Lithium Batteries

# A High-Performance Li–B–H Electrolyte for All-Solid-State Li Batteries

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Highly Li-ion conductive Li<sub>4</sub>(BH<sub>4</sub>)<sub>3</sub>I@SBA-15 is synthesized by confining the LiI doped LiBH<sub>4</sub> into mesoporous silica SBA-15. Uniform nanoconfinement of *P*6<sub>3</sub>*mc* phase Li<sub>4</sub>(BH<sub>4</sub>)<sub>3</sub>I in SBA-15 mesopores leads to a significantly enhanced conductivity of  $2.5 \times 10^{-4}$  S cm<sup>-1</sup> with a Li-ion transference number of 0.97 at 35 °C. The super Li-ion mobility in the interface layer with a thickness of 1.2 nm between Li<sub>4</sub>(BH<sub>4</sub>)<sub>3</sub>I and SBA-15 is believed to be responsible for the fast Li-ion conduction in Li<sub>4</sub>(BH<sub>4</sub>)<sub>3</sub>I@SBA-15. Additionally, Li<sub>4</sub>(BH<sub>4</sub>)<sub>3</sub>I@SBA-15 also exhibits a wide apparent electrochemical stability window (0 to 5 V vs Li/Li<sup>+</sup>) and a superior Li dendrite suppression capability (critical current density 2.6 mA cm<sup>-2</sup> at 55 °C) due to the formation of stable interphases. More importantly, Li<sub>4</sub>(BH<sub>4</sub>)<sub>3</sub>I@SBA-15-based Li batteries using either high-capacity sulfur cathode or high-voltage oxide cathode show excellent electrochemical performances, making Li<sub>4</sub>(BH<sub>4</sub>)<sub>3</sub>I@SBA-15 a very attractive electrolyte for next-generation all-solid-state Li batteries.

# 1. Introduction

Exploration of the rechargeable Li batteries with high energy and power densities is considered to be one of the key challenges to the widespread application of clean and renewable energy sources, especially for electric vehicles and smart grid.<sup>[1]</sup> Extensive efforts have been devoted to develop advanced electrolytes with high ionic conductivity, wide electrochemical stability window, and excellent electrode compatibility.<sup>[2]</sup> However, most of the investigations focus on the liquid organic electrolytes,

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which exhibit high Li-ion conductivity but suffer from low stability (e.g., decompose at excessive potentials, vaporize, and combust at high temperatures) and poor compatibility to electrodes (e.g., shuttle effect for sulfur cathode and dendrite formation for Li anode).<sup>[3]</sup> These disadvantages of the liquid organic electrolytes usually cause severe safety issues and reversible capacity decay, and thus stimulate the research of Li-ion super conductors as solid electrolytes for Li batteries.

Replacement of liquid electrolytes with solid electrolytes can significantly enhance the battery safety and performance.<sup>[4]</sup> Oxide-<sup>[5]</sup> and sulfide-<sup>[6]</sup> based solid electrolytes with ionic conductivity similar to or just slightly lower than that of liquid electrolytes have been developed in the last decade. However, the stability and compati-

bility of these solid electrolytes still cannot simultaneously fulfill the demands of all-solid-state Li batteries (ASSLBs) up to now.<sup>[7]</sup>

Recently, complex hydrides, which mainly consist of Li<sup>+</sup> and  $(BH_4)^{-,[8]}$   $(B_{12}H_{12})^{2-,[9]}$   $(AlH_6)^{3+,[10]}$   $(NH_2)^{-,[11]}$   $(NH)^{2-,[12]}$  have drawn intense interest as solid electrolytes for ASSLBs. Among them, LiBH<sub>4</sub> exhibits a wide apparent electrochemical stability window of 0 to 5 V (vs Li/Li<sup>+</sup>, same below),<sup>[13]</sup> and is compatible to most electrodes.<sup>[14]</sup> Its main disadvantage is the poor conductivity (<10<sup>-7</sup> S cm<sup>-1</sup>) at room temperature (RT) although it shows a high conductivity of 10<sup>-3</sup> S cm<sup>-1</sup> at 120 °C. This is because the highly conductive *P*6<sub>3</sub>*mc* phase transforms to the less conductive *Pnma* phase when temperature reduces to <110 °C.

Two effective strategies have been reported to increase the ionic conductivity of LiBH<sub>4</sub> at low temperatures. It is found that partial substitution of  $(BH_4)^-$  by Cl<sup>-</sup>, Br<sup>-</sup>, and I<sup>-</sup> can stabilize the highly conductive *P6*<sub>3</sub>*mc* phase of LiBH<sub>4</sub> to RT, and thus leads to a remarkably enhanced Li-ion conduction at low temperatures.<sup>[15]</sup> In addition, researchers found that LiBH<sub>4</sub> nanoconfined in mesoporous silica MCM-41 scaffold possesses much higher conductivity due to the fast Li-ion mobility in the interface layer between LiBH<sub>4</sub> and SiO<sub>2</sub>.<sup>[16]</sup> However, further improvement in the RT conductivity of LiBH<sub>4</sub>-based materials is still highly desired for practical application, and the electrochemical stability and electrode compatibility of the modified LiBH<sub>4</sub> still need to be investigated in depth in ASSLBs.

Inspired by the success in enhancing the bulk conductivity through halide substitution and in improving the interface

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conductivity through scaffold nanoconfinement, we synergically combined these two strategies by nanoconfining the highly conductive  $P6_3mc$  Li<sub>4</sub>(BH<sub>4</sub>)<sub>3</sub>I phase into SBA-15 mesopores, which resulted in significantly enhanced conductivity, electrochemical stability, and electrode compatibility of Li<sub>4</sub>(BH<sub>4</sub>)<sub>3</sub>I@SBA-15, as demonstrated by super performances of Li<sub>4</sub>(BH<sub>4</sub>)<sub>3</sub>I@SBA-15-based Li–Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub>, Li–S, and Li–LiCOO<sub>2</sub> ASSLBs.

## 2. Results and Discussion

Li<sub>4</sub>(BH<sub>4</sub>)<sub>3</sub>I@SBA-15 is prepared via a two-step process (**Figure 1**a). First, the partial substitution of I<sup>-</sup> for BH<sub>4</sub><sup>-</sup> to form Li<sub>4</sub>(BH<sub>4</sub>)<sub>3</sub>I is performed by heating LiBH<sub>4</sub> and LiI under 250 °C and 100 bar hydrogen for 12 h. Then, Li<sub>4</sub>(BH<sub>4</sub>)<sub>3</sub>I is nanoconfined into SBA-15 by heating the Li<sub>4</sub>(BH<sub>4</sub>)<sub>3</sub>I and SBA-15 mixtures at 340 °C for 1 h under 130 bar hydrogen to form Li<sub>4</sub>(BH<sub>4</sub>)<sub>3</sub>I@SBA-15.

X-ray diffraction (XRD) is used to characterize the phase composition of  $Li_4(BH_4)_3I$ . As shown in Figure 1b,  $Li_4(BH_4)_3I$  at RT is in  $P6_3mc$  phase, which is a solid solution of LiI in LiBH<sub>4</sub>. The peak intensities of  $Li_4(BH_4)_3I$  ( $P6_3mc$ ) phase in  $Li_4(BH_4)_3I$ @SBA-15 become weaker, which is attributed to the existence of amorphous SBA-15. These XRD results confirm the successful stabilization of high-temperature  $P6_3mc$  phase of  $Li_4(BH_4)_3I$  to RT in  $Li_4(BH_4)_3I$ @SBA-15. Since LiBH<sub>4</sub> tends to decompose into amorphous phase at high temperatures, which

cannot be detected by XRD,<sup>[17]</sup> we employ Fourier transform infrared (FTIR, Figure 1c) and Raman (Figure 1d) spectroscopy to further detect the phase composition. All the peaks in both FTIR and Raman spectra can be assigned to LiBH<sub>4</sub>, Li<sub>4</sub>(BH<sub>4</sub>)<sub>3</sub>I, or SiO<sub>2</sub>, and no signal for possible decomposition products of LiBH<sub>4</sub>, such as Li<sub>2</sub>B<sub>12</sub>H<sub>12</sub> and B, is detected, which confirms that the decomposition of LiBH<sub>4</sub> is completely suppressed by the high-pressure hydrogen atmosphere during the preparation process. Additional XRD, FTIR, and Raman results for LiI and SBA-15 are shown in Figure S1 in the Supporting Information.

The mesoporous structure of SBA-15 and Li<sub>4</sub>(BH<sub>4</sub>)<sub>3</sub>I@ SBA-15 is observed by transmission electron microscope (TEM). SBA-15 exhibits well defined 2D hexagonally ordered parallel mesopores with a uniform diameter of 8 nm (Figure 1e,g). After melt infiltration, the ordered mesoporous structure of SBA-15 remains almost intact, while the pore regions become darker than the wall regions (Figure 1f,h), which indicate that the mesopores of SBA-15 are filled with Li4(BH4)3I. Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS) mapping of Li<sub>4</sub>(BH<sub>4</sub>)<sub>3</sub>I@SBA-15 are applied to reveal its morphology and elemental distribution. Intersecting fibers with a diameter of 3-5 µm are found in the SEM image (Figure 1i), which are quite similar to the pristine SBA-15. The I and Si mapping images (Figure 2j,k) show that the distributions of both elements apparently match well with the shape of the intersecting fibers, indicating that Li<sub>4</sub>(BH<sub>4</sub>)<sub>3</sub>I is homogeneously distributed in SBA-15. The melt-infiltration method can



**Figure 1.** a) A schematic diagram of the preparing process of  $Li_4(BH_4)_3I$  in SBA-15; b) XRD patterns, c) FTIR spectra, and d) Raman spectra of LiBH<sub>4</sub>,  $Li_4(BH_4)_3I$ , and  $Li_4(BH_4)_3I@SBA-15$ ; TEM images of e,g) SBA-15 and f,h)  $Li_4(BH_4)_3I@SBA-15$ ; i–k) SEM-EDS mapping images of  $Li_4(BH_4)_3I@SBA-15$ ; l) nitrogen adsorption isotherms of SBA-15,  $Li_4(BH_4)_3I@SBA-15$ , and  $Li_4(BH_4)_3I/SBA-15$ .



effectively confine  $Li_4(BH_4)_3I$  into SBA-15 mesopores without changing the morphology of SBA-15.

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Since the infiltration of  $Li_4(BH_4)_3I$  into SBA-15 may change the porosity of SBA-15, the nitrogen adsorption (normalized to 1 g of SBA-15) is applied to characterize the pore parameters of SBA-15, 30 wt% Li<sub>4</sub>(BH<sub>4</sub>)<sub>3</sub>I@SBA-15, 60 wt% Li<sub>4</sub>(BH<sub>4</sub>)<sub>3</sub>I@ SBA-15, and 60 wt% Li<sub>4</sub>(BH<sub>4</sub>)<sub>3</sub>I/SBA-15 mixture (Figure 11). SBA-15 exhibits typical steep capillary condensation step and a hysteresis loop. The nitrogen adsorption amounts are remarkably decreased for the two melt-infiltrated Li<sub>4</sub>(BH<sub>4</sub>)<sub>3</sub>I@SBA-15 samples, while it remains unchanged for the mixed Li4(BH4)3I/ SBA-15 sample. These results, combined with the pore parameters (Table S1, Supporting Information), suggest that Li<sub>4</sub>(BH<sub>4</sub>)<sub>3</sub>I is filled into the mesopores of SBA-15, and 90% of SBA-15 mesopores are occupied by Li4(BH4)3I in 60 wt% Li4(BH4)3I@ SBA-15. This value agrees with the theoretical calculation on maximum effective loading content of Li4(BH4)3I in SBA-15 (59 wt%) according to the pore volume of SBA-15 (1.1 cm<sup>3</sup> g<sup>-1</sup>) and the density of  $Li_4(BH_4)_3I$  (1.3 g cm<sup>-3</sup>).

All the characterizations above demonstrate that LiI dissolves into LiBH<sub>4</sub> at 250 °C, forming a highly conductive solid solution Li<sub>4</sub>(BH<sub>4</sub>)<sub>3</sub>I phase and this  $P6_3mc$  phase is stable at RT. At above 320 °C, melted Li<sub>4</sub>(BH<sub>4</sub>)<sub>3</sub>I (Figure S2, Supporting Information) fills into the mesopores of SBA-15 by a capillary action. After cooling and degassing, Li<sub>4</sub>(BH<sub>4</sub>)<sub>3</sub>I with  $P6_3mc$  highly conductive phase is uniformly nanoconfined in SBA-15. The decomposition of LiBH<sub>4</sub> during the preparing process is suppressed by the high-pressure hydrogen (Figure S3, Supporting Information).

The temperature-dependent conductivities of LiBH<sub>4</sub>, Li<sub>4</sub>(BH<sub>4</sub>)<sub>3</sub>I, LiBH<sub>4</sub>@SBA-15, and Li<sub>4</sub>(BH<sub>4</sub>)<sub>3</sub>I@SBA-15 are measured using electrochemical impedance spectroscopy (EIS, **Figure 2**a; Figures S4 and S5, Supporting Information). The conductivity for LiBH<sub>4</sub> exhibits an abrupt drop (three orders of magnitude) when the temperature decreases to 105 °C, which corresponds to the phase transformation from  $P6_3mc$  phase to *Pnma* phase.<sup>[8]</sup> For Li<sub>4</sub>(BH<sub>4</sub>)<sub>3</sub>I, the abrupt reduction in conductivity at 105 °C disappears and the logarithmic conductivity is linearly decreased with reciprocal temperature (1/*T*), demonstrating that high-temperature *P*6<sub>3</sub>*mc* phase is stabilized to RT by I<sup>-</sup> substitution.<sup>[15a]</sup> LiBH<sub>4</sub>@SBA-15 shows even higher conductivities than Li<sub>4</sub>(BH<sub>4</sub>)<sub>3</sub>I in the temperature range of 35–125 °C, which is closely relative to the formation of interface layer between LiBH<sub>4</sub> and SBA-15.<sup>[16a]</sup> As for Li<sub>4</sub>(BH<sub>4</sub>)<sub>3</sub>I@SBA-15, the logarithmic conductivity is nearly linear with 1/*T*, and reaches as high as  $1.0 \times 10^{-2}$  S cm<sup>-1</sup> at 125 °C and  $2.5 \times 10^{-4}$  S cm<sup>-1</sup> at 35 °C. The conductivity of Li<sub>4</sub>(BH<sub>4</sub>)<sub>3</sub>I@SBA-15 at RT is almost four orders of magnitude higher than that of LiBH<sub>4</sub>. These results prove that the conductivity of LiBH<sub>4</sub> is improved by synergic effect of I<sup>-</sup> substitution and SBA-15 nanoconfinement. The activation energies of Li<sub>4</sub>(BH<sub>4</sub>)<sub>3</sub>I@SBA-15 is calculated to be 0.46 eV, which is a typical activation energy for super ionic conductors (<0.5 eV).<sup>[18]</sup>

 $Li_4(BH_4)_3I@SBA-15$  should be a single-ion conductor. The transference number of  $Li_4(BH_4)_3I@SBA-15$  at 35 °C is measured using direct current polarization and EIS techniques (Figure 2b,c). The steady current of Mo|Li\_4(BH\_4)\_3I@SBA-15|Mo cell at 10 mV is very small, suggesting an electronic transference number of close to 0 for  $Li_4(BH_4)_3I@SBA-15$ . Moreover, the Li-ion transference number is determined to be 0.97 according to the initial and steady currents at 10 mV and resistances before and after polarization of  $Li|Li_4(BH_4)_3I@SBA-15|Li cell$ . These results prove that the electronic transference is neglectable and the migration Li-ion contributes the majority of the charge transference for  $Li_4(BH_4)_3I@SBA-15$ .

The Li-ion mobility of  $\text{Li}_4(\text{BH}_4)_3\text{I}@\text{SBA-15}$  is measured using solid-state <sup>7</sup>Li nuclear magnetic resonance (NMR) spectroscopy at different temperatures. For solid-state sample, the transverse relaxation time (*T*2), which is inversely proportional to the full width at half maximum of the NMR peaks, is closely related to the ionic mobility of the sample, because high ionic mobility can average the anisotropic dipolar and quadrupolar interactions.<sup>[19]</sup> Therefore, in this case, higher *T*2 is an indication of higher Li-ion mobility. In Figure 2d, clear <sup>7</sup>Li resonance signals centered at -0.2 kHz at different temperatures are detected and each signal consists of a narrow peak and a



**Figure 2.** a) Temperature-dependent conductivities of LiBH<sub>4</sub>, Li<sub>4</sub>(BH<sub>4</sub>)<sub>3</sub>I, LiBH<sub>4</sub>@SBA-15, and Li<sub>4</sub>(BH<sub>4</sub>)<sub>3</sub>I@SBA-15; b,c) transference number measurements of Li<sub>4</sub>(BH<sub>4</sub>)<sub>3</sub>I@SBA-15 by direct current polarization and EIS techniques; d) solid-state <sup>7</sup>Li NMR spectra of Li<sub>4</sub>(BH<sub>4</sub>)<sub>3</sub>I@SBA-15 at different temperatures; e) T2 and f) contents of the narrow and broad NMR peaks at different temperatures.



broad peak. Calculation of T2 from the narrow and broad peaks at different temperatures (Figure 2e) reveals that higher temperature induces better Li-ion mobility, and the narrow peak corresponds to a high Li-ion mobility component and the broad peak corresponds to a low Li-ion mobility component. The contents of the two components are estimated to be 50% and 50%, respectively, by the integral intensities of the two peaks (Figure 2f). As only one Li-containing phase is identified by the structural characterizations, we believe that the two components both correspond to the nanoconfined Li<sub>4</sub>(BH<sub>4</sub>)<sub>3</sub>I in SBA-15. In other words, half of the nanoconfined Li<sub>4</sub>(BH<sub>4</sub>)<sub>3</sub>I possesses high Li-ion mobility and the other half possesses low Li-ion mobility. We believe that this phenomenon can be explained by the significant enhancement in the Li-ion mobility of the interface layer between Li<sub>4</sub>(BH<sub>4</sub>)<sub>3</sub>I and SiO<sub>2</sub>. The thickness of the interface layer is estimated to be 1.2 nm according to the content of the high Li-ion mobility component and the diameter of the mesopores of SBA-15. For comparison, more NMR data of LiBH<sub>4</sub> at different temperatures are shown in Figure S6 in the Supporting Information.

Only fast Li-ion conduction is not sufficient for practical solid electrolyte materials, because electrochemical stability and electrode compatibility are also key properties that determine the overall performances of ASSLBs.



Electrochemical stability of Li4(BH4)3I@SBA-15 is characterized by cyclic voltammetry (CV) of Li|Li4(BH4)3I@SBA-15|Mo cell at 0.5 mV s<sup>-1</sup> and 55 °C. In the -0.2 to 5 V curve (Figure 3a), only apparent current peaks (mA level) near 0 V is observed, which correspond to the Li plating (negative potentials) and Li stripping (positive potentials) on the Mo electrode. To reveal its real resistances to electrochemical oxidation and reduction without the interference of huge Li plating/ stripping peaks, Li|Li4(BH4)3I@SBA-15|Mo cells are repeatedly scanned from open-circuit voltage (OCV) to 5 V (Figure 3b) and 0 V (Figure 3c), respectively. Current signals centered at 3.1 V (1.8 µA) and 0.2 V (3.0 µA) can be observed in the first scan, but both signals disappear in the following scans (0.1 µA at 5 V, 0.7 µA at 0 V). These indicate the formation of cathode electrolyte interphase (CEI) and solid electrolyte interphase (SEI) films, which prevent Li<sub>4</sub>(BH<sub>4</sub>)<sub>3</sub>I@SBA-15 from further decomposition at excessive potentials (Figure S7, Supporting Information). Combining these results with those of LiBH<sub>4</sub> and Li<sub>4</sub>(BH<sub>4</sub>)<sub>3</sub>I (Figures S8 and S9, Supporting Information), we believe that the CEI and SEI films of Li<sub>4</sub>(BH<sub>4</sub>)<sub>3</sub>I@ SBA-15 are more structurally stable due to the support of SBA-15 scaffold. It is noteworthy that the anodic current of SiO<sub>2</sub> at low potentials is not detected, demonstrating that the lithiation reaction of SiO<sub>2</sub> is suppressed by the uniform



**Figure 3.** CV curves of  $Li_4(BH_4)_3|@SBA-15$  within the potential windows of a) -0.2 to 5 V, b) OCV to 5 V, and c) OCV to 0 V; galvanostatic cycling curves of the  $Li_4(BH_4)_3|@SBA-15$ -based symmetrical Li cell at d) constant and e) increasing current densities; galvanostatic charge/discharge curves of the  $Li_4(BH_4)_3|@SBA-15$ -based f) Li– $Li_4Ti_5O_{12}$ , g) Li–S, and h) Li– $LiCOO_2$  cells.

coating of Li<sub>4</sub>(BH<sub>4</sub>)<sub>3</sub>I on its surface. Therefore, we believe that Li<sub>4</sub>(BH<sub>4</sub>)<sub>3</sub>I@SBA-15 is stable enough to work in the potential window of 0 to 5 V with the help of in situ formed CEI and SEI films.

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The compatibility of Li<sub>4</sub>(BH<sub>4</sub>)<sub>3</sub>I@SBA-15 to Li anode, as well as the Li dendrite suppression capability, is evaluated by galvanostatic cycling of Li|Li<sub>4</sub>(BH<sub>4</sub>)<sub>3</sub>I@SBA-15|Li cell at a constant current of 0.5 mA cm<sup>-2</sup> (Figure 3d) and increased current densities from 0.1 to 3 mA cm<sup>-2</sup> (Figure 3e) at 55 °C. The cell exhibits flat over voltages of  $\pm 35$  mV at  $\pm 0.5$  mA cm<sup>-2</sup> and shows excellent long-term cycling stability (350 h) without significant voltage fluctuations. For the increased current experiment, the over voltage raises with current and suddenly drops at 2.6 mA cm<sup>-2</sup>, which corresponds to the critical current density for Li dendrite formation in Li<sub>4</sub>(BH<sub>4</sub>)<sub>3</sub>I@SBA-15. It should be highlighted that this critical current density is the highest among all reported solid electrolyte materials under identical conditions (Figure S10, Supporting Information).<sup>[20]</sup> The area specific resistance is 70  $\Omega$  cm<sup>2</sup> calculated using Ohm's law, which is comparable to that of liquid electrolytes.<sup>[21]</sup> The above results indicate that the stable interphase between Li and Li<sub>4</sub>(BH<sub>4</sub>)<sub>3</sub>I@SBA-15 can effectively suppress the growth of Li dendrite. Moreover, the low hardness of Li4(BH4)3I@SBA-15 may also be beneficial to the Li dendrite suppression (Table S2, Supporting Information).

To demonstrate the compatibility of Li<sub>4</sub>(BH<sub>4</sub>)<sub>3</sub>I@SBA-15 to cathodes, we investigate three representative types of cells, i.e., Li–Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub> cell, Li–S cell, and Li–LiCoO<sub>2</sub> cell, by galvanostatic charge/discharge measurements at 0.05 C and 55 °C. Cycling performances of these batteries are shown in Figure S11 in the Supporting Information.

Li|Li<sub>4</sub>(BH<sub>4</sub>)<sub>3</sub>I@SBA-15|Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub>–Li<sub>4</sub>(BH<sub>4</sub>)<sub>3</sub>I@SBA-15–C cell (Figure 3f) delivers a comparable discharge and charge profiles to that of Li|LiPF<sub>6</sub>–EC–DMC–EMC|Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub>–C cells.<sup>[22]</sup> Little steeper plateaus at 1.55 V for both discharge and charge curves indicate small polarization. The specific capacity for the first cycle is 166 mAh g<sup>-1</sup> with a coulombic efficiency of near 100%, and it gradually reduces to 158 mAh g<sup>-1</sup> for the third cycle, suggesting a high active material utilization and an acceptable capacity retention during cycling.

The discharge/charge profiles of Li|Li<sub>4</sub>(BH<sub>4</sub>)<sub>3</sub>I@SBA-15|S–Li<sub>4</sub>(BH<sub>4</sub>)<sub>3</sub>I@SBA-15–C cell (Figure 3g) are a little different to that of corresponding Li|LiPF<sub>6</sub>–DME–DOL|S–C cells.<sup>[23]</sup> Only one plateau exists for both discharge and charge curves, which suggests a solid-state electrochemical reaction for the lithiation and delithiation of S. Moreover, the polarization is a little larger indicated by the steeper plateaus. The initial discharge capacity is 1397 mAh g<sup>-1</sup> (83% S utilization), and the coulombic efficiencies rise to near 100% after the second cycle, indicating no shuttle effect of sulfides.

For LiCoO<sub>2</sub> electrode, LiNbO<sub>3</sub>, and sulfide are introduced to decrease the interfacial resistance between LiCoO<sub>2</sub> and Li<sub>4</sub>(BH<sub>4</sub>)<sub>3</sub>I@SBA-15 by forming Li-ion conductive CEI film.<sup>[24]</sup> Li|Li<sub>4</sub>(BH<sub>4</sub>)<sub>3</sub>I@SBA-15|LiCoO<sub>2</sub>@LiNbO<sub>3</sub>-80Li<sub>2</sub>S-20P<sub>2</sub>S<sub>5</sub> cell exhibits typical high-voltage plateaus for charge and discharge. The reversible specific capacity reaches 122 mAh g<sup>-1</sup> for the first cycle (87% LiCoO<sub>2</sub> utilization), and decreases to 111 mAh g<sup>-1</sup> for the third cycle with a coulombic efficiency of close to 100% (Figure 3h).

The above preliminary attempts provide strong evidences that  $Li_4(BH_4)_3I@SBA-15$  is a promising electrolyte material for ASSLBs. We believe that the overall properties of the ASSLBs with  $Li_4(BH_4)_3I@SBA-15$  electrolyte can be further improved by electrode optimization and interface modification, which will be done in our future works.

#### 3. Conclusion

In summary, Li<sub>4</sub>(BH<sub>4</sub>)<sub>3</sub>I@SBA-15 is successfully prepared by nanoconfining Li<sub>4</sub>(BH<sub>4</sub>)<sub>3</sub>I into SBA-15 mesopores, which shows a conductivity as high as  $2.5 \times 10^{-4}$  S cm<sup>-1</sup>, a neglectable electronic transference number, and a Li-ion transference number of 0.97 at 35 °C. This improvement can be attributed to the synergic effect of halide substitution and scaffold nanoconfinement and, more specifically, to the fast Li-ion conduction in the 1.2 nm thick interface layer between Li<sub>4</sub>(BH<sub>4</sub>)<sub>3</sub>I and SBA-15. Furthermore, Li<sub>4</sub>(BH<sub>4</sub>)<sub>3</sub>I@SBA-15 exhibits a wide apparent electrochemical stability window of 0 to 5 V due to the formation of stable CEI and SEI films. The Li dendrite suppression capability of Li4(BH4)3I@SBA-15 is also very distinguished, as the critical current density for dendrite formation is 2.6 mA cm<sup>-2</sup> at 55 °C. More importantly, excellent overall performances are achieved for ASSLBs using Li<sub>4</sub>(BH<sub>4</sub>)<sub>3</sub>I@SBA-15 as electrolyte and Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub>, S or LiCoO<sub>2</sub> as cathode.

#### 4. Experimental Section

Materials Preparation: LiBH<sub>4</sub> (95%, Sigma-Aldrich) and LiI (99.99%, Sigma-Aldrich) was used as received without further purification. SBA-15 was synthesized using the method described in the literature<sup>[25]</sup> and dried under dynamic vacuum at 250 °C for 12 h prior to use. Li<sub>4</sub>(BH<sub>4</sub>)<sub>3</sub>I was prepared by heating a mixture of LiBH<sub>4</sub> and LiI at a molar ratio of 3:1 under 250 °C and 100 bar hydrogen for 12 h. Li<sub>4</sub>(BH<sub>4</sub>)<sub>3</sub>I@SBA-15 with different Li<sub>4</sub>(BH<sub>4</sub>)<sub>3</sub>I loadings were obtained by heating a mixture of Li<sub>4</sub>(BH<sub>4</sub>)<sub>3</sub>I and SBA-15 at various weight ratios (30:70, 50:50, 60:40, and 70:30) under 340 °C and 130 bar hydrogen for 1 h. LiBH<sub>4</sub>@SBA-15 was prepared using a similar method with a LiBH<sub>4</sub> loading of 46 wt%.

Structural Characterizations: XRD measurements were performed on Rigaku MiniFlex 600 at a scan rate of 5° min<sup>-1</sup>. FTIR spectra were recorded by Bruker Vector 22 in transmission mode. Raman spectra were obtained by Bruker Optics Senterra R200-L with a laser wavelength of 532 nm. TEM observations were conducted on JEOL JEM-2100F. SEM observations and EDS mapping were performed on FEI Nova SEM 230 equipped with INCA X-Max 80. Specific surface areas and pore volumes of the samples were characterized on Micromeritics ASAP2020 using the Brunauer–Emmett–Teller (BET) and Barrett–Joyner–Halenda (BJH) methods. Solid state NMR experiments were performed on Bruker Ascend 600 MHz (14.1 T) with resonance frequencies at 233 MHz for <sup>7</sup>Li. A Bruker 3.2 mm magic angle spinning probe head was used for the 15 kHz MAS experiments.

*Cell Assemblies*: Cells were assembled using homemade Swagelok type dies. The electrolyte pellets with a diameter of 10 mm and a thickness of 3 mm (for Li-ion conduction measurements) and 0.5 mm (for electrochemical stability and electrode compatibility measurements) were made by pressing the target materials under 100 MPa pressure. For different measurements, different electrodes were used, i.e., Mo foil, Li foil, Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub>-based composite (70 wt% Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub>, 20 wt% Li<sub>4</sub>(BH<sub>4</sub>)<sub>3</sub>I@ SBA-15, 10 wt% C), S-based composite (60 wt% S, 25 wt% Li<sub>4</sub>(BH<sub>4</sub>)<sub>3</sub>I @SBA-15, 15 wt% C), LiCOO<sub>2</sub>-based composite (70 wt% LiCOO<sub>2</sub>@LiNbO<sub>3</sub>,<sup>[26]</sup> 30 wt% 80Li<sub>2</sub>S-20P<sub>2</sub>S<sub>5</sub><sup>[27]</sup>).

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*Electrochemical Measurements*: EIS, direct current polarization, and CV were conducted on Gamry Interface 1000E. Galvanostatic charge/discharge measurements were performed using LAND CT2001A. The conductivities ( $\sigma$ ) were calculated from the EIS of Molelectrolyte|Mo cells. Each Nyquist plot consists of a depressed semicircle and a linear tail, and the intersection of the semicircle with the Z' axis corresponds to the resistance (*R*). The conductivity can be calculated by the following equation

$$\sigma = \frac{d}{AR} \tag{1}$$

where *d* is the thickness and *A* is the area of the electrolyte pellet. The activation energies ( $E_a$ ) are then evaluated according to the Nernst–Einstein equation and Arrhenius equation

$$\ln(\sigma T) = -\frac{E_a}{k_B T} + C \tag{2}$$

where  $k_{\rm B}$  is the Boltzmann constant.

The electronic transference number was obtained from the ratio of steady current to initial current in the 10 mV potential step curve of Mo|Li<sub>4</sub>(BH<sub>4</sub>)<sub>3</sub>I@SBA-15|Mo cell. The Li-ion transference number was calculated from the ratio of steady current to initial current in the 10 mV potential step curve of Li|Li<sub>4</sub>(BH<sub>4</sub>)<sub>3</sub>I@SBA-15|Li cell, because the electronic transference number was close to 0 and the interface impedance between Li<sub>4</sub>(BH<sub>4</sub>)<sub>3</sub>I@SBA-15 and Li was very small after polarization.<sup>[28]</sup>

### **Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

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## **Conflict of Interest**

The authors declare no conflict of interest.

## Keywords

all-solid-state Li battery, halide substitution, ionic conductor, lithium borohydride, nanoconfinement

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