B_{12}H_{12}]^{2-}$, $[CB_{11}H_{12}]^{-}$, and $[CB_9H_{10}]^{-}$ have been reported to exhibit high lithium-ion conductivities [3-4].

Despite their impressive ionic conductivities, the unique complex anion structure formed by strong covalent bonding between the boron and hydrogen atoms greatly complicate efforts to modify crystal structures, which are directly related to their ionic conductivities. For example, systematic cationic and/or anionic substitutions, which have been widely adopted to control the crystal structures (and thus ionic conductivities) of various ionic conductors, are largely inappropriate because the structural stabilities of complex anions are significantly lowered by such substitutions, leading to structural collapse. For these reasons, substitution of the complex anions themselves to form so-called mixed complex anions, has been explored, but usable candidates are very limited. Therefore, a more general approach is required to broaden the structure and conduction property scopes of complex hydrides.

In this study, we report an atom deficiency approach to enhance lithium-ion conductivity of *closo*-type complex hydrides [6]. We find that lithium and hydrogen could be simultaneously extracted from lithium dodecahydro-*closo*-dodecaborate ($Li_2[B_{12}H_{12}]$) by applying a small external energy, enabling the formation of atom deficiencies. These atom deficiencies lead to an increase in carrier concentration, improving lithium-ion conductivity by three orders of magnitude compared to that of a pristine material. An all solid-state TiS_2/Li battery employing atom-deficient $Li_2B_{12}H_{12}$ as a solid electrolyte exhibits superior battery performance during repeated discharge–charge cycles. The current study suggests that the atom deficiency can be a useful strategy to develop high ion-conducting complex hydride solid electrolytes.

References:

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