Turning Sodium borohydride into superionic conductors for All-Solid-State battery

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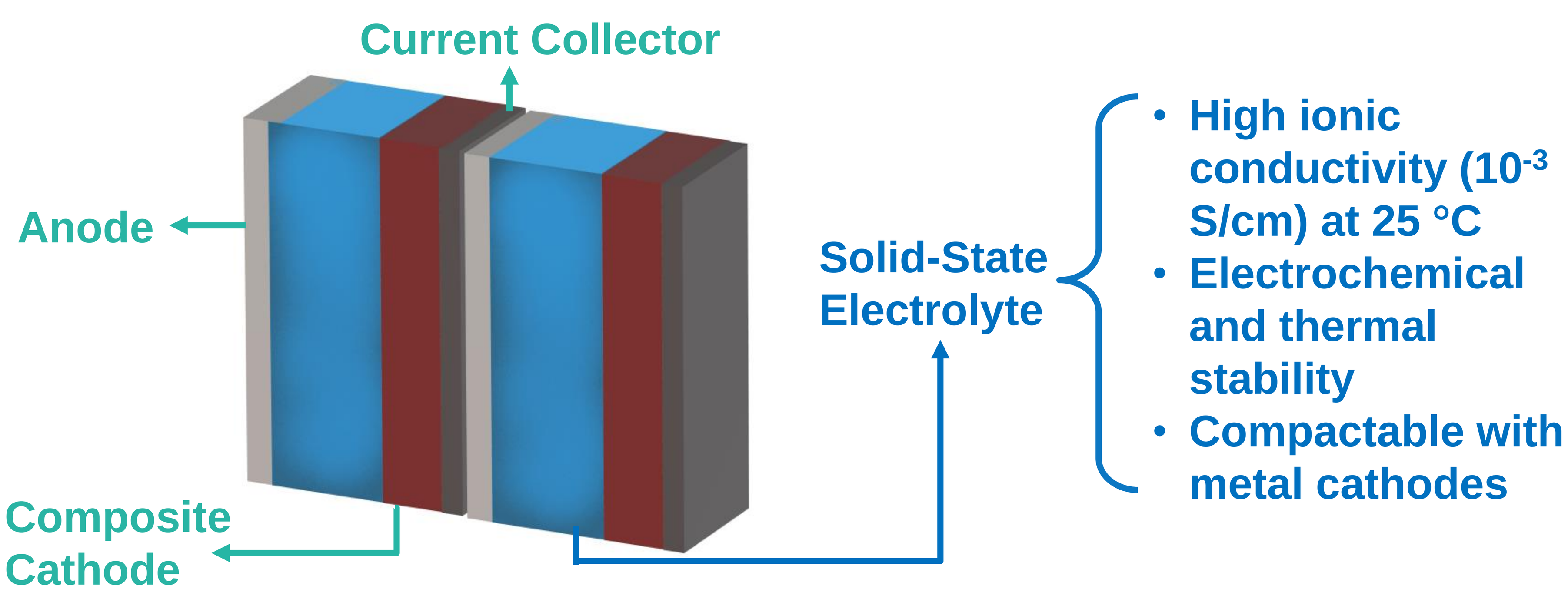
Background and Objectives

The all-solid-state concept can enable batteries of higher energy density and improved safety. For this, adequate solid-state electrolytes with high ionic conductivity and electrochemical stability need to be developed.

Complex borohydrides as electrolytes shows a high transference number and good compatibility with metal anodes, e.g. Na. However, the low ionic conductivity of $NaBH_4$ (10^{-10} S cm^{-1} at RT) hinders practical application.

Figure 1: Concept of the All-Solid-State battery



Observations

Figure 2: a) TEM of nanoconfined $NaBH_4$, b) TEM of $NaBH_4@Na_2B_{12}H_{12}$, c) NMR of pristine $NaBH_4$ and $NaBH_4$ oxidized by 5% O_2, d) the ionic conductivity of $NaBH_4$ oxidized at different O_2 levels as function of temperature , d) Arrhenius plot of $NaBH_4@MCM-41$, $NaBH_4@Na_2B_{12}H_{12}$ partial oxidized $NaBH_4$ and pristine $NaBH_4$.

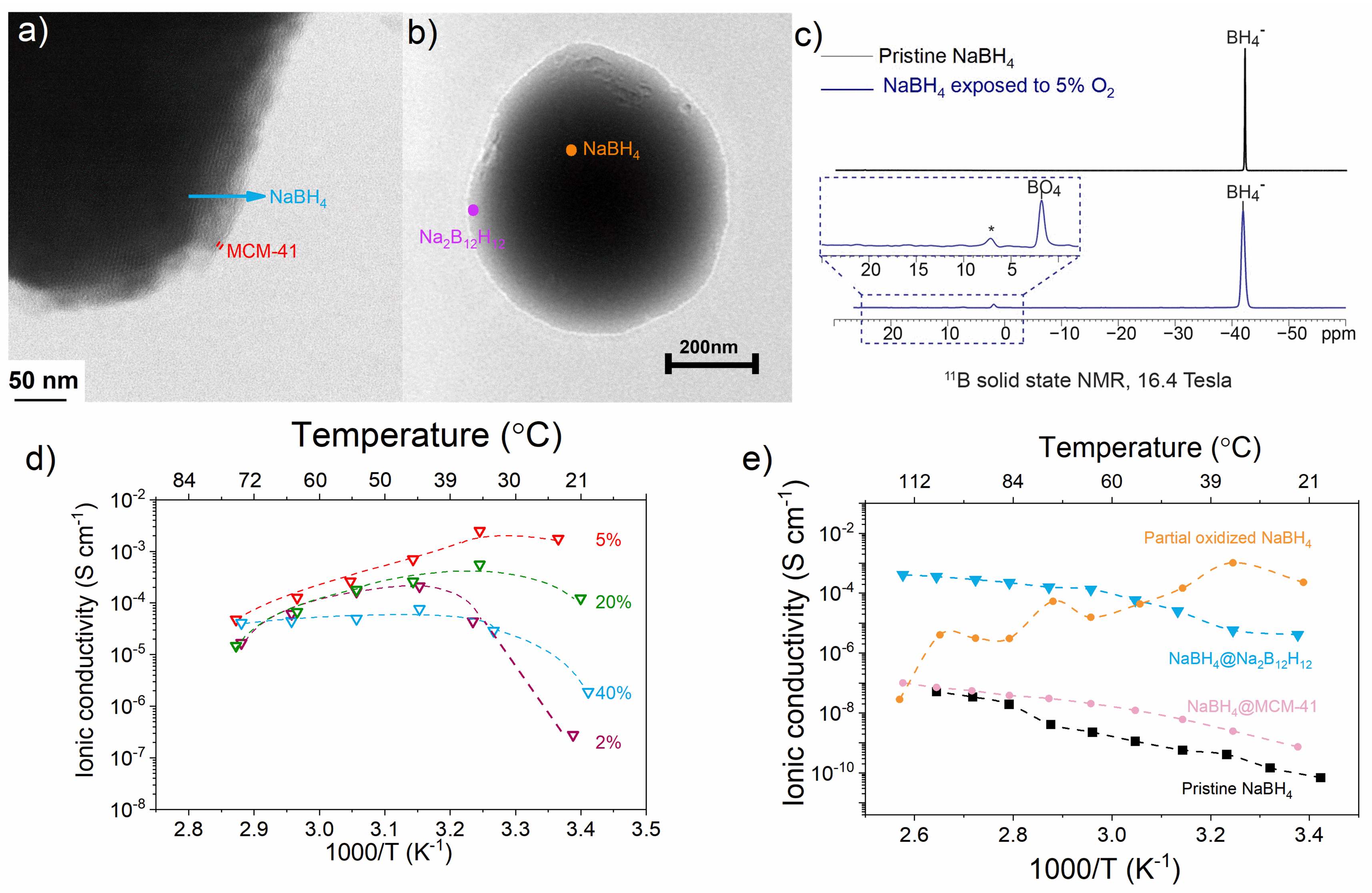


Table 1: Summary of the strategies investigated

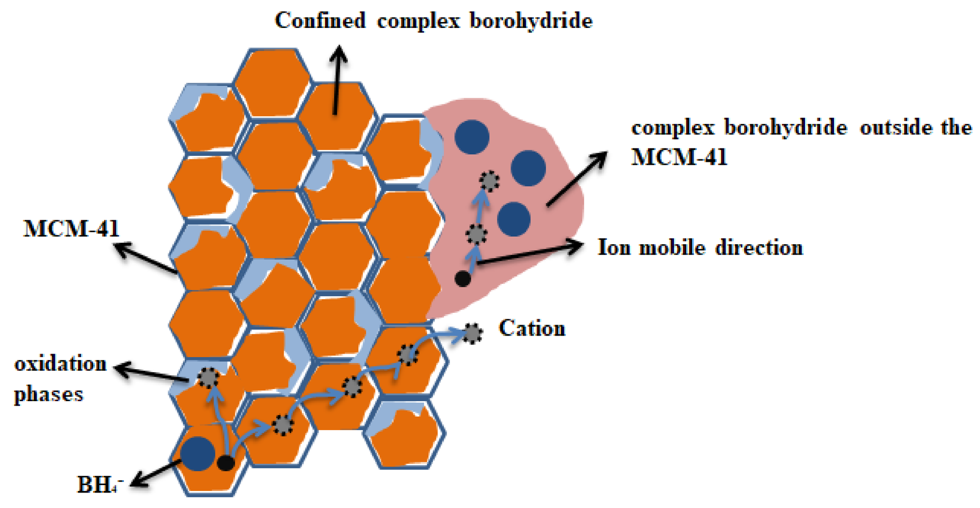
Method	Material	Potential reason
Nanoconfinement	$NaBH_4@MCM-41$[1]	Presence of the high ionic conductor $Na_2B_{12}H_{12}$
Core-shell structure	$NaBH_4@Na_2B_{12}H_{12}$	Conductive interface between $NaBH_4@Na_2B_{12}H_{12}$
Partial surface oxidation	Partial oxidized $NaBH_4$[2]	Creating a defective structure by partial oxidation

Strategies to enhance the ionic conductivity

a. Nanoconfinement into scaffold material (MCM-41)

Confining $NaBH_4$ into silica oxides scaffold MCM-41 via melt infiltration under H_2 pressure.

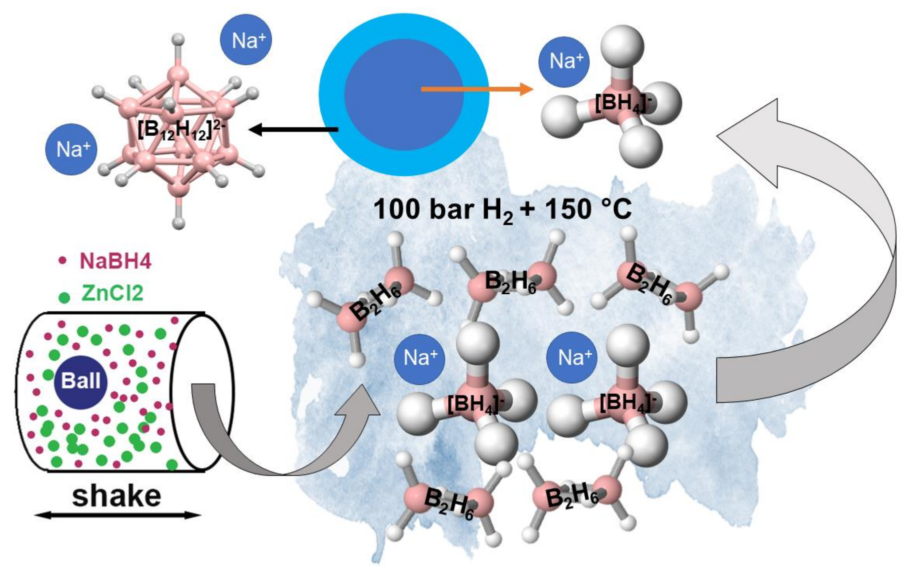
$NaBH_4@MCM-41$ ~ 10^{-7} S cm^{-1} at 115 °C



b. Core-shell structure by solid-gas reaction

Exposing $NaBH_4$ to B_2H_6 gas to synthesize $Na_2B_{12}H_{12}$ at the surface of $NaBH_4$ to create a defective interface of high ionic mobility

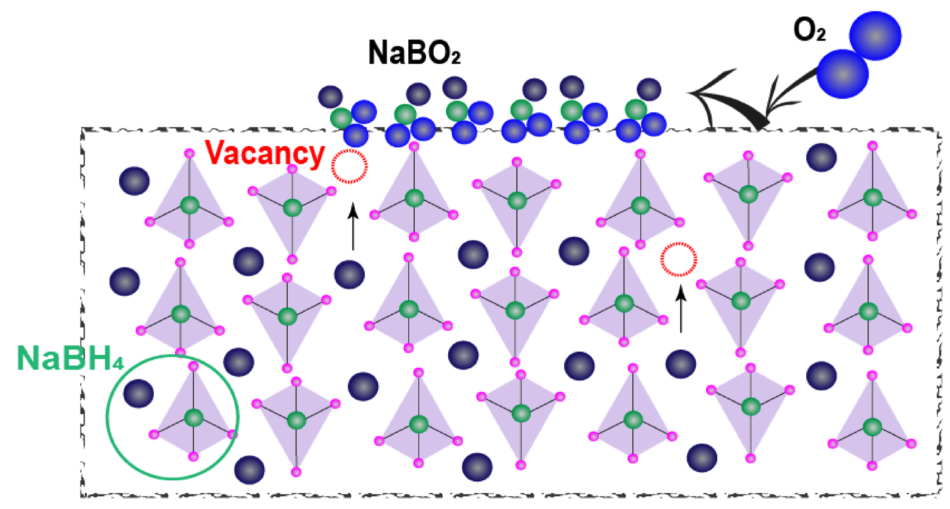
$NaBH_4@Na_2B_{12}H_{12}$ ~ 10^{-4} S cm^{-1} at 115 °C



c. Partial surface oxidation in complex borohydride

Partial oxidation of $NaBH_4$ surface by exposing $NaBH_4$ to controlled amounts of O_2 to create a defective $NaBH_4$ structure.

$NaBH_4$ 5% O_2 ~ 2.50×10^{-3} S cm^{-1} at 35°C



Conclusion

Through proper modifications, the ionic conductivity of $NaBH_4$ can be elevated to 10^{-3} S cm^{-1} at near room temperature. Our studies show the potential of $NaBH_4$ as a solid-state electrolyte.

We also expanded the partial oxidation method to $LiBH_4$ and $Mg(BH_4)_2$ and a significant increase in ionic conductivity was observed. The details can be seen in ref 2.

Future studies focus on further enhancing the ionic conductivity of complex borohydride at room temperature and incorporating modified complex borohydride electrolyte into All-Solid-State battery.

References

1.Luo, X., Rawal, A., & Aguey-Zinsou, K. F. (2021). Investigating the Factors Affecting the Ionic Conduction in Nanoconfined $NaBH_4$. Inorganics, 9(1), 2.

2.Luo, X., Rawal, A., Cazorla, C., & Aguey-Zinsou, K. F. (2020). Facile Self-Forming Superionic Conductors Based on Complex Borohydride Surface Oxidation. Advanced Sustainable Systems, 4(3), 1900113.