# Effects of specific surface area and pore volume of activated carbon nanofibers on nanoconfinement and dehydrogenation of LiBH$_4$

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## ARTICLE INFO

## ABSTRACT

The effects of specific surface area (S$_{BET}$) and total pore volume (V$_{tot}$) of activated carbon nanofibers (ACNF) on nanoconfinement and dehydrogenation of LiBH$_4$ are investigated. By varying activation time from 15 to 75 min, S$_{BET}$ and V$_{tot}$ of ACNF are altered in the ranges of 509–2752 m$^2$/g and 0.38–2.17 mL/g, respectively. Melt infiltration of LiBH$_4$ in ACNF is improved with the increment of S$_{BET}$ and V$_{tot}$. Due to effective melt infiltration, not only high hydrogen content desorbed (up to 81% of theoretical capacity), but also the release of B$_2$H$_6$ is suppressed. All nanoconfined LiBH$_4$ in ACNF show the main dehydrogenation at comparable temperature of 347–352 °C, implying that kinetic improvement is mainly from catalytic effects of carbon surface. However, effective nanoconfinement yields considerable reduction of onset and main dehydrogenation temperatures to 275 and 305 °C, respectively (ΔT = 125 and 170 °C, respectively, as compared with bulk LiBH$_4$). Via re-melting the as-prepared sample, further melt infiltration of LiBH$_4$ into voids and/or small pores of ACNF can be obtained. The latter leads to closer contact and more interaction with carbon surface, resulting in the reduction of onset dehydrogenation temperature toward 268 °C and the enhancement of relative content of hydrogen released at low temperature (305 °C). Thus, multiple times or long length of time for melt infiltration can be an interesting choice to increase LiBH$_4$ content up to the maximum loading of ACNF.

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## Introduction

Via particle size reduction, kinetic properties of hydrides are considerably improved due to shorter hydrogen diffusion pathway and higher surface area exposed to hydrogen [1–3]. High energy ball milling has been intensively used to decrease particle size of hydrides. However, upon cycling particle agglomeration and sintering are observed, resulting in poorer de/rehydrogenation kinetics. Confinement into nanoporous

scaffolds, which act as the structural directing agent to constrain particle size of hydrides in nanoscale, has been of interest in solid state hydrogen storage field. For thermodynamics, particle size reduction and interaction with scaffold pore wall can result in either stabilization or destabilization of hydrides, which depends on the surface energy of hydrogenated and dehydrogenated states [2]. For example, $MgH_2$ nanoparticles embedded in LiCl salt matrix (~7 nm in size) were relatively destabilized due to increase of surface energy from particle size reduction [4]. Nevertheless, $NaAlH_4$ was stabilized after nanoconfinement because Na confined in carbon scaffold provided additional binding enthalpy to destabilize NaH (dehydrogenated product of $NaAlH_4$) [5–7]. Therefore, thermodynamics of nanoconfined hydrides can be altered by modifying surface chemistry of scaffold [8].

Lithium borohydride ($LiBH_4$) is one of the most promising materials for solid state hydrogen storage due to high reversible capacity of 13.6 wt. % $H_2$. However, its thermodynamic stability (decomposition temperature up to 460 °C) and severe rehydrogenation condition ($T = 600$ °C under 350 bar $H_2$) hamper practical uses as hydrogen storage material [9]. As compared with physically mixed $LiBH_4$-nonporous graphite, melt infiltrated $LiBH_4$ in carbon aerogel scaffold (13 nm pore size) showed considerable reduction of onset dehydrogenation temperature and activation energy ($\Delta T = 100$ °C and $\Delta E_A = 43$ kJ/mol, respectively) together with 50 times faster dehydrogenation rate [10]. This improvement could be related to the enhancement of ionic mobility at nanoscale [11–13]. In addition, suppression of $B_2H_6$ release observed in nanoconfined $LiBH_4$ in carbon scaffold could be explained by fast reaction of $B_2H_6$ and $LiBH_4$ in the tight pores of carbon [13]. The latter hinted at the decomposition mechanisms via $Li_2B_{12}H_{12}$ according to the reaction $2LiBH_4 + 5B_2H_6 \rightarrow Li_2B_{12}H_{12} + 13H_2$ [13,14]. Moreover, ordered mesoporous silica (SBA-15) [15], multiwall carbon nanotubes (MWCNT) [16], Cu-metal-organic framework (Cu-MOF) [17], and activated carbon nanofibers (ACNF) [18] have been used for $LiBH_4$ nanoconfinement. Enhancement of surface area and pore volume of SBA-15 yielded effective infiltration of $LiBH_4$, leading to significant reduction of dehydrogenation temperature ($\Delta T =$ up to 120 °C). However, undesired reaction between the decomposition products of $LiBH_4$ and $SiO_2$ to form $Li_2SiO_3$ and $Li_4SiO_4$ resulted in irreversibility of $LiBH_4$ [15]. In the case of MWCNT, reduction of dehydrogenation temperature ($\Delta T \sim 100$ °C) was detected in $LiBH_4$ confined in ball-milled MWCNT. High vacancies, defects in the nanotube walls, and shortening nanotube length of MWCNT obtained after ball milling favored kinetic properties of $LiBH_4$ [16]. For Cu-MOF, nanoconfinement of $LiBH_4$ in the pores of Cu-MOF initiated the interaction between $LiBH_4$ and $Cu^{2+}$ ions, leading to significant reduction of decomposition temperature ($\Delta T = 320$ °C with respect to bulk $LiBH_4$) [17].

Furthermore, our group has recently reported a new material of activated carbon nanofibers (ACNF) with high specific surface area and pore volume (995 $m^2$/g and 0.71 mL/g, respectively) for nanoconfinement of $LiBH_4$ [18]. Not only remarkable reduction of dehydrogenation temperature ($\Delta T_{onset} = 128$ °C with respect to milled $LiBH_4$) and suppression of $B_2H_6$ release were obtained, but also reversibility up to 10.1 wt. % $H_2$ after three hydrogen de/absorption cycles

under milder condition than pristine $LiBH_4$ ($T = 350$ °C and $p(H_2) = 80$ bar) [18]. In the present study, various activation times during heating (15, 45, and 75 min) are applied to discover the best condition for preparation of ACNF with high specific surface area and pore volume. The effects of specific surface area and pore volume of ACNF on nanoconfinement of $LiBH_4$ as well as dehydrogenation temperature and kinetics are investigated. Dehydrogenation pathways of the most competitive nanoconfined sample are discussed to be a guideline for further improvement of nanoconfinement.

## Experimental details

### Sample preparation

Polyacrylonitrile (PAN)-based activated carbon nanofibers were prepared by the electrospinning technique, carbonization, and chemical activation with concentrated potassium hydroxide (KOH) solution [19]. PAN ($M_w = 150,000$ g/mol, Sigma-Aldrich) was dissolved in N,N-dimethylformamide (DMF, Carlo Erba Reagents) and stirred for 12 h to prepare 10% w/v PAN solution for electrospinning. PAN solution was loaded into a 10 mL polypropylene syringe assembled with a stainless steel needle connected to an anode of a DC power supply. Electrospinning was carried out at 35 °C and at a voltage of 10 kV. The tip-to-collector distance and the flow rate were 15 cm and 1.0 mL/h, respectively. A grounded stainless steel roll wrapped with aluminum foil was employed as a collector. The obtained PAN-based nanofibers were stabilized in air at 280 °C for 45 min and pyrolyzed under nitrogen ($N_2$) atmosphere at 1000 °C for 1 h to obtain carbon nanofibers, denoted as CNF. Activation of CNF was done by immersing in concentrated KOH solution (30% w/v) under 1:4 (CNF:KOH solution) weight ratio at 80 °C for 2 h and dried at room temperature for 24 h. CNF treated with KOH solution was heated from room temperature to 800 °C (5 °C/min) under $N_2$ atmosphere, kept at 800 °C for 15, 45, and 75 min, and cooled to room temperature to obtain activated carbon nanofibers, denoted as ACNF15, ACNF45, and ACNF75, respectively. Residual KOH in ACNF were neutralized by immersing in 0.5 M hydrochloric acid for 30 min at room temperature. ACNF were filtered and washed with distilled water until the pH of filtrate was neutral (pH ~ 6). The obtained ACNF were dried at 120 °C for 24 h. Prior to melt infiltration, ACNF were treated at 500 °C under vacuum for 6 h.

$LiBH_4$ ($\geq$90%, hydrogen storage grade, Sigma-Aldrich) was milled by using a SPEX Sample Prep 8000D Dual Mixer/Mill. The milling time and the ball-to-powder weight ratio were 1 h and 30:1, respectively. Treated ACNF15, ACNF75, and ACNF45 were mixed with milled $LiBH_4$ under 2:1 (ACNF:$LiBH_4$) weight ratio in the mortar. Nanoconfinement was carried out by heating the mixtures of $LiBH_4$-ACNF15, $LiBH_4$-ACNF45, and $LiBH_4$-ACNF75 from room temperature to 310 °C (5 °C/min) under 90 bar $H_2$, dwelling at isothermal and isobaric condition for 45 min, and cooling to room temperature to achieve nanoconfined $LiBH_4$ in ACNF, denoted as nano $LiBH_4$-ACNF15, nano $LiBH_4$-ACNF45, and nano $LiBH_4$-ACNF75, respectively.