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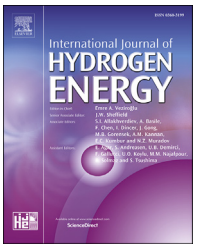

Hydrogen storage properties of activated carbon confined $LiBH_4$ doped with CeF_3 as catalyst

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ABSTRACT

CeF_3 as a catalyst is first added to activated carbon (AC) by ball milling under low rotation speed. Then the treated AC was used as the scaffold to confine $LiBH_4$ by melt infiltration process. The combined effects of confinement and CeF_3 doping on the hydrogen storage properties of $LiBH_4$ are studied. The experimental results show that $LiBH_4$ and CeF_3 are well dispersed in the AC scaffold and occupy up to 90% of the pores of AC. Compared with pristine $LiBH_4$, the onset dehydrogenation temperature for $LiBH_4$-AC and $LiBH_4$-AC-CeF_3 decreases by 150 and 190 °C, respectively. And the corresponding dehydrogenation capacity increases from 8.2 wt% to 13.1 wt% for $LiBH_4$-AC and 12.8 wt% for $LiBH_4$-AC-CeF_3, respectively. The maximum dehydrogenation speed of $LiBH_4$-AC and $LiBH_4$-AC-CeF_3 is 80 and 288 times higher than that of pristine $LiBH_4$ at 350 °C. And $LiBH_4$-AC and$LiBH_4$-AC-CeF_3 show good reversible hydrogen storage properties. On the during 4th dehydrogenation cycle, the hydrogen release capacity of $LiBH_4$-AC and $LiBH_4$-AC-5 wt% CeF_3 reaches 8.1 and 9.3 wt%, respectively.

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Introduction

In order to develop a new energy carrier system, different kinds of hydrogen storage materials have been extensively studied to optimize their properties [1–4]. Among these materials, complex hydrides (e.g. $LiBH_4$, $Mg(BH_4)_2$, and $NaBH_4$) comprised of light metal cations and borohydride have received much attentions due to their high gravimetric hydrogen density (e.g. 18.3 wt% H_2 for $LiBH_4$) [5–8]. These hydrides are considered to be potential candidates for solid state hydrogen storage system [2,9]. However, the B–H covalent bonds in these borohydrides are too thermodynamically stable that they hamper the de/rehydrogenation process [10,11]. For example, the decomposition of $LiBH_4$ requires over 400 °C with sluggish kinetics and inferior reversibility [12–14].

In order to achieve a better dehydrogenation condition, several attempts have been made to increase the dehydrogenation properties of hydrides. One of the methods is catalysts

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additions, which is mixing the hydrides with metal oxides, chlorides or fluoride [15–17]. Such catalysts could lower the onset dehydrogenation temperature. Guo et al. [18] reported that when doped with TiF_3, the decomposition temperature of $LiBH_4$ could be reduced to 100 °C while the system reaches a hydrogen capacity of 5.0 wt% at 250 °C. Nielsen et al. [19] reported that nanoconfined $NaAlH_4$ in carbon aerogel catalyzed with 3.0 wt% $TiCl_3$ showed superior dehydrogenation kinetics over both nanoconfined $NaAlH_4$ and bulk catalyzed $NaAlH_4$. Kim et al. [7] reported that when doped with NbF_5, $6LiBH_4 + CaH_2$ composite shows a reversible hydrogen capacity of 6 wt% at 450 °C. Sun et al. [20] reported that nano Ni particles could significantly decrease the activation energy of $LiBH_4$ in the $LiBH_4$-AC system to 88 kJ/mol, which is much lower than that of pristine $LiBH_4$ (156 kJ/mol) [10]. Zhou et al. [21] proved that addition of REF_3 (RE = Y, La, Ce) not only reduces the peak temperatures of both dehydrogenation steps of $LiAlH_4$, but also reduces the activation energy for the two desorption steps.

Another effective approach to improve the dehydrogenation properties is the adoption of nanoconfinement [22–26]. After space confinement, the metal hydrides are confined in the nano-structure of the scaffold materials, hence decrease the particle size of the hydrides while prevent agglomeration and phase segregation during decomposition [23]. Many reports have confirmed great enhancement in the thermodynamic and kinetic properties of metal hydrides using this method. Fang et al. [27] reported incorporation of $LiBH_4$ into activated carbon using chemical impregnation. The sample starts to release hydrogen at over 220 °C. Liu et al. [28] proved that when $LiBH_4$ was confined with nanoporous hard carbon with hexagonally pores of 2 nm diameter, the onset dehydrogenation temperature reduced drastically while emission of diborane (B_2H_6) gas was suppressed. Xu et al. [29] confirmed that the onset dehydrogenation temperature of $LiBH_4$-graphene ball-milling sample could be reduced from 420 °C to 195 °C. Ward et al. [30] showed that $LiBH_4$:C_{60} nanocomposite had great reversible hydrogen storage properties as well as the ability to absorb hydrogen under mild conditions. Shao et al. [31] used a mesoporous carbon scaffold containing dispersed NbF_5 to load $LiBH_4$ and reported a combined effect of nanoconfinement and nanocatalysis on the dehydrogenation properties of $LiBH_4$.

Although their hydrogen storage properties have been greatly enhanced using these methods, complex hydrides still could not meet the requirement for onboard applications. Some works have been focused on combining the effect of catalyst doping and nano-confinement [8,16,17,19,20,32]. In this paper, the scaffold we used was activated carbon (AC) doped with CeF_3 as catalyst. Activated carbon is a very commonly used porous structure and is very easy to obtain. CeF_3 was added to activated carbon through ball milling and melt infiltration was used to prepare $LiBH_4$-AC-CeF_3 confined sample. The hydrogen storage properties of $LiBH_4$ were greatly enhanced.

Experimental

$LiBH_4$ (95% purity) was purchased from Acros Organics and used without further purification. Activated carbon (AC, 99% purity) was also purchased from Acros Organics and was purified under 500 °C and vacuum in a reactor for 5 h to remove moisture and other possible impurities. CeF_3 (99.99% purity) was purchased from Alfa Aesar. First, different amount of CeF_3 catalyst was added to activated carbon in a milling vessel and they were ball milled for 1 h using a QM-3SP4 planetary ball mill with a rotation speed of 100 rpm. Then the mixed samples were removed from the vessel and used as scaffold in further preparation. The $LiBH_4$-AC-CeF_3 melt infiltration (MI) nanocomposite was prepared following a two-step procedure. First, the scaffold AC-CeF_3 and $LiBH_4$ (mass ratio 3:1) were mixed using the same planetary mill at 100 rpm for 5 min. The mixture was then delivered into a reactor and calcined at 290 °C under 5 MPa H_2 pressure for 1 h. All sample operations were performed in an Ar atmosphere.

Dehydriding/rehydriding measurements were carried out on a homemade Sieverts-type apparatus. About 200 mg of sample was loaded into a stainless steel reactor, which was connected to a thermocouple and a pressure sensor to monitor the temperature and pressure inside the reactor. For the non-isothermal desorption measurements, i.e. the temperature programmed desorption (TPD) measurements, the samples were heated gradually from room temperature to 500 °C at a heating rate of 2 °C/min. For the isothermal desorption measurements, the samples were heated quickly to 350 °C under a back pressure of 8 MPa H_2 to prevent the decomposition of the samples. Then the reactor was evacuating quickly to start the isothermal measurements. Hydrogen capacity was estimated by the ideal gas equation using the temperature and pressure previously obtained. The rehydriding process was carried out under the conditions of 350 °C and 6 MPa H_2. The reactor was filled with H_2 and then heated to 350 °C rapidly and kept at that temperature for 5 h.

The AC scaffold was characterized by gas absorption and desorption using an Autosorb-1-C surface area and pore size analyzer from Quantachrome. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TG) were conducted using a differential scanning calorimeter (Netzsch STA449F3), which was equipped with a mass spectrometer (MS, Netzsch QMS403C) to detect the hydrogen desorption synchronously. X-ray diffraction (XRD) analysis was performed on a PANalytical X-ray diffractometer (X'Pert Pro, Cu-Kα, 40 kV, 40 mA) where the samples were sealed with an amorphous membrane during the measurements to avoid oxidation. Field emission scanning electronic microscopes (SEM, Hitachi S-4800) were applied to analyze the morphology of the samples, while the energy dispersive spectroscopy (EDS) detector was used to study the elemental distributions.

Results and discussion

Sample preparation

In order to characterize the effect of melt infiltration, the surface area and pore volume were determined by BET measurements. Fig. 1 shows the results of N_2 adsorption measurements for the as received activated carbon (AC), the activated carbon ball milled with CeF_3 to be used as scaffold (AC-CeF_3). Table 1 lists the surface area and pore volumeof the

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