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Electrochemical Oxidative Stability of Hydroborate-Based Solid-State Electrolytes

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ABSTRACT

We report a robust methodology based on linear sweep voltammetry to determine experimentally the electrochemical oxidative stability of hydroborate-based solid-state electrolytes for all-solid-state batteries. To accelerate kinetics and improve the sensitivity to decomposition, we explore different solid-state electrolyte/carbon composites and employ a low scan rate of $10 \mu\text{V s}^{-1}$. Using LiBH_4 as a model system, we show that proper selection of the conductive carbon and its ratio in the composite are important for an accurate determination of the intrinsic oxidative stability. This method is robust with respect to the choice of the current collector material and the ionic conductivity of the solid-state

electrolyte. The measured oxidative stability of LiBH_4 of 2.0 V vs. Li^+/Li is in good agreement with the value predicted by first principles calculations. The irreversible electrochemical decomposition of LiBH_4 outside the oxidative stability limit is independently confirmed by galvanostatic cycling. We apply this method to re-assess the electrochemical oxidative stability of selected, highly conductive hydroborate-based solid-state electrolytes, including $\text{Li}_2(\text{CB}_9\text{H}_{10})(\text{CB}_{11}\text{H}_{12})$, $\text{Na}_3(\text{BH}_4)(\text{B}_{12}\text{H}_{12})$, $\text{Na}_4(\text{B}_{12}\text{H}_{12})(\text{B}_{10}\text{H}_{10})$, and $\text{Na}_4(\text{CB}_{11}\text{H}_{12})_2(\text{B}_{12}\text{H}_{12})$, and emphasize the necessity of selecting cathode materials for all-solid-state batteries based on the accurate understanding of the oxidative stability of the solid-state electrolytes.

TEXT

Introduction

All-solid-state batteries, which employ solid-state electrolytes (SSEs) instead of liquid electrolytes, have recently drawn wide attention due to their potential for higher energy and power density and for a wider operating temperature range. These advantages arise from their high ion transference number, non-volatility, and improved thermal stability of SSEs.¹ Liquid-like ionic conductivity has been achieved in several material classes including sulfides, oxides, and hydroborates.^{2,3} Hydroborates are particularly interesting, because they combine (i) low gravimetric density, (ii) high thermal stability due to the strong covalency of their anions, and (iii) high deformability guaranteeing a robust ionic contact to the electrode materials.^{4,5} Superionic conduction ($\sigma_{\text{ion}} > 10^{-3} \text{ S cm}^{-1}$) in hydroborates was first discovered in the high-temperature (HT) phase of LiBH_4 above 110 °C and applied in prototype all-solid-state batteries.^{6,7} Lithium and sodium hydro-*closo*-borates ($[\text{B}_n\text{H}_n]^{2-}$) and hydro-*closo*-monocarbaborates ($[\text{CB}_{n-1}\text{H}_n]^-$) show even higher thermal stability and ionic conductivity in

their respective HT phases.^{8–11} The HT phase of hydroborates can be stabilized at lower temperatures by ball milling,^{12,13} partial dehydrogenation,¹⁴ nano confinement,^{15,16} or anion/cation substitution,^{17–27} which leads to the increase in the room-temperature ionic conductivity. For instance, $\text{Na}_4(\text{B}_{12}\text{H}_{12})(\text{B}_{10}\text{H}_{10})$ (also named $\text{Na}_2(\text{B}_{12}\text{H}_{12})_{0.5}(\text{B}_{10}\text{H}_{10})_{0.5}$ in literature), an equimolar mixture of $\text{Na}_2\text{B}_{12}\text{H}_{12}$ and $\text{Na}_2\text{B}_{10}\text{H}_{10}$, exhibits a room-temperature ionic conductivity of $10^{-3} \text{ S cm}^{-1}$ by stabilizing the HT phase of $\text{Na}_2\text{B}_{10}\text{H}_{10}$.²² This enabled a stable 3 V all-solid-state sodium battery with more than 85% capacity retention after 250 cycles at C/5.²⁸

Integrating SSEs into all-solid-state battery cells with high energy and power density, and long cycle life,²⁹ requires not only high ionic conductivity, but also a wide electrochemical stability window. SSEs with high oxidative stability facilitate the use of high-voltage cathodes that increase the battery's energy density. However, the experimental determination of the electrochemical stability window of SSEs is more challenging than that of liquid electrolytes due to the slow decomposition kinetics.^{30,31} One approach to circumvent this problem is to establish an interpenetrating network of ionic and electronic conduction pathways by forming a composite consisting of a SSE material and conductive carbon additives.³² This has proven to be a good solution for the soft sulfide-based SSEs, such as $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$, which can be compacted by simple cold pressing.^{32,33} For hard oxide-based SSEs, such as $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$, sintering at high temperatures is required to establish ionic contact between individual grains, making it more difficult to establish the electronic network.³²

The thermodynamic electrochemical stability window of various inorganic SSEs, including hydroborates, was predicted by first principles calculations using grand-potential phase diagram.^{29,32,34–39} The experimental proof of the electrochemical stability window of $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ agrees well with first principles computation.³² On the other hand, previous experimental estimations of the electrochemical oxidative stability of hydroborates are

inconsistent with computationally predicted values, claiming the oxidative stability beyond 5 V vs. Li^+/Li .^{14–16,20,23,27,40} Some of us measured anodic currents by linear sweep voltammetry on the nA scale and extracted an oxidative stability of ~ 3 V vs. Na^+/Na for $\text{Na}_4(\text{B}_{12}\text{H}_{12})(\text{B}_{10}\text{H}_{10})$.²² However, so far, none of the previous studies provides a comprehensive assessment of the oxidative stability of hydroborate-based SSEs measured under relevant and unified conditions.

Here we report a robust methodology to experimentally determine the electrochemical oxidative stability of the yet under-explored hydroborate-based SSEs by linear sweep voltammetry (LSV). Using LiBH_4 as a model material, we show in a systematic study that low scan rates and proper selection of the type and amount of conductive carbon additives are critical for an accurate determination of the intrinsic oxidative stability. The re-examined oxidative stability of LiBH_4 is in good agreement with the computationally predicted value. We also identify factors resulting in overestimation of the electrochemical stability in previous studies. We apply our methodology to re-assess the electrochemical oxidative stability of recently discovered, highly conductive hydroborate-based SSEs including $\text{Li}_2(\text{CB}_9\text{H}_{10})(\text{CB}_{11}\text{H}_{12})$, $\text{Na}_3(\text{BH}_4)(\text{B}_{12}\text{H}_{12})$, $\text{Na}_4(\text{B}_{12}\text{H}_{12})(\text{B}_{10}\text{H}_{10})$, and $\text{Na}_4(\text{CB}_{11}\text{H}_{12})_2(\text{B}_{12}\text{H}_{12})$.^{19,22–24}

Experimental Section

Commercial LiBH_4 (95%, Sigma-Aldrich) was ground for 15 min with mortar and pestle and used without further purification. $\text{Na}_3(\text{BH}_4)(\text{B}_{12}\text{H}_{12})$ and $\text{Na}_4(\text{CB}_{11}\text{H}_{12})_2(\text{B}_{12}\text{H}_{12})$ were prepared by ball milling and heat treatment as described elsewhere.^{23,24} $\text{Na}_4(\text{B}_{12}\text{H}_{12})(\text{B}_{10}\text{H}_{10})$ was prepared by a solution-based method.⁴¹ An equimolar mixture of as-purchased $\text{Na}_2\text{B}_{12}\text{H}_{12}$ (Katchem) and pre-dried $\text{Na}_2\text{B}_{10}\text{H}_{10}$ (Katchem) at 160 °C for 6 h under vacuum (10^{-3} mbar) was dissolved into anhydrous isopropanol (99.9%, VWR). Excess solvent was removed in a rotary evaporator. The obtained powder was further dried at 100 °C for 1 h under vacuum, and heat-treated at 180 °C for 4 h under vacuum.

Li₂(CB₉H₁₀)(CB₁₁H₁₂) was prepared in a similar way to Na₄(B₁₂H₁₂)(B₁₀H₁₀) with changes in drying conditions. LiCB₉H₁₀ (Katchem) and LiCB₁₁H₁₂ (Katchem) were pre-dried at 200 and 160 °C for 12 h under vacuum, respectively. The equimolar mixture of these two compounds after dissolution in anhydrous isopropanol and rotary evaporation was further dried 150 °C for 1 h under vacuum, and heat-treated at 200 °C for 4 h under vacuum. Five types of conductive carbon with different BET specific surface areas S_{BET} and densities ρ , i.e. Ketjenblack EC-600JD ($S_{\text{BET}} = 1362 \text{ m}^2 \text{ g}^{-1}$, $\rho_{\text{bulk}} = 0.11 \text{ g cm}^{-3}$), Super P ($S_{\text{BET}} = 58 \text{ m}^2 \text{ g}^{-1}$, $\rho_{\text{bulk}} = 0.16 \text{ g cm}^{-3}$, Imerys Graphite & Carbon), Super C65 ($S_{\text{BET}} = 60 \text{ m}^2 \text{ g}^{-1}$, $\rho_{\text{bulk}} = 0.16 \text{ g cm}^{-3}$, Imerys Graphite & Carbon), TIMREX KS6 ($S_{\text{BET}} = 16 \text{ m}^2 \text{ g}^{-1}$, $\rho_{\text{bulk}} = 0.07 \text{ g cm}^{-3}$, Imerys Graphite & Carbon), and mesocarbon microbeads (MCMB, $S_{\text{BET}} = 1.2 \text{ m}^2 \text{ g}^{-1}$, $\rho_{\text{tap}} = 1.3 \text{ g cm}^{-3}$, MTI), were dried at 100–150 °C for 24 h under vacuum. S_{BET} of dried conductive carbon were measured by five-point nitrogen adsorption using a surface area and porosity analyzer (ASAP 2020, micrometrics). All chemicals were stored and handled in an argon-filled glovebox (O_2 and $\text{H}_2\text{O} < 0.1 \text{ ppm}$).

LiBH₄/carbon composites were prepared by mixing LiBH₄ and conductive carbon in a weight ratio of 95:5 (Ketjenblack), 90:10 (Super P), 75:25 (Super P, C65, KS6, and MCMB), ~~70:30 (KS6)~~, and 50:50 (Super P) with mortar and pestle for 15 min. The 5 wt.% was chosen for Ketjenblack due to its hollow structure with a void fraction of 0.8 in order to ensure similar electronic conductivity to other types of conductive carbon. To avoid an electrical short circuit during measurements, a powder stack composed of the first layer of 2 or 5 mg of the LiBH₄/carbon composite and the second layer of 80 mg of LiBH₄ was uniaxially pressed under 450 MPa to form a pellet with 12 mm diameter and 1.0–1.3 mm thickness (see Figure 1a). The volume fraction of carbon was calculated from the density and weight of LiBH₄ and the respective conductive carbon in the composite, while the total surface area of carbon was obtained from the specific surface area and weight of the respective conductive carbon. As shown in Figure 1a, a Pt disk (99.997%, 0.25 mm in

thickness, Alfa Aesar) and an Al foil (>99.3%, 15 μm in thickness, MTI) with 12 mm diameter were attached to the carbon composite side of the pellet, and a surface-scratched Li metal foil (99.9%, 0.5 mm in thickness, China Energy Lithium) with a diameter of 10 mm was attached to the other side. A glassy carbon disk (0.2 mm in thickness, Goodfellow) was employed as an alternative to the Pt disk in selected experiments. All components were fixed between two stainless-steel rods and assembled in a Swagelok-type cell in a two-electrode configuration. To assess the oxidative stability of selected, highly conductive hydroborate-based SSEs, SSE/Super C65 composites were mixed for 15 min in a weight ratio of 75:25. Super C65 was chosen as it has similar material specifications to Super P at a lower impurity level. For Na-ion conductors, a Li metal foil was replaced by a surface-scratched Na metal foil which was rolled out from a Na metal cube (99.9%, Sigma-Aldrich).

All electrochemical measurements were carried out using a multi-channel potentiostat (VMP3, BioLogic). Electrochemical oxidative stability was determined by LSV at a scan rate of 10 or 100 $\mu\text{V s}^{-1}$. We choose to define the oxidative stability limit as the onset potential E_{onset} , at which the electrochemical oxidation reactions start. As shown in Figure 1b, E_{onset} was determined from the intersection of two linear regression lines ($R^2 > 0.99$) of (i) the non-faradaic background current associated with the double layer capacitance and (ii) the faradaic anodic (= oxidative) current in order to extract the onset of the anodic current. In LSV scans of LiBH_4 and $\text{Na}_3(\text{BH}_4)(\text{B}_{12}\text{H}_{12})$, the voltage was first swept down from the open circuit voltage to 1.5 V vs. Li^+/Li or vs. Na^+/Na , respectively, and subsequently swept up to obtain a sufficient number of data points of the background current for the linear regression. For $\text{Na}_4(\text{B}_{12}\text{H}_{12})(\text{B}_{10}\text{H}_{10})$ and $\text{Na}_4(\text{CB}_{11}\text{H}_{12})_2(\text{B}_{12}\text{H}_{12})$, the voltage was directly swept upwards from the open circuit voltage because of the sufficient number of data points before the onset of anodic currents. The linear fit method was chosen as it enables a more accurate determination of E_{onset} compared to other arbitrary criteria such as a specified cut-off current density.⁴² This method has also been suggested to quantify the electrochemical stability limits

of liquid electrolytes and ionic liquids, where errors of less than ± 0.05 V were reported.⁴³ Galvanostatic cycling of LiBH_4 was conducted between 1.5–4.0 V vs. Li^+/Li at a constant current density of $30 \mu\text{A cm}^{-2}$. The specific capacity was obtained based on the weight of LiBH_4 in the LiBH_4 /carbon composite.

Results and Discussion

LiBH_4 has been investigated as a model superionic conductor^{15,18,27,44–48} and was reported to exhibit high electrochemical stability over 5 V vs. Li^+/Li ,⁴⁰ which is not consistent with the value of ~ 2.0 V vs. Li^+/Li predicted by first principles calculation.^{34,35} In order to determine experimental conditions allowing an accurate assessment of the electrochemical oxidative stability of LiBH_4 , its sensitivity on the following parameters was investigated: the type and amount of carbon in the composite, the voltage scan rate, and the current collector material.

Figure 1c shows the linear sweep voltammograms of $\text{Li}/\text{LiBH}_4/\text{LiBH}_4\text{-C}/\text{Pt}$ cells (Super P, 25 wt.%) at scan rates of 10, 100, and $500 \mu\text{V s}^{-1}$ in comparison to a $\text{Li}/\text{LiBH}_4/\text{Pt}$ cell without carbon addition at a scan rate of $10 \mu\text{V s}^{-1}$. All LSVs were recorded at 60°C to prevent Li dendrite formation from the Li counter electrode. The onset potentials E_{onset} for LiBH_4 oxidation extracted from the pellets with and without carbon addition at $10 \mu\text{V s}^{-1}$ are 2.04 V and 3.10 V vs. Li^+/Li , respectively. The value of E_{onset} with carbon addition is in good agreement with the computationally predicted value from grand-potential phase diagrams (~ 2.0 V vs. Li^+/Li),^{34,35} despite the low ionic conductivity of LiBH_4 at 60°C on the order of $10^{-7} \text{ S cm}^{-1}$. We attribute the overestimation of E_{onset} without carbon addition even at a low scan rate of $10 \mu\text{V s}^{-1}$ to insufficient electronic contact area between SSE and current collector, resulting in slow kinetics of the electrochemical oxidative decomposition.³² The use of a SSE/conductive carbon composite increases the electronic contact area between SSE and conductive carbon and thereby accelerates the decomposition reactions.

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3 In order to examine the effect of the current collector and potential catalytic
4 decomposition of LiBH_4 in contact with Pt, the Pt disk was replaced by a glassy carbon disk.
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6 LSV with carbon addition was carried out as before at a scan rate of $10 \mu\text{V s}^{-1}$ at 60°C . As
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8 shown in Figure S1, the experiments with glassy carbon and Pt current collectors yield very
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10 similar values for E_{onset} . The negligible difference in E_{onset} indicates that the catalytic activity
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12 of Pt is negligible for LiBH_4 oxidation in this configuration, and that the electrochemical
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14 oxidative decomposition of LiBH_4 in the $\text{LiBH}_4/\text{carbon}$ composite dominates the
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16 contributions from the interface between LiBH_4 and the current collector. Therefore, as long
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18 as the current collector serves as inert, non-porous, semi-blocking electrode, the determination
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20 of E_{onset} is robust against the choice of the current collector material.
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26 Figure 1c also shows the influence of the scan rate on E_{onset} in a $\text{Li}/\text{LiBH}_4/\text{LiBH}_4\text{-C}/\text{Pt}$
27 cell (see Figure S2 for the detailed linear sweep voltammograms measured at different scan
28 rates). The faster scans at 100 and $500 \mu\text{V s}^{-1}$ result in a larger contribution from the
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30 capacitive background current because capacitive currents are expected to be linearly
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32 proportional to the scan rate after a sufficiently long sweeping time.⁴³ The higher background
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34 current shifts E_{onset} for 100 and $500 \mu\text{V s}^{-1}$ upwards by more than 100 and 500 mV,
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36 respectively, compared to $10 \mu\text{V s}^{-1}$. Note that the selected scan rates (10 , 100 , and
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38 $500 \mu\text{V s}^{-1}$) are much lower than those employed in previous LSV tests of hydroborate-based
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40 SSEs (e.g. 1 or 5 mV s^{-1}).^{20,40,47} As shown in Figure S2, higher scan rates significantly
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42 increase the contribution of capacitive background currents and consequently lead to an
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44 overestimation of E_{onset} . Below scan rates of $20 \mu\text{V s}^{-1}$, capacitive background currents have a
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46 minor effect on E_{onset} determination. Therefore, we consider a scan rate of $10 \mu\text{V s}^{-1}$ to be a
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48 suitable compromise between suppression of capacitive currents and time constraints.
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56 To investigate the role of the type of conductive carbon in the determination of the
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58 oxidative stability, $\text{LiBH}_4/\text{carbon}$ composites were investigated under the same conditions
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60 with five different types of conductive carbon (Ketjenblack, Super P, Super C65, KS6, and

MCMB). Figure 2a shows the representative linear sweep voltammograms at 10 and 100 $\mu\text{V s}^{-1}$, using conductive carbon with higher (Ketjenblack, 5 wt.%) or lower (MCMB, 25 wt.%) specific surface area and density than Super P. The use of low surface-area MCMB results in an overestimation of E_{onset} (2.61 V vs. Li^+/Li), even at the lower scan rate. Higher scan rates result in an even larger overestimation. As was the case without carbon addition, we attribute this to an insufficiently large electronic contact area. The value of E_{onset} obtained with high surface-area Ketjenblack at 10 $\mu\text{V s}^{-1}$ (2.08 V vs. Li^+/Li) lies close to the value of E_{onset} observed with Super P (2.04 V vs. Li^+/Li), while the shift of E_{onset} from 10 to 100 $\mu\text{V s}^{-1}$ (>200 mV) is higher than with Super P (>100 mV) mainly due to the larger capacitive current resulting from the larger specific surface area.

The effect of the amount of conductive carbon in terms of volume fraction and total surface area (Super P in this case) is summarized in Figures 2b and S4. As shown in Figure 2b, the 2 and 5 mg composites with the same carbon volume fraction of 0.58 (corresponding to 25 wt.%) exhibited almost the same E_{onset} . On the other hand, the 2 mg, 25 wt.% and 5 mg, 10 wt.% composites with the same total carbon surface area of 292 cm^2 (corresponding to 0.5 mg Super P) exhibit more than 100 mV difference in E_{onset} . This suggests that the carbon volume fraction in the composite is a more decisive parameter for the accuracy of E_{onset} , than the total surface area (see Figure S4 for a plot of E_{onset} vs. total surface area). The shift to higher E_{onset} for lower carbon volume fractions than 0.58 can be explained by insufficient electronic contact area, slowing the kinetics of electrochemical decomposition. On the other hand, the shift to higher E_{onset} for higher carbon volume fractions than 0.58 might be due to decreased decomposition currents resulting from the lower fraction of LiBH_4 in the composite. Overall, 25 wt.% Super P, 25 wt.% Super C65, or 5 wt.% Ketjenblack provided low E_{onset} below 2.1 V vs. vs. Li^+/Li among other results. However, the deviation of E_{onset} stays within 150 mV for all types of investigated carbons except for MCMB. This can be attributed to both the lower volume fraction (~ 0.15) and total surface area ($\sim 15 \text{ cm}^2$) of

MCMB compared to the other types of carbon. A robust determination of E_{onset} requires (i) a conductive carbon volume fraction between 0.2 and 0.8, and (ii) a carbon surface area of $>200 \text{ cm}^2$ in a 5 mg LiBH_4 /carbon composite.

In order to assess the impact of the ionic conductivity of the SSE, LSV using optimized conditions (25 wt.% Super P, $10 \mu\text{V s}^{-1}$) was conducted for the HT phase of LiBH_4 ($>10^{-3} \text{ S cm}^{-1}$) at 120°C , as shown in Figure 3a. The enhanced ionic conductivity in the HT phase increases the anodic current substantially and enables a clearer distinction between background and SSE decomposition currents. The measured E_{onset} at 120°C (1.96 V vs. Li^+/Li) turns out to be only slightly lower than the E_{onset} at 60°C (2.04 V vs. Li^+/Li), which we attribute to the thermodynamically facilitated decomposition reactions at higher temperatures and the accelerated kinetics in the HT phase. The value of E_{onset} at 120°C is also in good agreement with the computational prediction, confirming the robustness of this method with respect to variations in ionic conductivity over several orders of magnitude ($>10^{-3} - 10^{-7} \text{ S cm}^{-1}$ in the case of the high- and low-temperature phase of LiBH_4).

Sweeping the voltage from 1.5 V to 4.0 V vs. Li^+/Li , two distinct anodic peaks appear (see Figure 3a) that are absent when sweeping back down from 4.0 V to 1.5 V vs. Li^+/Li (also shown in Figure 3a), suggesting multi-step, irreversible electrochemical decomposition reactions of LiBH_4 . Galvanostatic measurements shown in Figure 3b confirm the irreversible nature of the oxidative decomposition. Using the same cell setup, we applied a constant current density of $30 \mu\text{A cm}^{-2}$ to reach the total capacity obtained during LSV after around 100 h ($\sim C/100$). In agreement with the LSV experiment, the electrochemical oxidation starts at around 2.0 V vs. Li^+/Li during the 1st charge, and over 90% of the total capacity was obtained below 2.5 V vs. Li^+/Li , followed by almost no capacity during the 1st discharge and subsequent charge-discharge cycles (see the inset in Figure 3b). A similar constant-current method was employed to estimate the electrochemical stability of SSEs using slurry-based working electrodes of SSE materials in liquid electrolyte cells.²⁹ However, the all-solid-state

cell setup is much closer to the configuration of all-solid-state batteries and allows focusing on electrochemical decomposition reactions of the SSE, excluding possible side reactions of the SSE with the liquid electrolyte, binder, and impurities (e.g. residual H₂O) in liquid electrolyte cells.

Accurate determination of the electrochemical stability limit provides an interpretation of the electrochemical reactions in all-solid-state batteries outside the stability limit of SSEs. For instance, the initial irreversible discharge capacity of the Li/LiBH₄/LiBH₄-TiS₂ cell reported previously⁴⁹ can be attributed to the electrochemical oxidation of LiBH₄ as it was cycled up to 2.7 V vs. Li⁺/Li, i.e. beyond its oxidative stability limit of ~2.0 V vs. Li⁺/Li.

In order to investigate the general applicability of this protocol for hydroborate-based SSEs, we re-evaluated the oxidative stability of four kinds of recently reported, superionic SSEs ($\sigma_{\text{ion}} > 10^{-3} \text{ S cm}^{-1}$ at 60 °C) for all-solid-state battery applications, i.e. Li₂(CB₉H₁₀)(CB₁₁H₁₂), Na₃(BH₄)(B₁₂H₁₂), Na₄(B₁₂H₁₂)(B₁₀H₁₀), and Na₄(CB₁₁H₁₂)₂(B₁₂H₁₂).^{19,22–24} Both Li- and Na-ion conductors were selected because the oxidative stability of Li and Na hydroborates can be measured in the same way when their respective alkali metal is used as a reference electrode, i.e. vs. M⁺/M (M = Li or Na).^{29,32,35} Figure 4a shows the voltammogram of Li₂(CB₉H₁₀)(CB₁₁H₁₂), displaying a step-wise increase of the anodic current with an E_{onset} of 2.86 V vs. Li⁺/Li. As with LiBH₄, this result revealed much lower oxidative stability of Li hydro-*closo*-monocarbaborate compounds than the value (>5 V vs. Li⁺/Li) previously measured at scan rates of >200 $\mu\text{V s}^{-1}$ without carbon addition.¹⁹ The linear sweep voltammogram of Na₃(BH₄)(B₁₂H₁₂) in Figure 4b also shows two step-wise onsets of the anodic current at 1.90 V and 2.41 V vs. Na⁺/Na, indicating a multi-step decomposition process. The first step at 1.90 V vs. Na⁺/Na coincides with the computationally predicted oxidative stability limit of NaBH₄ (~1.9 V vs. Na⁺/Na).^{35,36} Note that this value is significantly lower than the oxidative stability of NaBH₄-based SSEs (>6 V vs. Na⁺/Na) previously measured at much higher scan rates without carbon addition (e.g. 1 and

50 mV s^{-1}).^{20,23} We tentatively attribute the second step at 2.41 V vs. Na^+/Na to further electrochemical oxidation of $[\text{BH}_4]^-$ decomposition products as $[\text{B}_{12}\text{H}_{12}]^{2-}$ ions are stable at least up to 3 V vs. Na^+/Na .²² Figure 4c depicts the result for $\text{Na}_4(\text{B}_{12}\text{H}_{12})(\text{B}_{10}\text{H}_{10})$, showing two onsets at 3.02 V and 3.22 V vs. Na^+/Na , which we tentatively attribute to the onset of decomposition of the less stable $[\text{B}_{10}\text{H}_{10}]^{2-}$ and more stable $[\text{B}_{12}\text{H}_{12}]^{2-}$ ions, respectively. In our earlier measurement without carbon addition at a scan rate of $100 \mu\text{V s}^{-1}$, these two peaks could not be distinguished and instead overlapped into one broad onset.²² The voltammogram of $\text{Na}_4(\text{CB}_{11}\text{H}_{12})_2(\text{B}_{12}\text{H}_{12})$ in Figure 4d exhibits a large contribution to the anodic current above 4 V vs. Na^+/Na with an E_{onset} of 4.07 V vs. Na^+/Na , which is a similar value to the previously reported E_{onset} of ~ 4.1 V vs. Na^+/Na at a scan rate of $500 \mu\text{V s}^{-1}$.²⁴ However, we also observe smaller contributions to the anodic current with an E_{onset} of 2.93 V vs. Na^+/Na which were concealed in the background current in the previous study. The four examples shown in Figure 4 confirm the applicability of this method to other hydroborate-based SSEs and the possibility to unveil their oxidative stability limit with enhanced sensitivity, which again stresses the importance of carefully selected experimental conditions for accurate determination of oxidative stability of SSEs. Additionally, almost no cathodic (= reductive) current was observed in all of the cyclic voltammograms in Figure S5, which suggests a general irreversible nature of electrochemical oxidation reactions of hydroborates at high voltages. For a definitive attribution of the various faradaic contributions to the anodic current, a more detailed understanding of the multi-step decomposition reaction pathways needs to be developed in the future.

Conclusion

Using LiBH_4 as a model system, we established a methodology to determine the electrochemical oxidative stability of hydroborate-based SSEs in solid-state cells by LSV. Robust determination of E_{onset} (2.0 V vs. Li^+/Li for LiBH_4) is accomplished by linear fitting of background and anodic current contributions, a low scan rate of $10 \mu\text{V s}^{-1}$, and increasing the

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3 electronic contact area by means of SSE/carbon composites. We confirmed the applicability
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5 of this method to other SSEs and found that previous reports overestimated the oxidative
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7 stability, from which it is proven to be important to select experimental conditions carefully
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9 for accurate determination of the oxidative stability.
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12 The understanding of the intrinsic electrochemical oxidative stability of SSEs and their
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14 electrochemical decomposition reaction pathways determines the choice of cathode materials
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16 in all-solid-state batteries. Decent all-solid-state battery performance was attributed to the
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18 slow kinetics of decomposition reactions when all-solid-state batteries are cycled to an upper
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20 cut-off voltage slightly above the oxidative stability of SSEs.²⁸ However, to enable stable
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22 cycling with cathode materials with redox potentials far outside the oxidative stability, it is
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24 important to identify decomposition products and determine their ionic and electronic
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26 transport properties as well as their mechanical properties. If no passivating interphase is
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28 spontaneously formed by the decomposition products, artificial protective coatings need to be
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30 applied to allow stable cycling beyond the electrochemical stability limit of the electrolyte.
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32 The experimental methodology in this study provides key information to direct appropriate
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34 selection of cathode materials and define interface engineering strategies.
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FIGURES

Figure 1. (a) Schematic of the solid-state cell setup for electrochemical oxidative stability tests. (b) Example of E_{onset} estimation from two linear regression lines ($R^2 > 0.99$) of the non-faradaic background current and faradaic anodic current. (c) Linear sweep voltammograms of Li/LiBH₄/LiBH₄-C/Pt cells with 25 wt.% Super P in the 5 mg LiBH₄/carbon composite at scan rates of 10, 100, and 500 $\mu\text{V s}^{-1}$ and of a Li/LiBH₄/Pt cell at a scan rate of 10 $\mu\text{V s}^{-1}$ from 1.5 V to 4.0 V vs. Li⁺/Li at 60 °C. The inset shows the magnified linear sweep voltammograms of a Li/LiBH₄/Pt cell at scan rates of 10 and 100 $\mu\text{V s}^{-1}$ between 2.7 V and 4.0 V vs. Li⁺/Li.

Figure 2. (a) Linear sweep voltammograms of Li/LiBH₄/LiBH₄-C/Pt cells with 5 wt.% Ketjenblack (green) 25 wt.% MCMB (red) and in the 5 mg LiBH₄/carbon composite at scan rates of 10 and 100 $\mu\text{V s}^{-1}$ from 1.5 V to 4.0 V vs. Li⁺/Li at 60 °C. (b) E_{onset} at a scan rate of 10 $\mu\text{V s}^{-1}$ at 60 °C plotted against the volume fraction of the conductive carbon in the LiBH₄/carbon composite. The circle symbol stands for a 5 mg composite, while the diamond symbol stands for a 2 mg composite. The volume fraction was calculated from the density and weight of LiBH₄ and the respective conductive carbon in the composite.

Figure 3. (a) Cyclic voltammogram at a scan rate of $10 \mu\text{V s}^{-1}$ and (b) initial galvanostatic charge-discharge curves at a current density of $30 \mu\text{A cm}^{-2}$ for $\text{Li}/\text{LiBH}_4/\text{LiBH}_4\text{-C}/\text{Pt}$ cells with 25 wt.% Super P in the $\text{LiBH}_4/\text{carbon}$ composite cycled between 1.5 V and 4.0 V vs. Li^+/Li at 120°C . The inset shows the galvanostatic charge-discharge curves after the first charge. The specific capacity was obtained based on the weight of LiBH_4 in the composite (= 3.75 mg).

Figure 4. Linear sweep voltammograms of Li or Na/SSE/SSE-C/Pt cells using (a) $\text{Li}_2(\text{CB}_9\text{H}_{10})(\text{CB}_{11}\text{H}_{12})$ between 2.5 V and 4.0 V vs. Li^+/Li , (b) $\text{Na}_3(\text{BH}_4)(\text{B}_{12}\text{H}_{12})$ between 1.5 V and 3.0 V vs. Na^+/Na , (c) $\text{Na}_4(\text{B}_{12}\text{H}_{12})(\text{B}_{10}\text{H}_{10})$ between 2.5 V and 3.5 V vs. Na^+/Na , and (d) $\text{Na}_4(\text{CB}_{11}\text{H}_{12})_2(\text{B}_{12}\text{H}_{12})$ between 2.5 V and 4.5 V vs. Na^+/Na , with 25 wt.% Super C65 in the 5 mg SSE/carbon composite at a scan rate of $10 \mu\text{V s}^{-1}$ at 60°C .

ASSOCIATED CONTENT

Supporting Information

The following files are available free of charge.

Linear sweep voltammograms of Li/LiBH₄/LiBH₄-C/Pt or Glassy Carbon cells with different scan rates or types of conductive carbon in the LiBH₄/carbon composite. E_{onset} plotted against the total surface area of the conductive carbon in the LiBH₄/carbon composite. Cyclic voltammograms of Li or Na/SSE/SSE-C/Pt cells using other hydroborate-based SSEs.

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Notes

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TOC Graphic

109x49mm (300 x 300 DPI)

Figure 1. (a) Schematic of the solid-state cell setup for electrochemical oxidative stability tests. (b) Example of E_{onset} estimation from two linear regression lines ($R^2 > 0.99$) of the non-faradaic background current and faradaic anodic current. (c) Linear sweep voltammograms of Li/LiBH4/LiBH4-C/Pt cells with 25 wt.% Super P in the 5 mg LiBH4/carbon composite at scan rates of 10, 100, and 500 $\mu\text{V s}^{-1}$ and of a Li/LiBH4/Pt cell at a scan rate of 10 $\mu\text{V s}^{-1}$ from 1.5 V to 4.0 V vs. Li^+/Li at 60 $^{\circ}\text{C}$. The inset shows the magnified linear sweep voltammograms of a Li/LiBH4/Pt cell at scan rates of 10 and 100 $\mu\text{V s}^{-1}$ between 2.7 V and 4.0 V vs. Li^+/Li .

80x73mm (300 x 300 DPI)

Figure 2. (a) Linear sweep voltammograms of Li/LiBH₄/LiBH₄-C/Pt cells with 5 wt.% Ketjenblack (green) 25 wt.% MCMB (red) and in the 5 mg LiBH₄/carbon composite at scan rates of 10 and 100 $\mu\text{V s}^{-1}$ from 1.5 V to 4.0 V vs. Li⁺/Li at 60 °C. (b) E_{onset} at a scan rate of 10 $\mu\text{V s}^{-1}$ at 60 °C plotted against the volume fraction of the conductive carbon in the LiBH₄/carbon composite. The circle symbol stands for a 5 mg composite, while the diamond symbol stands for a 2 mg composite. The volume fraction was calculated from the density and weight of LiBH₄ and the respective conductive carbon in the composite.

80x39mm (300 x 300 DPI)

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79x40mm (300 x 300 DPI)

Figure 4. Linear sweep voltammograms of Li or Na/SSE/SSE-C/Pt cells using (a) $\text{Li}_2(\text{CB9H}_{10})(\text{CB11H}_{12})$ between 2.5 V and 4.0 V vs. Li^+/Li , (b) $\text{Na}_3(\text{BH}_4)(\text{B12H}_{12})$ between 1.5 V and 3.0 V vs. Na^+/Na , (c) $\text{Na}_4(\text{B12H}_{12})(\text{B10H}_{10})$ between 2.5 V and 3.5 V vs. Na^+/Na , and (d) $\text{Na}_4(\text{CB11H}_{12})_2(\text{B12H}_{12})$ between 2.5 V and 4.5 V vs. Na^+/Na , with 25 wt.% Super C65 in the 5 mg SSE/carbon composite at a scan rate of $10 \mu\text{V s}^{-1}$ at 60°C .

80x100mm (300 x 300 DPI)