

Supplementary Information

The *In-situ* Formation of an Electrolyte via the Lithiation of $\text{Mg}(\text{BH}_4)_2$ in an All-solid-state Lithium Battery

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Experimental

Material synthesis

All operations were carried out in a glove box filled with Ar gas. Commercially available LiBH_4 ($\geq 95\%$, Sigma-Aldrich) was hand milled for 5 min before use. A sulfide-based solid electrolyte was synthesized by the continuous ball milling (370 rpm) of Li_2S (98%, Strem Chemicals, Inc.) and P_2S_5 (99%, Sigma-Aldrich) in an 80:20 molar ratio for 20 h to obtain $80\text{Li}_2\text{S} \cdot 20\text{P}_2\text{S}_5$ glass (LPS).^{13, 14} Milling was performed using a planetary-type mill (FRITSCH Pulverisette 6). The LiBH_4 and LPS samples prepared as above were subsequently used as solid electrolytes. Two composites containing $\text{Mg}(\text{BH}_4)_2$ (95%, Sigma-Aldrich) were also prepared, one containing a solid electrolyte and the other without the solid electrolyte. These materials were respectively obtained by the mechanical milling of $\text{Mg}(\text{BH}_4)_2$ with LiBH_4 and acetylene black (AB) in a 40:30:30 mass ratio or $\text{Mg}(\text{BH}_4)_2$ and AB in a 70:30 mass ratio at 400 rpm for 30 min. Each mixture was subsequently used as an electrode.¹⁵

Battery assembly

A coin cell set with a sleeve made out of poly(ether ether ketone) (EQ-PSC, AA Portable Power Corp.) was used to fabricate a battery having an inside diameter of 10 mm. Li foil (Honjo Metal Co., Ltd) was pressed by hand onto an SUS plate inside the cell as a counter electrode. Following this, a quantity of LiBH_4 was placed on the same Li foil and pressed at 255 MPa. Finally, a portion of either the $\text{Mg}(\text{BH}_4)_2 + \text{LiBH}_4 + \text{AB}$ or $\text{Mg}(\text{BH}_4)_2 + \text{AB}$ mixture was placed on top of the LiBH_4 layer and pressed at 382 MPa. A second all-solid-state battery was fabricated by hand pressing Li foil onto an SUS plate, after which In foil (Nilaco Co.) was hand pressed over top of the Li foil to produce a Li-In counter electrode. A quantity of the LPS was then placed on the Li-In foil and pressed at 127 MPa. Finally, a portion of the $\text{Mg}(\text{BH}_4)_2 + \text{AB}$ mixture was placed over top of the LPS layer and pressed at 255 MPa.

Herein, the batteries having Li/ LiBH_4 / $\text{Mg}(\text{BH}_4)_2 + \text{LiBH}_4 + \text{AB}$ (40:30:30 by mass), Li/ LiBH_4 / $\text{Mg}(\text{BH}_4)_2 + \text{AB}$ (70:30 by mass) and Li-In/LPS/ $\text{Mg}(\text{BH}_4)_2 + \text{AB}$ (70:30 by mass) structures are referred to as samples 1, 2 and 3, respectively. Sample 3 was prepared to provide evidence for the formation of LiBH_4 during the lithiation process, because it was challenging to remove the effect of the LiBH_4 in the solid electrolyte layer when obtaining nuclear magnetic resonance (NMR) spectra and X-ray diffraction (XRD) patterns.

Sample preparation for solid state NMR

Prior to acquiring solid state magic angle spinning (MAS) NMR spectra of the initial electrode materials, quantities of the $\text{Mg}(\text{BH}_4)_2 + \text{AB}$ (70:30 by mass) mixture and the LPS were hand milled for 5 min. In addition, pellets of these same materials in the discharged (lithiated) and charged (delithiated) states were milled by hand after extraction from the cell.

Electrochemical measurements

The discharge/charge properties of the batteries were examined using a galvanostat (Hokuto Denko Co.) at a current density of 0.5 mA/cm^2 and at 120°C , to obtain high ionic conductivity from the LiBH_4 . Samples 1 and 2 were assessed between 0.3 and 1.5 V (vs Li/Li⁺) while sample 3 was tested between 0.0 and 1.2 V (vs Li-In). The capacity of each device was calculated based on the mass of $\text{Mg}(\text{BH}_4)_2$ in the anode mixture, not including the masses of the solid electrolyte and AB. The capacity was also calculated based on the mass of anode mixture including $\text{Mg}(\text{BH}_4)_2$, the solid electrolyte and the AB.

Characterization

The crystal structures of the electrode mixtures at various stages during the discharge/charge process were determined based on *ex-situ* XRD analyses (MiniFlex600, Rigaku Corp.) using Cu-K α radiation at room temperature over the 2θ range of 10° to 60° at a scanning rate of $4^\circ/\text{min}$. The samples were sealed in an airtight holder with polyimide film to prevent any effects of ambient oxygen or moisture. Solid state MAS NMR spectra were acquired using a JNM-ECA400 (JEOL Ltd.) spectrometer with a 9.4 T magnetic field at frequencies of 58.9 and 128.3 MHz for ^6Li and ^{11}B single pulse experiments, respectively. The NMR spectrometer was equipped with a 4 mm MAS probe. In case of ^{11}B experiments, a B-free cap was adopted for the MAS probe. Samples were packed in ZrO_2 tubes and sealed with tight-fitting Kel-F caps in an Ar-filled glovebox, then spun at 10 kHz under dry N_2 gas at room temperature. The ^6Li chemical shifts were determined with reference to an aqueous 1.0 M LiCl solution, assigned a chemical shift of 0 ppm, while the ^{11}B chemical shifts were determined based on assigning a chemical shift of 19.5 ppm to a saturated aqueous H_3BO_3 solution.

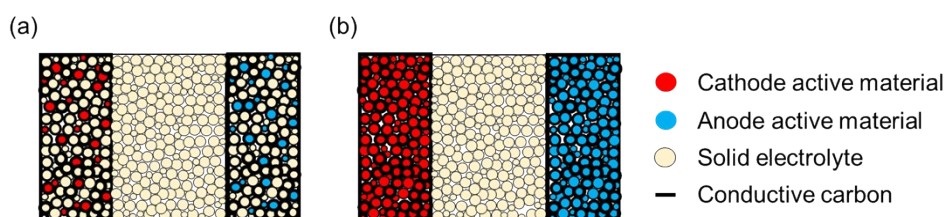


Figure S1. Diagrams of (a) a typical all-solid-state battery with electrodes consisting of an active material, solid electrolyte and conductive carbon and (b) a new all-solid-state battery with electrodes consisting only of an active material and a conductive aid, without a solid electrolyte.

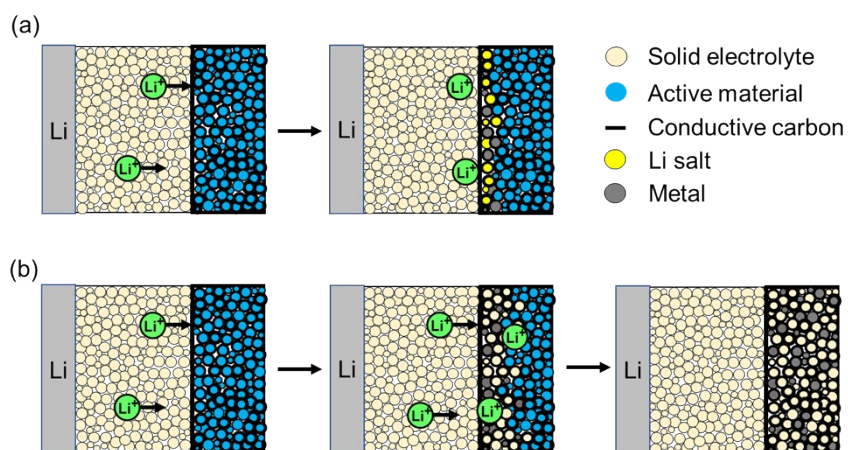


Figure S2. Diagrams showing the lithiation of an all-solid-state battery electrode without a solid electrolyte. (a) A typical active material reaction producing materials with low ionic conductivity and (b) the reaction of an active material that generates a solid electrolyte with high ionic conductivity *in-situ*.

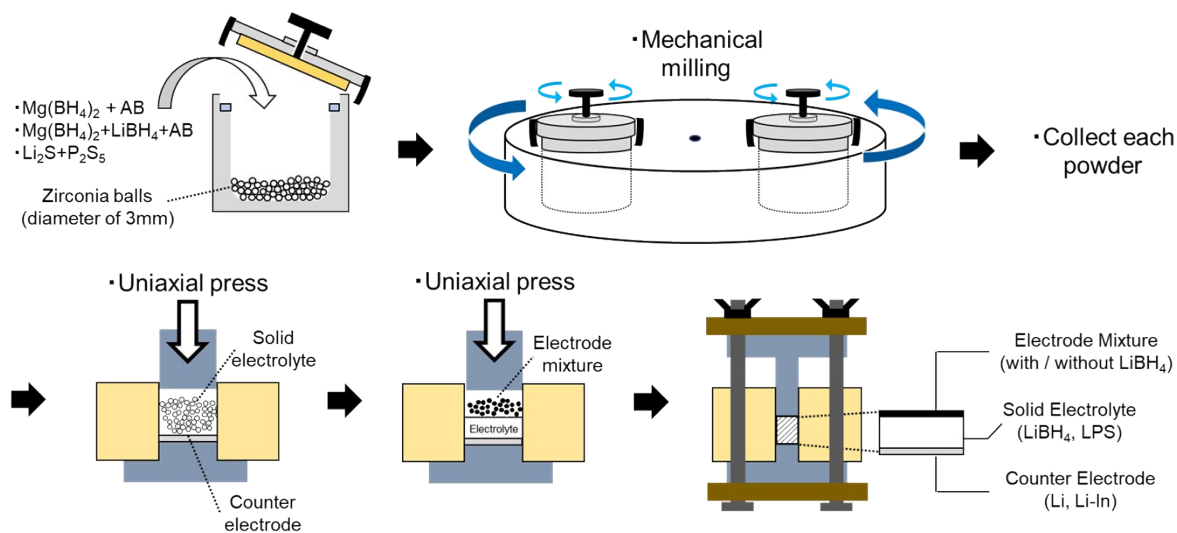


Figure S3. The detailed schematic diagram of the preparation of the electrode and cell.

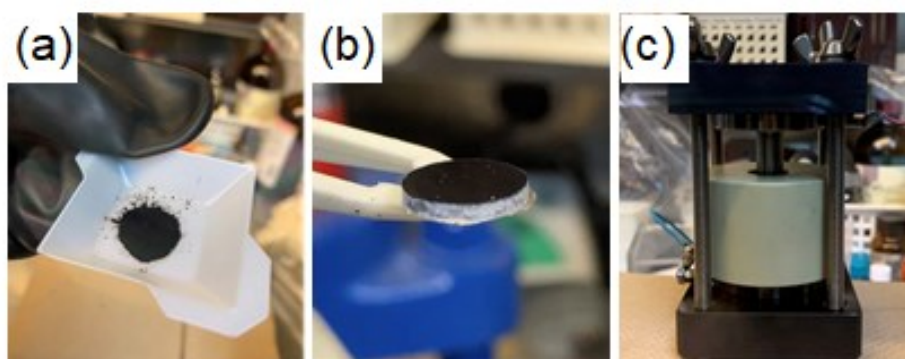


Figure S4. Photo images of (a) prepared powder of electrode mixture, (b) prepared cell ($\text{Li}/\text{LiBH}_4/\text{Mg}(\text{BH}_4)_2, \text{AB}$) and (c) Fabricated cell for evaluation of the solid-state cell.

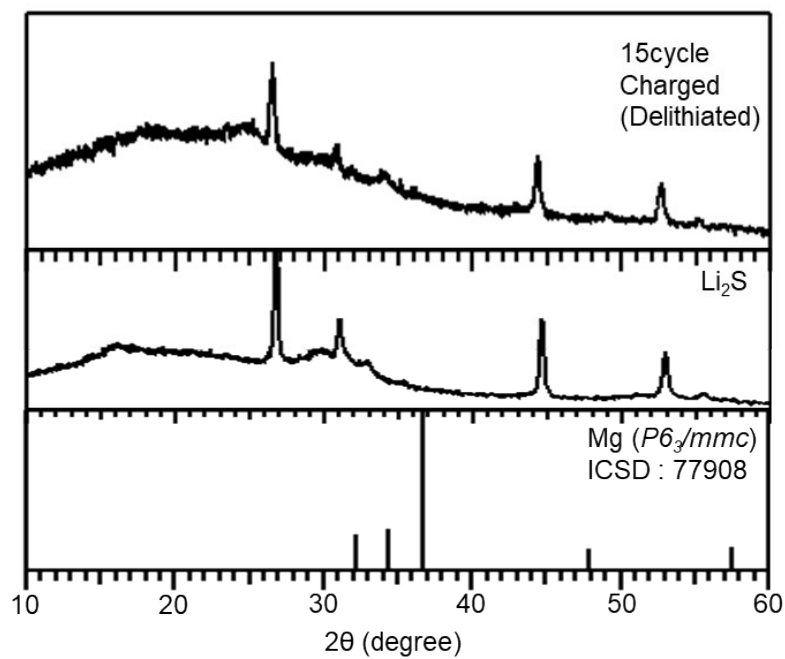


Figure S5. The *ex-situ* XRD patterns obtained from a $\text{Mg}(\text{BH}_4)_2$ -AB composite electrode after 15th cycles (charged state), together with reference ICSD patterns.

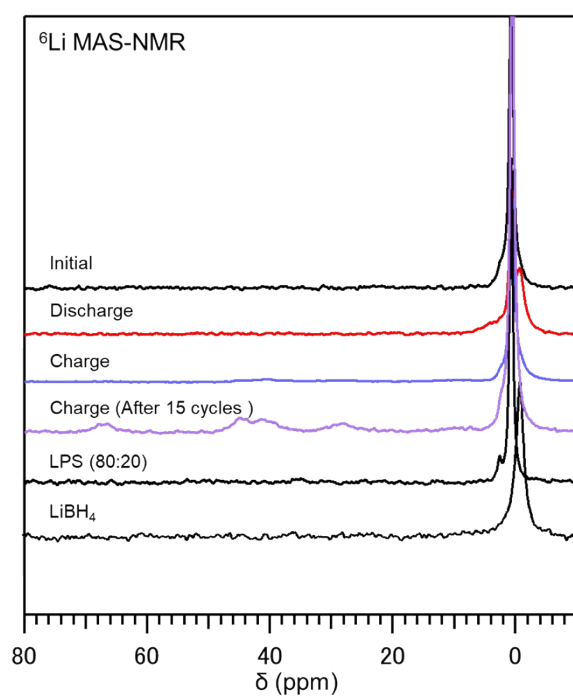


Figure S6. The solid state ^6Li MAS-NMR spectra of reagents and bilayer pellets ($\text{LPS}/\text{Mg}(\text{BH}_4)_2 + \text{AB}$ (70:30 by mass)) in the initial, 1st discharge, 1st charge and 15th charge states.

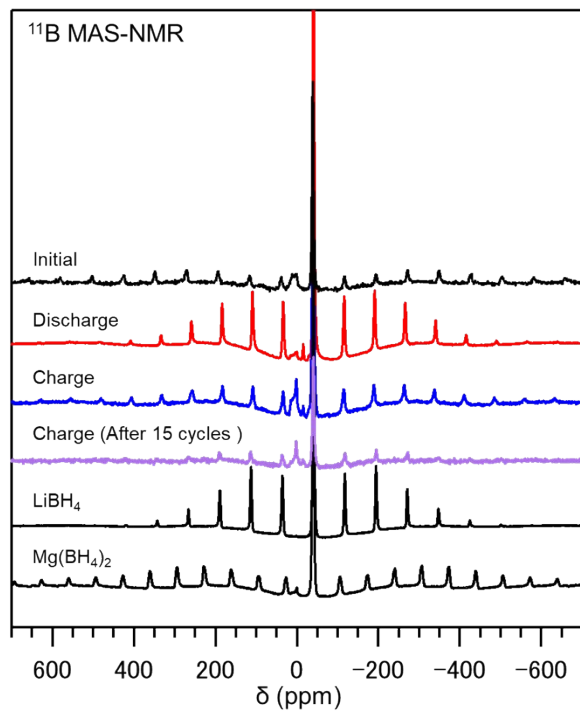


Figure S7. The solid state ^{11}B MAS-NMR spectra of reagents and bilayer pellets ($\text{LPS}/\text{Mg}(\text{BH}_4)_2 + \text{AB}$ (70:30 by mass)) in the initial, 1st discharge, 1st charge and 15th charge states over the full spectral window.

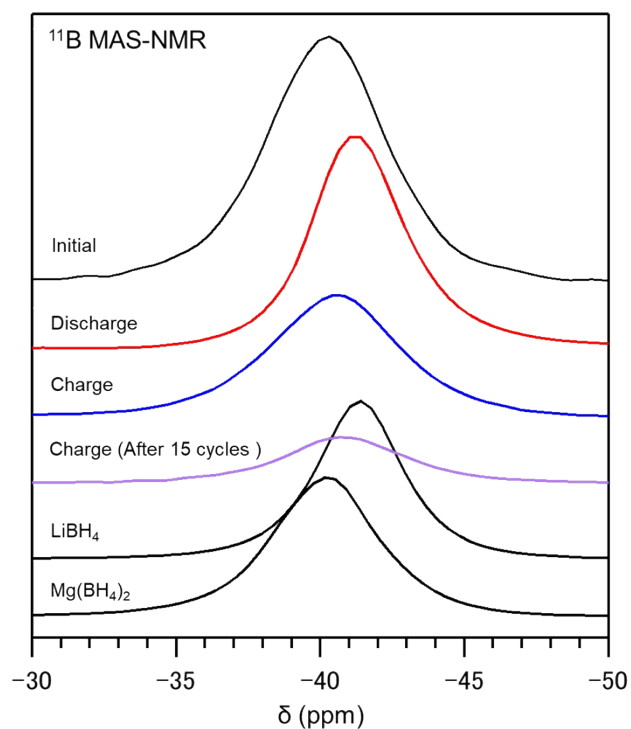


Figure S8. The expanded solid state ^{11}B MAS-NMR spectra of reagents and bilayer pellets ($\text{LPS}/\text{Mg}(\text{BH}_4)_2 + \text{AB}$ (70:30 by mass)) in the initial, 1st discharge, 1st charge and 15th charge states.

Table S1. Properties of $M(\text{BH}_4)_x$ -type active anode materials.

Active material	Theoretical capacity (mAh/g)
KBH_4	503
$\text{Ca}(\text{BH}_4)_2$	769
NaBH_4	721
$\text{Mg}(\text{BH}_4)_2$	993

Table S2. Proposed reactions of $\text{Mg}(\text{BH}_4)_2$ with Li.

Reaction	Theoretical capacity (mAh/g)
$\text{Mg}(\text{BH}_4)_2 + 8\text{Li}^+ + 8\text{e}^- \rightarrow 8\text{LiH} + 2\text{B} + \text{Mg}$	3970
$\text{Mg}(\text{BH}_4)_2 + 6\text{Li}^+ + 6\text{e}^- \rightarrow 6\text{LiH} + 2\text{B} + \text{MgH}_2$	2978
$\text{Mg}(\text{BH}_4)_2 + 4\text{Li}^+ + 4\text{e}^- \rightarrow \text{LiBH}_4 + 3\text{LiH} + \text{B} + 0.5\text{Mg} + 0.5\text{MgH}_2$	1985
$\text{Mg}(\text{BH}_4)_2 + 2\text{Li}^+ + 2\text{e}^- \rightarrow 2\text{LiBH}_4 + \text{Mg}$	993