ChemComm

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Journal:	*ChemComm*
Manuscript ID	CC-COM-09-2015-007793.R1
Article Type:	Communication
Date Submitted by the Author:	20-Oct-2015
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Fast lithium-ionic conduction in a new complex hydride–sulphide crystalline phase

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

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A new crystalline phase derived from a 90LiBH$_4$:10P$_2$S$_5$ mixture displays high lithium-ionic conductivity of log(σ / S cm^{-1}) = –3.0 at 300 K. It is stable up to 473 K and has both a wide potential window of 0–5 V and favorable mechanical properties for battery assembly. Its incorporation into a bulk-type all-solid-state TiS$_2$/InLi battery enabled repeated battery operation at 300 K.

The all-solid-state battery promises flexible battery design (broader choice of electrodes[1] and bipolar structure[2]) that meets required energy and power densities and improved safety (by inhibiting lithium dendrite growth, leakage and vaporization of organic liquid electrolytes).[3] Thus, the all-solid-state battery is considered as one of the future-generation energy reservoirs for use in large-scale applications including vehicles, stationary uses for load levelling, and so forth.

Research and development efforts of solid-state electrolytes for all-solid-state batteries have so far been focused mainly on oxides and sulphides.[4–9] Despite extensive explorations of these classes of materials, those that allow for repeated battery operation are limited to a few materials. Thus, interest in looking beyond the traditional electrolytes to other unexplored classes of materials such as complex hydrides[10] to achieve higher-performance batteries is growing. Matsuo et al. discovered fast lithium-ionic conduction in the high-temperature phase of LiBH$_4$ (HT-LiBH$_4$) accompanied by an order–disorder transition at around 390 K.[11] Since then, numerous complex hydride-based solid-state fast-ion conductors have been discovered,[12,13] some allowing for repeated all-solid-state battery operation.[14–19]

Despite their advantages for use in all-solid-state batteries, including nearly unity ion transport numbers, high-temperature durability, a wide potential window, high compatibility with reactive metallic electrodes and favorable mechanical properties for battery assembly,[13] fast-ion conductors comprised solely of complex hydrides discovered thus far exhibit structural-disorder-induced fast-ion conduction at transition temperatures generally higher than room temperature.[12,13,20,21] Realizing fast-ion conduction at reduced temperatures, especially below room temperature, is therefore urgently required.

High reorientational mobility of the complex anion, [BH$_4$]$^-$, in HT-LiBH$_4$ allows for inducing ionic carriers and lithium-ion transport channels in the LiBH$_4$ crystal lattice, and thereby fast lithium-ionic conduction takes place.[22–24] A recent theoretical study revealed that site-to-site lithium-ion migration is accompanied by rearrangements of the hydrogen coordination number to Li$^+$ mobile species.[25] Maekawa et al. were able to stabilize the HT-LiBH$_4$ phase down to room temperature by partial replacement of [BH$_4$]$^-$ by iodide ions, I$^-$. A larger activation energy, E_a, of 0.56 eV for Li$_4$(BH$_4$)$_3$I (compared to 0.53 eV for HT-LiBH$_4$)[11] reduced the ionic conductivity, σ, at 300 K to log(σ / S cm^{-1}) = –4.7.[26] Thus, a lower E_a is needed to maintain fast-ion conduction at reduced temperatures. More recently, Yamauchi et al. formed a fast lithium-ionic conductor by dispersing a small concentration of LiBH$_4$ into a 75Li$_2$S–25P$_2$S$_5$ glass matrix. It possesses the high lithium-ionic conductivity of log(σ / S cm^{-1}) = –2.8 at 298 K with a reduced E_a of 0.22 eV. The high conductivity and reduced E_a were attributed to a delocalized charge on the reorienting [BH$_4$]$^-$-unit within the glass matrix, weakening the electrostatic interaction between Li$^+$ and [BH$_4$]$^-$.[27] These studies indicate that a search for other hybrid complex-hydride/sulphide materials would be beneficial for finding additional promising Li$^+$ conductors with low activation energies.

Here we report on a pseudo-binary system comprised of a complex hydride and sulphide, namely xLiBH$_4$–(100–x)P$_2$S$_5$ ($0 \le x \le 100$). Within this system, a new crystalline phase appeared for x = 90 (hereafter denoted by "90LiBH$_4$:10P$_2$S$_5$"). It possessed high lithium-ionic conductivity of log(σ / S cm^{-1}) = –3.0 at 300 K, a low activation energy of 0.38 eV without phase transition within a wide temperature range of 4–473 K, a wide potential window of 0–5 V, and favourable mechanical properties for battery assembly. These allowed for repeated discharge–charge cycles of a bulk-type all-solid-state TiS$_2$/Li battery at 300 K.

The powder X-ray diffraction (XRD) patterns of the pseudo-binary system, xLiBH$_4$–(100–x)P$_2$S$_5$, indicate that a new crystalline phase precipitated with the highest concentration when x = 90, 90LiBH$_4$:10P$_2$S$_5$ (see powder X-ray and neutron powder diffraction patterns in ESI, Fig. S1). Although by no means certain, the XRD patterns could be indexed to a possible orthorhombic structure. Relative losses of B and H throughout the synthesis (with approximately 30 % and 45 %, respectively, and H/B ~ 3.2) evaluated by means of neutron prompt gamma-ray activation

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† Electronic Supplementary Information (ESI) available: Experimental procedures and additional experimental results. See DOI: 10.1039/x0xx00000x

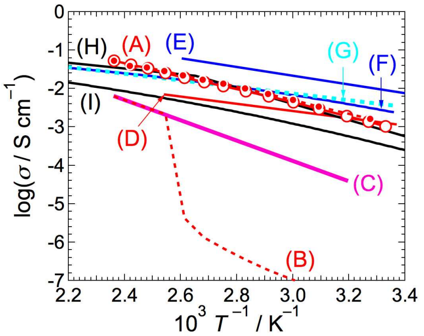

FIGURE 1. Lithium-ionic conductivities of (A) $90LiBH_4:10P_2S_5$, where closed and open symbols show the values obtained during heating and cooling runs, respectively. The conductivity is compared to other materials: (B) $LiBH_4$,[11] (C) $Li_4(BH_4)_3I$,[26] (D) 33LiBH$_4$–67(Li$_2$S–P$_2$S$_5$ glass),[27] (E) $Li_{10}GeP_2S_{12}$,[5] (F) $Li_7P_3S_{11}$ glass-ceramics,[6] (G) $Li_{0.325}Ge_{0.25}P_{0.75}S_4$ (thio-LISICON),[7] (H) $Li_{0.34}La_{0.51}TiO_{2.94}$,[8] and (I) $Li_7La_3Zr_2O_{12}$.[9]

analysis (PGAA), and neutron vibrational (NV) spectra of $90^7Li^{11}BH_4:10P_2S_5$ suggest that some or all of the original $[BH_4]^-$ ions may be transformed to $–BH_3$, $=BH_2$, and/or $\equiv BH$ fragments as part of a larger unknown complex anion (see NV spectra and elastic incoherent structure factor dependence on momentum transfer in ESI, Figs. S2 and S3, respectively). Differential scanning calorimetry (DSC) suggests that the new phase is stable upon cycling from room temperature to 473 K (see DSC profile in ESI, Fig. S4).

The pseudo-binary xLiBH$_4$–(100–x)P$_2$S$_5$ had the greatest conductivity regardless of the temperature, and the lowest E_a for x = 90, i.e., $90LiBH_4:10P_2S_5$ (also see the conductivities of xLiBH$_4$–(100–x)P$_2$S$_5$ in ESI, Fig. S5). DC measurements with symmetric cell configurations identified that the major carriers in $90LiBH_4:10P_2S_5$ were the lithium-ions (see ESI, Fig. S6). The lithium-ionic conductivity of $90LiBH_4:10P_2S_5$ at 300 K was as high as $\log\{\sigma$ (300 K)$\}$ = –3.0, and E_a was 0.38 eV (compared to 0.53 eV for HT-LiBH$_4$), as shown in Fig. 1.[11] The ionic conductivity and activation energy are comparable to $Li_{0.34}La_{0.51}TiO_{2.94}$.[8] Contrary to pure LiBH$_4$,[11] a conductivity jump accompanied by a structural transition was not observed within the studied temperature range (also see DSC profiles in ESI, Fig. S4). Although we explored within the pseudo-ternary system, LiBH$_4$–P$_2$S$_5$–Li$_2$S, no other new crystalline phase appeared by means of our synthetic route employed here (see conductivities in ESI, Figs. S7).

Owing to the complexity of the $90LiBH_4:10P_2S_5$ crystal chemistry, further investigations are required to solve its structure. On the other hand, fast-ion conduction in the complex hydrides is known to be associated with a high reorientational mobility for the resident anions, as seen for the high-temperature phases of LiBH$_4$,[22–25] $Na_2B_{12}H_{12}$[20] and $Na_2B_{10}H_{10}$.[21] We thus decided to investigate the dynamics of the hydrogen-containing anionic units in $90^7Li^{11}BH_4:10P_2S_5$ by means of quasielastic neutron scattering (QENS). Elastic-scattering fixed-window scans (FWSs)[28] for $90^7Li^{11}BH_4:10P_2S_5$ and $^7Li^{11}BH_4$ are shown in Fig. 2. A comparison of the relative decreases in intensity with temperature suggest that about one-fourth to one-third of the H atoms in $90LiBH_4:10P_2S_5$ are "reorientationally immobile" ($<10^8$ H jumps s^{-1}) on the neutron timescale up to at least 350 K. Different scenarios could explain this, e.g., by the presence of a mixture of (mobile) $[BH_4]^-$ anions and (immobile) $=BH_2$ fragments. The momentum-transfer dependences of the quasielastic fraction (see ESI, Fig. S3) and widths are consistent with this observation and suggest localized 2 Å H jumps, in agreement with the H-H distances in both $[BH_4]^-$ and $–BH_3$. The QENS spectrum at 300 K in Fig. 2 hints that there are two different quasielastic components of comparable intensities from two hydrogenous entities. The different widths (and thus reorientational mobilities) correspond to relative jump frequencies of the order of 10^{11} and 6×10^{11} s^{-1}. Although these values are reminiscent of what is observed for the relative $[BH_4]^-$ mobilities in orthorhombic and HT-LiBH$_4$,[29] we will not know the true nature of these mobile species until we are able to determine the corresponding crystal structure. Nonetheless, we may reasonably speculate that these high anion-related mobilities are a factor in promoting the fast-ion conductivity.[20–25]

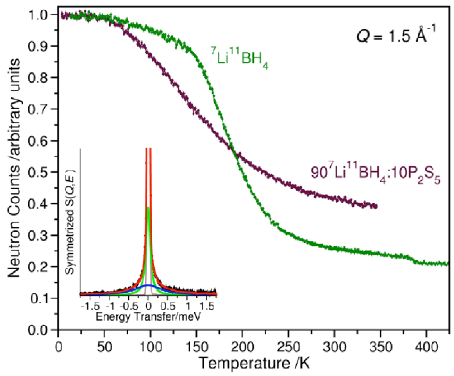

FIGURE 2. Neutron FWSs at +0.25 K min^{-1}, 0.8 μeV fwhm resolution, and 1.5 Å^{-1} neutron momentum transfer for $90^7Li^{11}BH_4:10P_2S_5$ and $^7Li^{11}BH_4$. Inset: corresponding 300 K QENS spectrum for $90^7Li^{11}BH_4:10P_2S_5$, fit with a resolution function (brown) and two Lorentzian components (green+blue).

Our new $90LiBH_4:10P_2S_5$ electrolyte had a wide potential window of 0–5 V at 300 K. In a cyclic voltammogram, reversible lithium dissolution/striping took place at nearly 0 V and no irreversible oxidation current was observed up to 5 V on the stainless-steel (SUS) electrode (see CV profile in ESI, Fig. S8). Thus, this new material has sufficient electrochemical stability to be incorporated into an all-solid-state battery.

High deformability of the constituent materials is also one of the important requirements for the "bulk-type" all-solid-state battery assembly,[30] which contains a high quantity of electrode-active materials in the electrode layer. Our $90LiBH_4:10P_2S_5$ consists of the highly deformable complex hydride[13,17,18] and sulphide.[30] It enables preparation of the compacted electrolyte and its intimate contact with the TiS_2 active material in the composite positive electrode layer merely by cold-pressing (see microstructure image of composite positive electrode layer in ESI, Fig. S9). Such a robust interface facilitates smooth charge transfer between layers during battery operation.[13,17–19,30]

As we expected, repeated operation of the bulk-type all-solid-state TiS_2/InLi battery with the $90LiBH_4:10P_2S_5$ electrolyte was successfully realized at 300 K and 0.1 C (114 μA cm^{-2}), as shown in Fig. 3 (the electrolyte thickness was 500 μm). TiS_2 has a theoretical capacity of 239 mAh g^{-1}.[31] Our battery exhibited initial and second

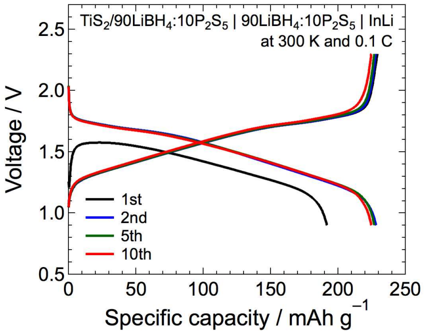

FIGURE 3. Discharge–charge profiles of the bulk-type all-solid-state TiS_2/InLi battery using the 90$LiBH_4$:10P_2S_5 electrolyte operated at 300 K and 0.1 C (114 μA cm^{-2}).

discharge capacities of 192 and 228 mAh g^{-1}, respectively. The reversible specific capacities with nearly 100 % coulombic efficiency were realized after the initial cycle (also see the battery test result with a different battery configuration, Fig. S11). As a result, the 10th discharge capacity retention ratio (to the 2nd discharge) remained as high as 98 %. We are currently evaluating, in more detail, cycle stability as well as power density of bulk-type all-solid-state batteries using this new 90$LiBH_4$:10P_2S_5 electrolyte.

In conclusion, a new crystalline, fast lithium-ionic conductor, 90$LiBH_4$:10P_2S_5, comprised of the complex hydride and sulphide was discovered in this study. Its fast lithium-ionic conduction may be assisted by the high reorientational mobility associated with the anions, similar to other complex hydride-based, solid-state, fast ionic conductors.[11,20,21] Unlike electrolytes comprised solely of complex hydrides,[11,20,21] no phase transition was observed in the wide temperature range of 4–473 K, and thereby a high lithium ionic conductivity, $\log(\sigma$ / S $cm^{-1}) = -3.0$ at 300 K was realized. The new phase also possesses a wide potential window of 0–5 V and high temperature durability up to 473 K. Highly deformable 90$LiBH_4$:10P_2S_5 allowed for assembling a bulk-type all-solid-state TiS_2/InLi battery merely by cold-pressing. Repeated operation of this battery was demonstrated at 300 K. The results obtained in this study provide principles for exploring new electrolytes for high-performance, all-solid-state, energy-storage devices.

The authors would like to thank Mr. K. Sato, Ms. H. Ohmiya and Ms. N. Warifune for technical assistances. Fruitful discussion and collaboration with Mr. G. Nogami and Dr. M. Taniguchi of Mitsubishi Gas Chemicals Co., Ltd. is also acknowledged. This study was performed in part as collaboration between members of IEA HIA Task 32, Hydrogen-based Energy Storage. The authors gratefully acknowledge support from DOE EERE through Grant No. DE-EE0002978; the Target Project 4 of WPI–AIMR, Tohoku University; the Integrated Materials Research Centre for the Low-Carbon Society (LC–IMR), Tohoku University; JSPS KAKENHI Grant No. 25220911; and the Advanced Low Carbon Technology Research and Development Program (ALCA) from the Japan Science and Technology Agency (JST).

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