

# Batteries & Supercaps

Supporting Information

## ***In situ* Electrolyte Design: Understanding the Prospects and Limitations of a High Capacity $\text{Ca}(\text{BH}_4)_2$ Anode for All Solid State Batteries**

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## EXPERIMENTAL SECTION

### Materials synthesis

The powdered starting materials,  $\text{LiBH}_4$  (95%, Sigma-Aldrich),  $\text{Ca}(\text{BH}_4)_2$  (95%, Sigma-Aldrich), AB (97%, Denka) and Boron (99%, Wako) were purchased and used without further purification. Two types of composite electrode materials (with or without  $\text{LiBH}_4$  electrolyte; hereafter named samples **1** and **2** respectively) were prepared by ball-milling. For the latter composite electrode without electrolyte included (sample **2**), a mixture of  $\text{Ca}(\text{BH}_4)_2$  and AB in a weight ratio of 70:30 was placed into a zirconia milling jar (45 ml) with zirconia balls (diameter: 3 mm) weighing 18 g (to give a ball:powder weight ratio of 36:1). The electrode mixture was milled at a rotation speed of 600 rpm for 2 h using a FRITSCH Pulvarisette 6 planetary mill. The composite electrode mixture including electrolyte (sample **1**) was prepared from  $\text{Ca}(\text{BH}_4)_2$ ,  $\text{LiBH}_4$  and AB with a weight ratio of 40:30:30. using otherwise the same milling conditions employed for sample **2**.

### Half cell assembly

Coin cells fitted with a polyether ether ketone (PEEK) sleeve were used in all electrochemical measurements. All-solid-state half cells were fabricated using a Li metallic disc counter electrode, a  $\text{LiBH}_4$  solid electrolyte layer and either composite electrode **1** or **2** with a weight of 6 mg. An Li metallic disc (Honjo Metal Co., LTD; diameter: 8 mm) was formed using a belt punch and was pressed by hand above a stainless steel (SS) plate (diameter: 10 mm). SS was used as the current collector. A layer of  $\text{LiBH}_4$  electrolyte was added and uniaxially pressed at 255 MPa. The respective composite electrodes were placed on top of the  $\text{LiBH}_4$  electrolyte and pressed at 318 MPa to complete the three-layered cell before sealing.

### Electrochemical measurements

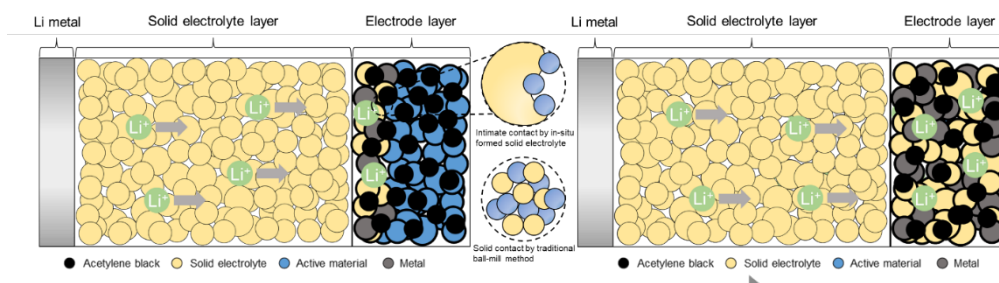
Each ASSB was charged and discharged galvanostatically at 120 °C using a Hokuto Denko-HJ1020mSD8 battery tester. Each cell was thus heated above the orthorhombic-hexagonal phase transition temperature of  $\text{LiBH}_4$  (using an electric furnace inside Ar globe box). All cycling was performed using a current density and voltage range of 0.5 mA  $\text{cm}^{-2}$  and 0.2-1.4 V (vs.  $\text{Li}/\text{Li}^+$ ) respectively.

### Characterization

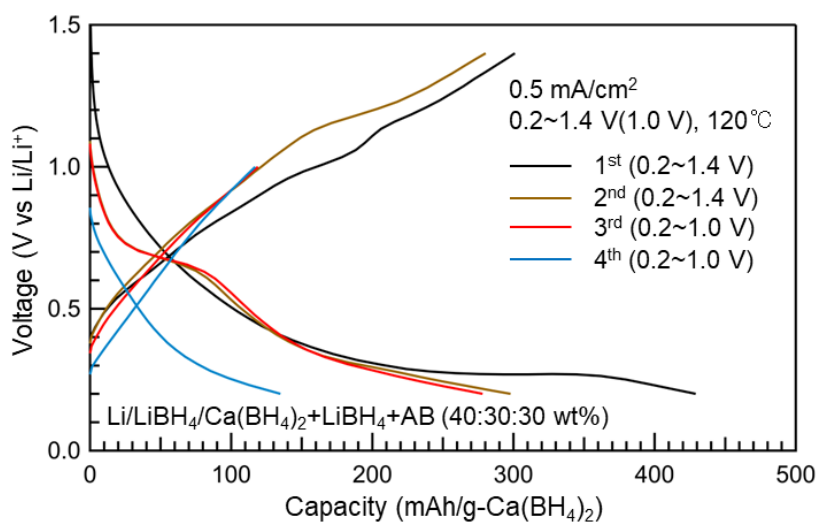
Measurements by *ex-situ* powder X-ray diffraction (XRD) (Rigaku RINT-TTRIII), magic angle spinning nuclear magnetic resonance spectroscopy (MAS NMR) (JNM-ECA400), extended X-ray absorption fine structure spectroscopy (EXAFS) (SAGA-LS BL12) and X-ray photoelectron spectroscopy (XPS) (JEOL JPS-9010MC/IV equipped with monochromatic Mg  $K\alpha$  radiation at 1253.6 eV) were performed at room temperature in order to identify the charge and discharge products and hence to assess the reaction mechanism of the  $\text{Ca}(\text{BH}_4)_2$ -based electrodes (The split in the binding energy between Ca  $2p_{1/2}$  and  $2p_{3/2}$  is 3.5 eV. The FWHM of the fitted doublets of different states are 2.26 eV (Initial and lithiated state) and 1.95 eV (delithiated state). The height ration between  $2p_{1/2}$  and  $2p_{3/2}$  is 0.51:1 ( $2p_{1/2} : 2p_{3/2}$ )). Subsequently, a series of cycling experiments were performed to investigate

the effect of electrode thickness on *in-situ* electrolyte formation. A selection of different composite electrode thicknesses was prepared by varying the total weight of the components (from 6 mg to either 20 mg or 30 mg). Otherwise, the same electrode configuration and charge-discharge conditions as above were employed. Since both  $\text{LiBH}_4$  and  $\text{Ca}(\text{BH}_4)_2$  are air- and moisture-sensitive, all operations (cell construction, charge-discharge measurement and other analyses were conducted under Ar atmosphere (dew point; lower than  $-80\text{ }^\circ\text{C}$ , oxygen; lower than 1 ppm))

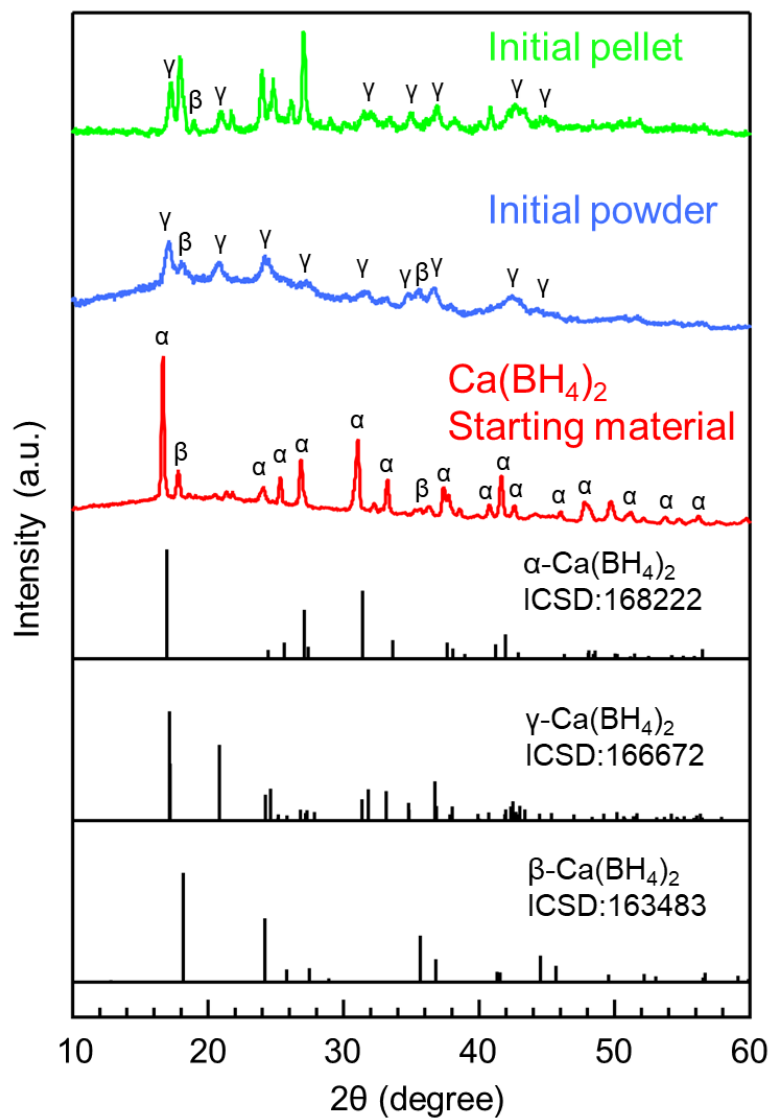
## ADDITIONAL FIGURES



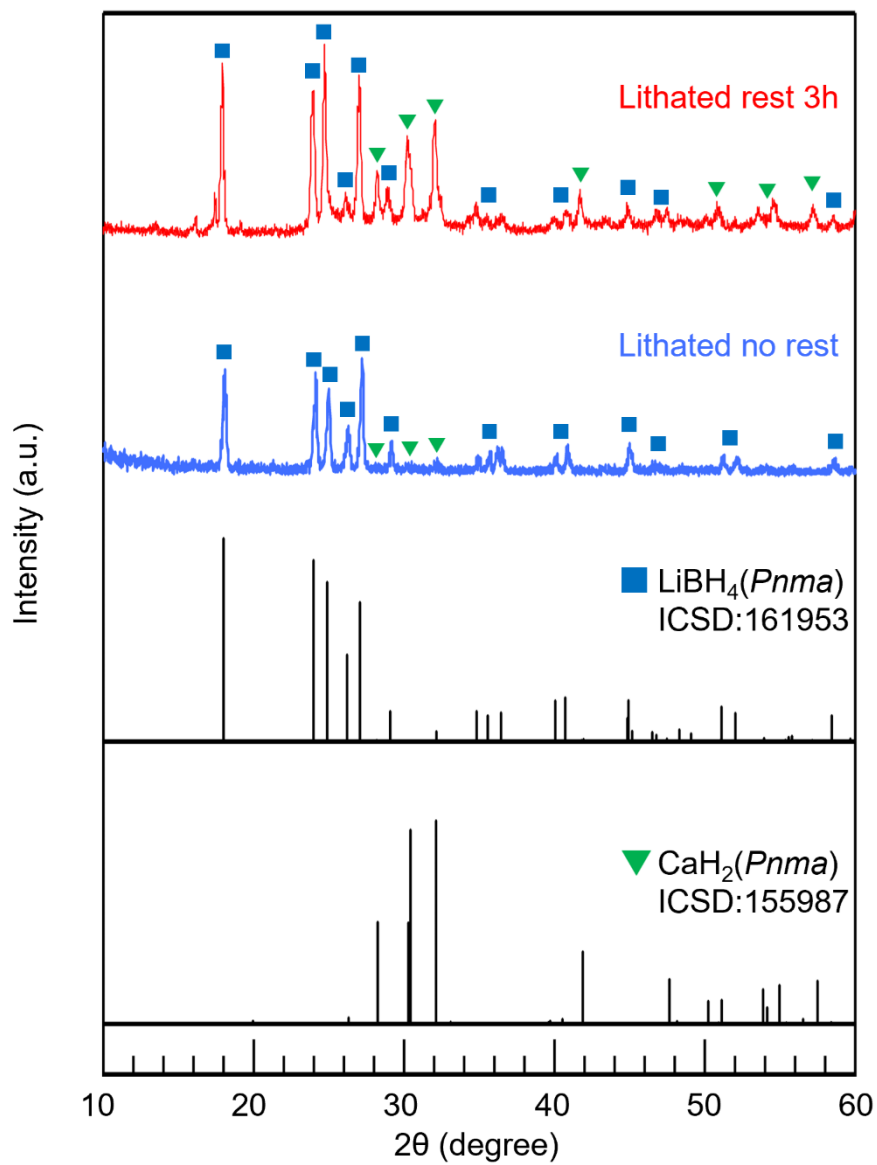
**Figure S1.** Schematic illustration of the solid electrolyte *in-situ* formation process in the electrode composite.



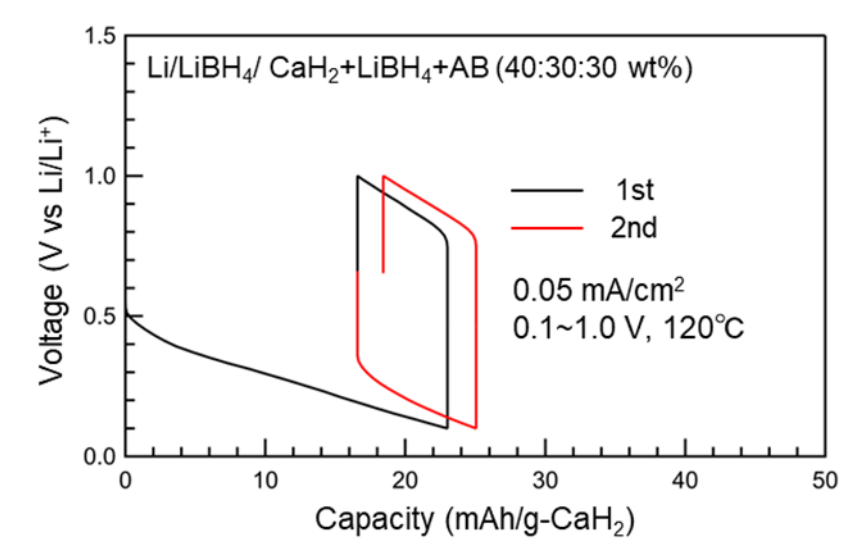
**Figure S2.** Charge-discharge voltage profiles of sample 1 (initially 40:30:30 wt.%  $\text{Ca}(\text{BH}_4)_2$ :  $\text{LiBH}_4$ : AB) with voltage ranges of 0.2~1.4 V and 0.2~1.0 V vs Li for cycles 1-2 and 3-4, respectively.



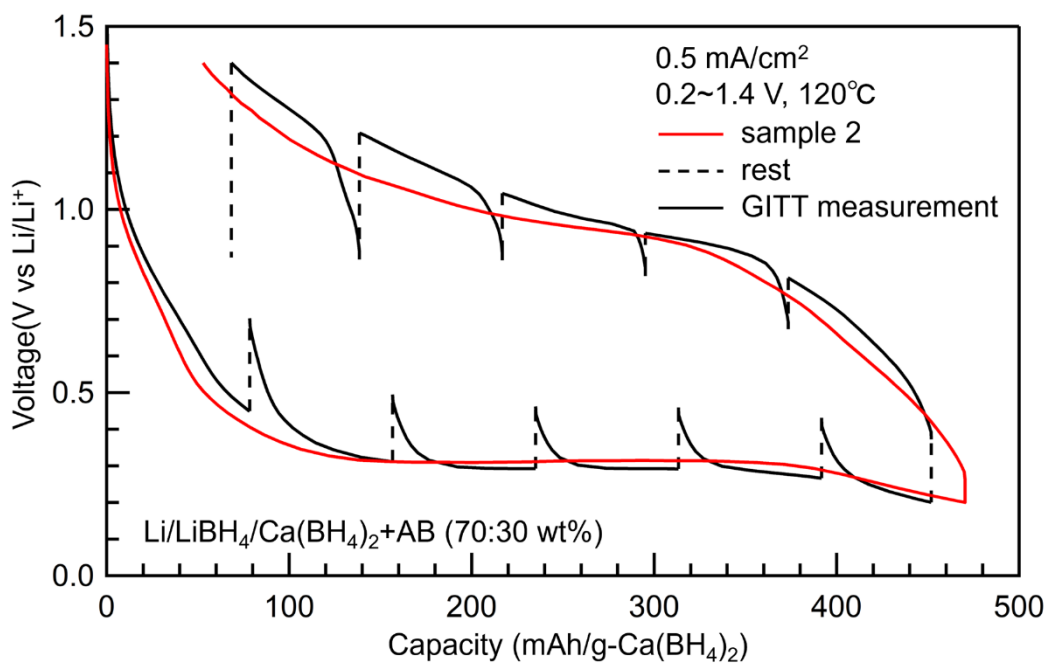
**Figure. S3** *Ex-situ* XRD patterns of: (a) the commercial  $\text{Ca}(\text{BH}_4)_2$  starting material; (b) the commercial borohydride powder following ball milling and (c) a pellet (formed from the milled powder). Patterns generated from ICSD entries for  $\text{Ca}(\text{BH}_4)_2$  phases are shown below and marked as  $\alpha$ :  $\alpha$ - $\text{Ca}(\text{BH}_4)_2$  (orthorhombic),  $\beta$ :  $\beta$ - $\text{Ca}(\text{BH}_4)_2$  (tetragonal),  $\gamma$ :  $\gamma$ - $\text{Ca}(\text{BH}_4)_2$  (orthorhombic).



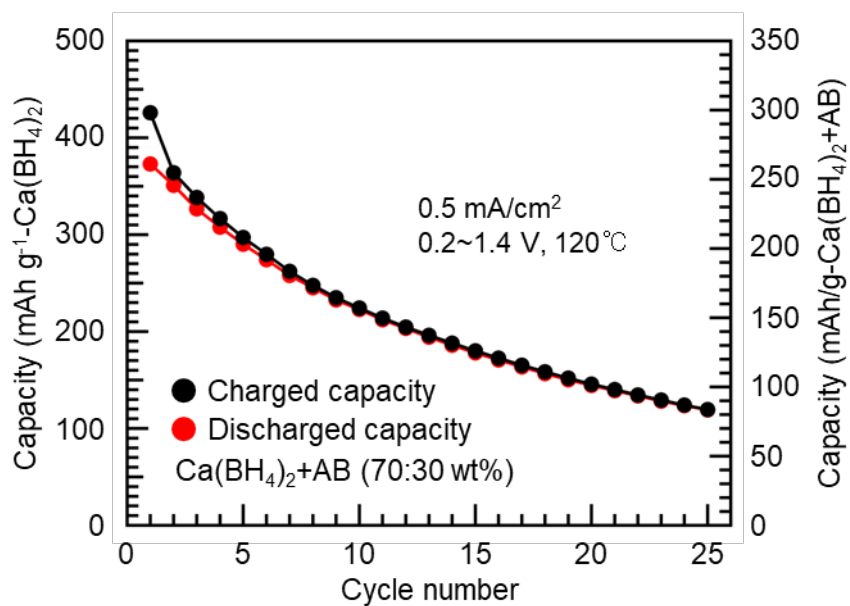
**Figure S4.** Comparison of *ex-situ* XRD patterns of sample 2 in the lithiated state with and without a “rest period” (3 h rest at open circuit voltage - OCV) between cycles. The CaH<sub>2</sub> peaks grow in relative intensity after the 3 h “rest period”.



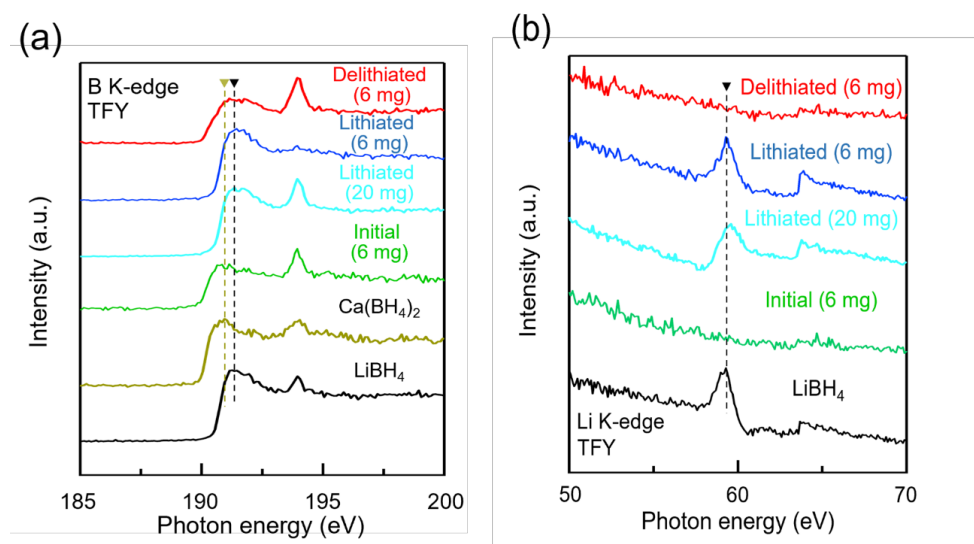
**Figure S5.** Charge-discharge voltage profiles of a  $\text{CaH}_2\text{-LiBH}_4\text{-AB}$  electrode composite (initially 40:30:30 wt.%  $\text{CaH}_2\text{:LiBH}_4\text{:AB}$ ).



**Figure S6.** GITT profiles of a  $\text{Ca(BH}_4)_2\text{-AB}$  composite electrode (2) following a 6 h "rest period" (black lines; constant current charge-discharge at  $0.5 \text{ mA cm}^{-2}$  for 50 min followed by application of an OCV for a "rest period" of 6 h). The discharge-charge curve for sample 2 without applying such a "rest period" is superimposed for comparison (red line).



**Figure S7.** The equivalent cycling performance of the  $\text{Ca}(\text{BH}_4)_2$ -AB composite electrode with a 290  $\mu\text{m}$  electrode layer over 25 cycles.



**Figure S8.** *Ex-situ* total fluorescence yield (TFY) mode EXAFS measurement of the  $\text{Ca}(\text{BH}_4)_2$ -AB composite electrodes (fabricated from electrode mixtures of 6 mg and 20 mg, respectively) in various charge states, showing: (a) B K-edge spectra (black dashed line:  $\text{LiBH}_4$ , green/yellow dashed line:  $\text{Ca}(\text{BH}_4)_2$ ) and (b) Li K-edge spectra (black dashed line:  $\text{LiBH}_4$ ).