FAST SOLID-STATE LI-ION CONDUCTIVITY IN $LiBH_4$, FACILITATED BY A NEUTRAL MOLECULE

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The rapidly growing demand for safer and cheaper energy storage devices has spurred an increased interest in solid-state batteries. However, fast Li-ion conductivity at room temperature is a major challenge for utilization of such devices. Complex metal hydrides exhibit an extreme structural and compositional flexibility, and have recently received significant attention as solid-state electrolytes. $LiBH_4$ has been extensively investigated as a solid-state Li-ion conductor, and exhibit a high ionic conductivity of $\sigma(Li^+) > 10^{-3}$ S cm^{-1} in the high temperature polymorph above T ~117 °C.[1] Several approaches have been used to suppress the transition temperature to achieve a high ionic conductivity at room temperature, including anion-substitution with halides, mechanochemical treatment, mixing with nanoparticles or incorporation into scaffold materials.[2, 3]

Recently, a new class of superionic conductors has been discovered, where metal borohydrides with a neutral ligand exhibit a high cationic conductivity. Here we present the synthesis and characterization of the first metal borohydride with a methylamine ligand, lithium borohydride mono-methylamine, $LiBH_4{\cdot}CH_3NH_2$. This compound demonstrate the highest reported Li^+ conductivity of any $LiBH_4$-based compound with $\sigma(Li^+) = 1.24{\cdot}10^{-3}$ S cm^{-1} at room temperature, which is five orders of magnitude higher than $LiBH_4$. The crystal structure is solved *ab initio* from powder X-ray diffraction data, revealing a new structural prototype built from two-dimensional layers held together by hydrophobic interactions. The layers contain large voids, which can accommodate an interstitial Li^+ migrating in a two-dimensional conduction network.

Electrochemical characterization revealed an oxidative stability of ~2.1 V vs. Li and reversible plating/stripping on a Mo-electrode. The first proof-of-concept solid state battery with $LiBH_4$ coordinated to a neutral ligand was demonstrated with a TiS_2 cathode, reaching a maximum discharge capacity of 69 mAh/g at 30 °C. An oxidative degradation is observed at >2.1 V, which was suppressed using constant current/constant voltage charging, resulting in a high coulombic efficiency of ~ 98 %.

References

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