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$LiBH_4$ nanoconfined in activated carbon nanofiber for reversible hydrogen storage

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ABSTRACT

New host material of activated carbon nanofiber (ACNF) prepared from carbonization and KOH activation of polyacrylonitrile (PAN)–based fibers is proposed for nanocofinement of $LiBH_4$. Nanocofinement and homogeneous distribution of $LiBH_4$ in ACNF are confirmed. Remarkable reduction of onset and main dehydrogenation temperatures of $LiBH_4$ ($\Delta T = 128$ and 118 °C, respectively) is obtained together with suppression of B_2H_6 release during dehydrogenation. Inferior hydrogen content released during cycling from nanoconfined $LiBH_4$ in ACNF at 350 °C under vacuum is due to partially unconfined $LiBH_4$ and formation of stable $Li_2B_{12}H_{12}$ phase. However, nanoconfined $LiBH_4$ in ACNF desorbs and preserves (after three release and uptake cycles) up to 11.7 and 10.1 wt.% H_2 with respect to $LiBH_4$ content, respectively. Also, $LiBH_4$ can be rehydrogenated at significantly milder condition after nanoconfinement in ACNF, that is, $\Delta T = 250$ °C and $\Delta p(H_2) = 270$ bar with respect to bulk $LiBH_4$. It could be claimed that not only positive influence of nanoconfinement as well known and frequently reported, but also catalytic effect and good thermal conductivity of ACNF itself can probably synergistically favors hydrogen sorption kinetics of $LiBH_4$.
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Introduction

Lithium borohydride ($LiBH_4$) has been one of the most promising materials for solid–state hydrogen storage due to its high gravimetric and volumetric hydrogen densities of 18.5 wt.% and 121 kg H_2/m^3, respectively [1–9]. However, its high thermal stability results in severe de/rehydrogenation condition, i.e., the main dehydrogenation starts above 380 °C and only half of hydrogen is obtained below 600 °C [4], while rehydrogenation can be achieved at 600 °C under 350 bar H_2 [3,5]. One of the most outstanding approaches to destabilize $LiBH_4$ is confinement into nanoporous host materials, which not only constrains particle agglomeration of $LiBH_4$ during cycling, but also shorten diffusion distance for hydrogen and increase surface area, leading to faster de/rehydrogenation rates. Gross et al. [10] reported that nanoconfined $LiBH_4$ in carbon aerogel scaffold (13 nm pore size) not only improved dehydrogenation rate (up to 50 times faster than bulk material at 300 °C), but also decreased dehydrogenation temperature ($\Delta T = 75$ °C) and enhanced cycling capacity up to 32%. Afterwards, via confinement of $LiBH_4$ in highly ordered nanoporous carbon with hexagonally packed 2 nm diameter columnar pores, significant reduction of onset dehydrogenation temperature ($\Delta T = 240$ °C) with respect to bulk $LiBH_4$ and suppression of toxic diborane (B_2H_6) release were achieved [11]. Recently, synergistic effects of nanoconfinement in carbon aerogel scaffold and nanocatalysts (e.g., NbF_5 and CoNiB) on

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reversible hydrogen storage performance of $LiBH_4$ were reported [12,13]. $LiBH_4$ nanoconfined in carbon aerogel loaded with NbF_5 showed remarkable reductions of onset temperature and activation energy for hydrogen desorption with respect to bulk $LiBH_4$ (ΔT (onset) = 225 °C and ΔE_A = 91.6 kJ/mol, respectively) as well as mild condition for rehydrogenation (T = 200 °C, $p(H_2)$ = 60 bar) [12]. In the case of nanoconfined $LiBH_4$ in CoNiB–loaded carbon aerogel, up to 15.9 wt.% H_2 released at temperature below 600 °C together with excellent desorption kinetics, for example, at 350 °C, 9.33 wt.% H_2 was obtained within 30 min. Also, onset and main dehydrogenation temperatures lowered to 192 and 320 °C, respectively (i.e., ΔT = 98 and 112 °C, respectively, as compared with bulk $LiBH_4$) [13].

Besides nanoporous carbon aerogel scaffold, other host materials of ordered mesoporous silica (SBA–15) [14,15], mesoporous TiO_2 [16], carbon nanotubes [17], CuS hollow nanospheres [17], and polymer host [18,19] have been used for nanoconfinement of $LiBH_4$. Ngene et al. [14] reported that confined $LiBH_4$ in nanoporous silica of SBA–15 by melt infiltration enhanced hydrogen desorption properties together with low onset desorption temperature at 150 °C. Afterwards, by loading 33 wt.% $LiBH_4$ into SBA–15 by incipient wetness impregnation, onset and main decompositions at very low temperatures of 45 and ~92 °C, respectively, and fast dehydrogenation kinetics at 105 °C (8.5 wt.% H_2 with respect to $LiBH_4$ content within 10 min) were achieved [15]. However, upon dehydrogenation, SiO_2 and decomposition products of $LiBH_4$ reacted to form Li_2SiO_3 and Li_4SiO_4, resulting in irreversible hydrogen loss [14,15]. Furthermore, $LiBH_4$ incorporated into mesoporous TiO_2 scaffold via chemical impregnation showed onset and main hydrogen release at 220 and 330 °C, respectively, as well as fast dehydrogenation kinetics at 300 °C (11 wt.% H_2 with respect to $LiBH_4$ content within 3 h) [16]. However, undesired reaction between TiO_2 and $LiBH_4$ to form $LiTiO_2$ and Li_2TiO_3, resulting in loss of reactive element for reversibility was found during cycling. For nanoconfined samples of $LiBH_4$ in carbon nanotubes and CuS hollow nanospheres, they released hydrogen from room temperature and at temperatures considerably below that of bulk $LiBH_4$. However, oxidation of $LiBH_4$ by oxygen–containing group on the surface of carbon nanotubes was observed, leading to decrease in hydrogen storage capacity during cycling, whereas capacity of $LiBH_4$ confined in CuS hollow nanospheses was maintained due to no undesirable reaction between $LiBH_4$ and CuS [17]. Recently, our group proposed new host material of poly(methyl methacrylate)–co–butyl methacrylate (PMMA–co–BM) for $LiBH_4$ nanoconfinement [18]. Due to hydrophobic properties of polymer matrix, deterioration of $LiBH_4$ by oxygen and humidity was avoided, resulting in simple handling in ambient condition. It was found that although the interaction between $LiBH_4$ and ester group of PMMA–co–BM yielded significantly destabilization of $LiBH_4$ based on lower onset and main dehydrogenation temperatures (~80 and 105 °C, respectively) as well as milder conditions for dehydrogenation (T = 120 °C under vacuum) and rehydrogenation (T = 140 °C under 50 bar H_2), reduction of hydrogen content released and reproduced due to loss of B was obtained. Moreover, partial thermal degradation of PMMA–co–BM polymer host was detected during cycling. To solve these problems, multi–wall carbon nanotube (MWCNT) and $NaAlH_4$ were doped into nanoconfined $LiBH_4$–PMMA–co–BM [19]. It was found that $NaAlH_4$ considerably improved thermal stability of PMMA–co–BM host and reduced $LiBH_4$/PMMA–co–BM interaction, leading to superior hydrogen content desorbed during cycling, whereas effects of MWCNT was not really significant.

In the present work, we would like to present our new host material of activated carbon nanofiber (ACNF) for nanoconfinement of $LiBH_4$. Polyacrylonitrile (PAN)–based fibers prepared by electrospinning technique are carbonized under inert atmosphere and activated with concentrated potassium hydroxide (KOH) solution to obtain ACNF with high porosity and large surface area [20]. Successful nanoconfinement of $LiBH_4$ in ACNF and morphological studies are determined by N_2 adsorption–desorption and scanning electron microscopy (SEM)–energy dispersive X–ray spectroscopy (EDS)–elemental mapping, respectively. Dehydrogenation temperature and kinetics of nanoconfined $LiBH_4$ in ACNF are investigated by simultaneous differential scanning calorimetry (DSC)–mass spectrometry (MS) and titration measurements. Reaction mechanisms and phases formed during de/rehydrogenation are studied by Fourier transform infrared spectroscopy (FTIR).

Experimental details

Sample preparation

Polyacrylonitrile (PAN)–based activated carbon nanofiber was prepared by electrospinning technique, carbonization, and chemical activation by KOH solution based on the previous report [20]. PAN (M_w = 150,000 g/mol, Sigma–Aldrich) was dissolved in N, N–dimetylformamide (DMF, Carlo Erba Reagents) to prepare 10 wt.% PAN precursor solution for electrospinning. After gentle stirring at room temperature for 12 h, PAN solution was loaded into a 10 ml polypropylene syringe equipped with a stainless steel needle connected to the anode of a DC power supply. Electrospinning was carried out at 35 °C and at a voltage of 7 kV. A tip–to–collector distance and a flow rate of 15 cm and 0.5 ml/h, respectively, were used. A grounded stainless steel roll wrapped with alluminium foil was employed as a collector. The obtained PAN–based nanofibers were stabilized in air at 280 °C for 90 min and carbonized under N_2 atmosphere at 1000 °C for 1 h to obtain carbonized nanofiber (CNF).

Activation of CNF was done by using KOH solution as a chemical reagent. CNF was immersed in concentrated KOH solution (30% w/v) at 80 °C for 2 h and dried at room temperature for 24 h. KOH–treated CNF was activated by heating to 800 °C (heating rate 5 °C/min) under N_2 atmosphere, dwelling at 800 °C for 45 min, and cooling to room temperature to obtain activated carbon nanofiber (ACNF). To neutralize residual KOH, ACNF was immersed in 0.5 M hydrochloric acid for 30 min at room temperature. ACNF was filtered and washed with distillated water until the pH of filtrated reached pH 6. The final ACNF was dried at 120 °C for 24 h.

Prior to confinement of $LiBH_4$, ACNF was treated at 500 °C under vacuum for 6 h. 0.0200 g of treated ACNF was soaked

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