Enhanced Low-Temperature Hydrogen Storage in Nanoporous Ni-Based Alloy Supported LiBH$_4$

Xi Chen, Zhao Li, Yue Zhang, Dongming Liu*, Chunyang Wang, Yongtao Li, Tinzhi Si and Qingan Zhang

School of Materials Science and Engineering, Anhui University of Technology, Maanshan, China

To reveal the synergistic effect of nanoconfinement and metallic catalysis on the hydrogen storage properties of LiBH$_4$, the nanoporous Ni-based alloy (np-Ni) was prepared herein by dealloying of the Mn$_{70}$Ni$_{30}$ alloy in (NH$_4$)$_2$SO$_4$ solution, and then LiBH$_4$ was loaded into np-Ni to construct the LiBH$_4$/np-Ni hydrogen storage system using wet impregnation. It was found that dehydrogenation of the LiBH$_4$/np-Ni (1:5) system starts at around 70°C and ends before 400°C, with ∼11.9 wt.% of hydrogen desorbed. The apparent dehydrogenation activation energy for the LiBH$_4$/np-Ni (1:5) system was remarkably decreased to about 11.4 kJ/mol. After rehydrogenation at 450°C under 8 MPa hydrogen pressure, ∼8.2 wt.% of hydrogen can be released from about 60°C upon second dehydrogenation. These obtained results would provide an efficient strategy for improving the hydrogen storage properties of other metal borohydrides.

Keywords: hydrogen storage, lithium borohydride, nanoporous metal, nanoconfinement, catalysis

INTRODUCTION

Nowadays, the issue of energy shortage has been called into public focus. Hydrogen is considered to be the most ideal secondary source because of its high caloric value, low environmental impact and abundant resources (Abe et al., 2019). To meet the need of storing hydrogen with high efficiency and safety, it is necessary to develop hydrogen storage materials with high mass and volume hydrogen density (Yang et al., 2010; Li H. W. et al., 2011; Abdalla et al., 2018). LiBH$_4$ has attracted much more attention due to its extremely high theoretical hydrogen storage capacity of 18.5 wt.%.

However, the elevated dehydrogenation temperature, complicated dehydrogenation behavior and poor reversibility limit its practical applications (Züttel et al., 2003; Orimo et al., 2005; Mauron et al., 2008; Li C. et al., 2011). In order to overcome these deficiencies, the strategies of constructing reactive hydride system (Liu D. M. et al., 2013; Liu et al., 2015, 2016; Ding et al., 2019), cation/anion substitution (Yin et al., 2008; Fang et al., 2011), adding catalyst (Zhang et al., 2017; Cai et al., 2018) and nanoconfinement (Guo et al., 2017; Xu et al., 2017; Meng et al., 2018) were developed in the last decade.

Nanoconfinement of LiBH$_4$ in nanoporous material can maintain the particle within a nanoscale structure, which is exceedingly beneficial to enlarge the reaction interface and shorten the element diffusion distance, thus significantly enhancing the de-/rehydrogenation properties (Ngene et al., 2010b; Shao et al., 2015; Meng et al., 2018; Gasnier et al., 2019). For example, Zhang et al. found that LiBH$_4$ nanoparticles supported by disordered mesoporous carbon (CMK-3) showed a single dehydrogenation peak at about 332°C and a large dehydrogenation amount of 14 wt.% below 600°C (Zhang et al., 2007). Fang et al. embedded LiBH$_4$ into active carbon (AC) by chemical impregnation.
Due to the enhancement of both the thermodynamic and kinetic properties, the LiBH$_4$/AC system began to release hydrogen at 220°C, which is 150°C lower than bulk LiBH$_4$ without nanostructure modulation (Fang et al., 2008b). Other nanoporous material scaffolds, such as carbon aerogel (Zhao et al., 2014; Surrey et al., 2016), ordered mesoporous carbon (Cai et al., 2016), metallic organic framework (MOFs) (Sun et al., 2011) and mesoporous silicon dioxide (SBA-15) (Ngene et al., 2010a), were also used as the confinement carriers to support LiBH$_4$.

However, the above reported nanoconfinement carriers are composed of non-metallic material that can only provide a single nanoconfinement role for LiBH$_4$ in general. Taking into account that transition metal elements (e.g., Ni and Co) can serve as the active catalyst in improving the hydrogen storage properties of complex hydrides owing to their high electronegativity0 (Ngene et al., 2011; Liu et al., 2018; Zhang et al., 2018), a synergistic effect of nanoconfinement and catalysis would be achieved by confining LiBH$_4$ in nanoporous transition metal. Based on this consideration, nanoporous Ni-based alloy was prepared by dealloying of the Mn$_{70}$Ni$_{30}$ alloy and then used as the carrier to support LiBH$_4$ in this work, and a significantly improved low-temperature hydrogen storage in LiBH$_4$ was successfully obtained.

**EXPERIMENTAL SECTION**

**Sample Preparation**

Commercial LiBH$_4$ powder (95%, Alfa Aesar), Mn bulk (99.5%, Alfa Aesar), Ni sheet (99.5%, Alfa Aesar) and tetrahydrofuran (THF) (99.8%, anhydrous, Alfa Aesar) were used in experiments. The Mn$_{70}$Ni$_{30}$ alloy was prepared by induction melting of appropriate amounts of Mn and Ni metals. For compensating the loss of Mn during melting, the extra 3 wt.% of Mn was added on the basis of stoichiometric amount. The as-cast Mn$_{70}$Ni$_{30}$ alloy was mechanically crushed into powders of 200 mesh, and the nanoporous Ni-based alloy (denoted as np-Ni) was prepared by dealloying of the Mn$_{70}$Ni$_{30}$ alloy powders in 1 mol/L (NH$_4$)$_2$SO$_4$ solution at 50°C for 2 h. The LiBH$_4$/np-Ni (1:5) system was prepared by loading LiBH$_4$ into np-Ni using wet impregnation method. Firstly, LiBH$_4$ was dissolved in anhydrous THF. Then, np-Ni was put in the LiBH$_4$ solution according to the LiBH$_4$/np-Ni weight ratio of 1:5. Finally, the mixture was evacuated for 24 h to remove THF solvent.

**Sample Characterization**

De-/rehydrogenation properties were examined based on the volumetric method by using a carefully calibrated Sieverts-type apparatus. Thermal dehydrogenation was performed by heating the sample from ambient temperature to 500°C at a rate of 2°C/min. Isothermal dehydrogenation was performed by quickly heating and then keeping the sample at a given temperature. The hydrogen back pressure for the above temperature ramp and isothermal dehydrogenation examinations was below 0.1 MPa. Isothermal rehydrogenation was carried out at 450°C under 4 MPa hydrogen pressure. The weight of np-Ni was not taken into account in calculating the hydrogen de-/absorption amounts.

X-ray diffraction (XRD) measurement was performed by a Rigaku D/Max 2500VL/PC diffractometer at 50 kV and 200 mA with Cu Kα radiation. A special Ar-filled holder was applied to seal the XRD sample to avoid contact with air in the course of measurement. To quantitatively investigate the phase structure change of the Mn$_{70}$Ni$_{30}$ alloy before and after dealloying, the XRD profiles were analyzed with the Rietveld refinement program RIETAN-2000 (Izumi and Ikeda, 2000). Scanning electron microscopy (SEM) was carried out using a Nova NanoSEM 430 microscope equipped with an energy dispersive X-ray spectrometer (EDS). Transmission electron microscopy (TEM) observation was performed on a JEM-2100F instrument. Pore size distribution, pore volume and specific surface area were determined by a Micromeritics ASAP 2020 fully-automatic analyzer based on the Brunauer–Emmett–Teller (BET) and Barrett–Joyner–Halenda (BJH) methods (Lowell et al., 2004). Fourier transform infrared (FTIR) spectrum was collected using a Nicolet 6700 FTIR spectrometer.

**RESULTS AND DISCUSSION**

**Structural Analysis of LiBH$_4$/np-Ni System**

Figure 1 gives the observed XRD patterns and the Rietveld analysis results of Mn$_{70}$Ni$_{30}$ alloy before and after dealloying, and the phase abundances and structural parameters refined by
the Rietveld analysis are listed in Table 1. It can be seen that the Mn<sub>70</sub>Ni<sub>30</sub> alloy before and after dealloying are both composed of a single phase of (Mn, Ni) solid solution with a Cu-type structure. However, the XRD peaks of np-Ni are relatively broadened and move toward higher angle as compared with the Mn<sub>70</sub>Ni<sub>30</sub> alloy. The results indicate that the grain size and cell parameters of the sample were both decreased with the extraction of Mn atom from (Mn, Ni) solid solution upon dealloying due to that Mn has a larger atomic radius relative to Ni.

| Sample         | Phase        | Space group | Lattice parameters (Å) | Abundance (%) |
|----------------|--------------|-------------|------------------------|---------------|
| Mn<sub>70</sub>Ni<sub>30</sub> alloy | (Mn, Ni)     | Fm-3m       | 3.6907(2) 3.6907(2) 3.6907(2) | 100           |
| np-Ni          | (Mn, Ni)     | Fm-3m       | 3.5601(1) 3.5601(1) 3.5601(1) | 100           |

Figure 2 presents the SEM images and corresponding EDS spectra of Mn<sub>70</sub>Ni<sub>30</sub> alloy and np-Ni. As seen from Figure 2A, the Mn<sub>70</sub>Ni<sub>30</sub> alloy has a smooth surface with a particle size of about ~70 µm. The EDS result (see Figure 2C) indicates that it consists of 70.22 at.% Mn and 29.78 at.% Ni, agreeing well with its nominal element composition. For np-Ni, as given in Figure 2D, the element content of Mn is decreased to 21.09 at.%.

It is reasonably considered that the massive lixiviation of Mn atom can bring large lattice distortion and physical shrinkage stress, thus leading to the formation of a nanoporous structure as shown in Figure 2B.

Figure 3A demonstrates the N\(_2\) adsorption/desorption isotherms for np-Ni and the LiBH\(_4\)/np-Ni (1:5) system. It can be seen that np-Ni has a typical IV-type adsorption isotherm with an obvious hysteresis loop. Those are the characteristics of mesoporous material. In comparison, the hysteresis loop has almost disappeared for the LiBH\(_4\)/np-Ni (1:5) system. The pore size distributions of np-Ni and the LiBH\(_4\)/np-Ni (1:5) system are compared in Figure 3B, which indicates that the peak in pore size distribution of np-Ni moves to a lower position with

![Figure 2](image-url)
an intensive decline in intensity after supporting LiBH₄. Table 2 gives the pore parameters and specific surface area of np-Ni and the LiBH₄/np-Ni (1:5) system. It is observed that np-Ni has the pore diameter, pore volume and specific surface area of 7.21 nm, 0.0586 cm³/g and 155 m²/g, respectively. However, those values reduce to 1.80 nm, 0.0339 cm³/g and 17 m²/g, respectively, for the LiBH₄/np-Ni (1:5) system. These results imply that LiBH₄ was loaded on the surface and impregnated into the pores of np-Ni. Figure 2E gives the TEM micrograph of the LiBH₄/np-Ni (1:5) system, and Figures 2F,G present the atomic lattice images of the square regions in Figure 2E obtained by inverse fast Fourier transform (IFFT). The fringe spacings of 0.200 nm in Figure 2F and 0.210 nm in Figure 2G correspond to (121) plane of LiBH₄ and (111) plane of Ni, respectively. The TEM results reveal that LiBH₄ and np-Ni indeed co-existed in the sample.

**Thermal Dehydrogenation Characteristics of LiBH₄/np-Ni System**

Figure 4 shows the temperature-programmed dehydrogenation curves of the LiBH₄/np-Ni (1:5) system and pristine LiBH₄. It can be seen that hydrogen release from the LiBH₄/np-Ni (1:5) system initiates at about 70°C and ends before 400°C, with ~11.9 wt.% of hydrogen desorbed. In contrast, the starting dehydrogenation temperature is as high as 330°C for pristine LiBH₄, and only 3.5 wt.% of hydrogen can be released when heating to 500°C. Evidently, the thermal dehydrogenation stability of LiBH₄ was notably reduced by np-Ni. In addition, Table 3 compares the dehydrogenation temperature of LiBH₄ supported on different carriers. It is observed that the present LiBH₄/np-Ni (1:5) system has lower starting and ending dehydrogenation temperatures as compared with the reported LiBH₄-based supporting systems. In other words, np-Ni can provide a stronger destabilization effect on LiBH₄ relative to other carriers due to its synergistic effect of nanoconfinement and metallic catalysis. On the one hand, nanoconfinement of LiBH₄ in np-Ni can decrease the particle size to nanoscale level, which is very helpful to facilitate the dehydrogenation by enlarging the reaction interface and shortening the element diffusion distance. On the other hand, Ni itself can act as the dehydrogenation catalyst for LiBH₄ by enhancing charge donation ability of Li atom to BH₄ unit and thus weakening the B–H bond due to its high electronegativity.

To further monitor the dehydrogenation process, Figure 5 gives the FTIR spectra of LiBH₄/np-Ni (1:5) systems after dehydrogenation at different temperatures. As can be seen
TABLE 3 | Hydrogen desorption temperature of LiBH₄ with different carriers.

| Carriers               | Starting temperature (°C) | Ending temperature (°C) | References                  |
|------------------------|---------------------------|-------------------------|------------------------------|
| ZnO/ZnCO₃O₄            | 169                       | <500                    | Xu et al., 2017              |
| CMK-3                  | 220                       | <600                    | Zhang et al., 2007           |
| Carbon aerogels@CoNiB  | 192                       | 600                     | Zhao et al., 2014            |
| SBA-15                 | 150                       | >500                    | Ngene et al., 2010a          |
| Single-walled carbon nanotubes | 270               | 550                     | Fang et al., 2008a           |
| Carbon nanotubes       | 250                       | <600                    | Yu et al., 2007              |
| Nanoporous carbon      | 220                       | 420                     | Liu et al., 2010             |
| Nanoscale SiO₂         | 200                       | 500                     | Chen et al., 2010            |
| np-Ni                  | 70                        | 400                     | This work                    |

![Figure 5](image-url)  
**FIGURE 5** | FTIR spectra of the LiBH₄/np-Ni (1:5) system dehydrogenated at different temperatures and rehydrogenated.

in Figure 5A, the obvious characteristic bands for B–H bond vibrations located at 2,379, 2,291, 2,224 and 1,126 cm⁻¹ (Zhang et al., 2011) confirm the existence of LiBH₄. With increasing the dehydrogenation temperature, the band intensity of B–H bond vibrations decreases gradually, indicating a continuous consumption of LiBH₄. Moreover, almost no FTIR bands can be observed in Figure 5D, which means that LiBH₄ was almost completely decomposed at 400°C. This result is in good agreement with the dehydrogenation phenomenon shown in Figure 4.

Dehydrogenation Kinetics of LiBH₄/np-Ni System
Figure 6A presents the isothermal dehydrogenation curves of the LiBH₄/np-Ni (1:5) system at the temperatures of 250, 300, and 350°C, respectively. It is observed that the dehydrogenation rate increases as the temperature rises. For example, the amounts of hydrogen desorbed within 5 min are 7.3, 9.4, and 10.4 wt.% at 250, 300, and 350°C, respectively. In order to further reveal the dehydrogenation mechanism, the experimental dehydrogenation data were fitted by the kinetic modeling of \( g(\alpha) = \int \frac{f(\alpha)}{f(\alpha_1)}k(\alpha) \, d\alpha \), where \( \alpha \) is the reacted fraction at time \( t \), and \( f(\alpha) \) are the functions representing different reaction mechanisms, and \( k \) is the rate constant (Li Y. et al., 2011; Liu D. M. et al., 2013). As the result, the function of \( -\ln(1-\alpha) \) gives the best linearity (see Figure 6B) over a broader \( \alpha \) range for each measurement with the correlation coefficient of \( R^2 > 0.99 \). This result indicates that dehydrogenation of the LiBH₄/np-Ni (1:5) system follows the first-order mechanism in the investigated temperature range.

According to the slope of the fitted straight line in Figure 6B, the \( k \) value at different temperatures can be obtained. Then the apparent activation energy for hydrogen desorption \( (E_a) \) can be determined based on the Arrhenius equation of \( k = k_0 \cdot \exp(-E_a/(RT)) \), where \( k_0 \) is the pre-exponential factor, \( R \) is the gas constant, and \( T \) is the temperature. Figure 6C gives the Arrhenius plot for the LiBH₄/np-Ni (1:5) system. From the slope \((-E_a/R)\) of the fitted straight line, \( E_a \) was calculated to be 11.4 kJ/mol. As reported in the literatures that \( E_a \) for LiBH₄ supported on CMK-3 and carbon aerogels@CoNiB are 40 and 46.39 kJ/mol, respectively (Zhang et al., 2007; Zhao et al., 2014). The lower \( E_a \) value for the present LiBH₄/np-Ni (1:5) system is originating from the synergistic effect of nanoconfinement and metallic catalysis of np-Ni, and can be regarded as one of the most important reasons for the enhanced dehydrogenation properties shown in Figures 4, 6A. Moreover, the preparation process of np-Ni carrier for LiBH₄ by dealloying method is far more convenient than that of CMK-3 based on template method.

Rehydrogenation Characteristics of LiBH₄/np-Ni System
The dehydrogenated residue of the LiBH₄/np-Ni (1:5) system was subjected to rehydrogenation, and Figure 7 demonstrates the isothermal rehydrogenation curve. It is observed that the LiBH₄/np-Ni (1:5) system can readily reabsorb 8.3 wt.% of hydrogen at 450°C under 8 MPa hydrogen pressure. The FTIR spectrum for the rehydrogenated product shown in Figure 5E gives the second hydrogen desorption curve of the LiBH₄/np-Ni (1:5) system. It can be seen that ~8.2 wt.% of hydrogen can be released during the second dehydrogenation process. Note that the starting dehydrogenation temperature keeps in a low value of about 60°C. The result indicates undoubtedly that the synergistic effect of nanoconfinement and metallic catalysis of np-Ni maintains well upon repeated dehydrogenation/hydrogenation.

CONCLUSIONS
In order to improve the hydrogen storage properties of LiBH₄, the nanoporous Ni-based alloy was prepared by dealloying of the precursor Mn₇₀Ni₃₀ alloy and then used as the carrier to support LiBH₄ by wet impregnation method. It was found that the constructed LiBH₄/np-Ni (1:5) system can release ~11.9
wt.% of hydrogen with the starting and ending dehydrogenation temperatures as low as about 70 and 400°C, respectively. Due to the synergistic effect of nanoconfinement and metallic catalysis of nanoporous Ni-based alloy, the apparent dehydrogenation activation energy of LiBH₄ was remarkably decreased to about 11.4 kJ/mol. The dehydrogenated residue can readily absorb hydrogen to regenerate LiBH₄ at 450°C under 8 MPa hydrogen pressure. Moreover, the starting dehydrogenation temperature keeps in a low value of about 60°C during the second dehydrogenation process.

**DATA AVAILABILITY STATEMENT**

All datasets generated for this study are included in the article.

**AUTHOR CONTRIBUTIONS**

XC and DL contributed conception and design of the study. XC and YZ were in charge of the analysis of data. ZL and CW prepared samples and performed characterization. All authors contributed to manuscript revision, read, and approved the submitted version.

**FUNDING**

This work was supported by the National Natural Science Foundation of China (Nos. U1503192 and 51371008).
REFERENCES

Abdalla, A. M., Hossain, S., Nisnidy, O. B., Azad, A. T., Dawood, M., and Azad., A. K. (2018). Hydrogen production, storage, transportation and key challenges with applications: a review. Energ. Convers. Manage. 165, 662–627. doi: 10.1016/j.enconman.2018.03.088

Abe, J. O., Popoola, A. P. I., Ajenifuja, E., and Popoola, O. M. (2019). Hydrogen energy, economy and storage: review and recommendation. Int. J. Hydr. Energy. 44, 15072–15086. doi: 10.1016/j.ijhydene.2019.04.068

Cai, R., Sun, L. X., Xu, F., Zou, Y. J., and Chu, H. L. (2016). LiBH4 confined in nitrogen-doped ordered mesoporous carbons for hydrogen storage. Mater. Sci. Forum. 852, 858–863. doi: 10.4028/www.scientific.net/MSF.852.858

Cai, W., Hou, J., Tao, P., and Yang, Y. (2018). An insight into the dehydrogenation behaviour of LiBH4 exhibiting remarkable kinetics enhanced by nanostructured b-Ni. J. Alloy Compd. 750, 443–450. doi: 10.1016/j.jallcom.2018.04.022

Chen et al. Nanoporous N-Based Alloy Supported LiBH4

Chen, X. Y., Guo, Y. H., Gao, L., and Yu, X. B. (2010). Improved dehydrogenation of LiBH4 supported on nanoscale SiO2 via liquid phase method. J. Mater. Res. 25, 2415–2421. doi: 10.1557/JMR.2010.0301

Ding, Z., Wu, P., and Shaw, L. (2019). Solid-state hydrogen desorption of 2MgH2 + LiBH4 nano-mixture: a kinetics mechanism study. J. Alloy Compd. 806, 350–360. doi: 10.1016/j.jallcom.2019.07.218

Fang, Z. Z., Kang, X. D., Wang, P., and Cheng, H. M. (2008a). Improved reversible dehydrogenation of lithium borohydride by milling with as-prepared single-walled carbon nanotubes. J. Phys. Chem. C. 112, 17023–17029. doi: 10.1021/php083916k

Fang, Z. Z., Kang, X. D., Yang, Z. X., Walker, G. S., and Wang, P. (2011). Combined effects of functional cation and anion on the reversible dehydrogenation of LiBH4. J. Phys. Chem. C. 115, 11839–11845. doi: 10.1021/jp200317n

Fang, Z. Z., Wang, P., Rufford, T. E., Kang, X. D., Lu, G. Q., and Cheng, H. M. (2008b). Kinetic- and thermodynamic-based improvements of lithium borohydride incorporated into activated carbon. Acta Mater. 56, 6257–6263. doi: 10.1016/j.actamat.2008.08.033

Gassner, A., Luguett, M., Pereira, A. G., Troiani, H., Zampieri, G., and Gennari, F. C. (2019). Entanglement of N-doped graphene in resorcinol-formaldehyde: Effect over nanoconfined LiBH4 for hydrogen storage. Carbon. 147, 284–294. doi: 10.1016/carbon.2019.02.090

Guo, L., Li, Y. M., Liu, Y., Peng, D., Zhang, L., et al. (2017). Enhanced hydrogen storage capacity and reversibility of LiBH4 encapsulated in carbon nanocages. Int. J. Hydr. Energy. 42, 2215–2222. doi: 10.1016/j.ijhydene.2016.11.184

Izumi, F., and Ikeda, T. (2000). A rietveld-analysis program RIETAN-98 and its applications to zeolites. Mater. Sci. Forum. 321–324, 198–205. doi: 10.1016/S1563-5287(00)80001-8

Li, C., Peng, F., Zhou, D. W., and Wan, L. (2011). Nanoconfinement of lithium borohydride in Cu-MOFs towards low temperature dehydrogenation. Dalton Trans. 40, 5673–5676. doi: 10.1039/c0dt01727b

Surrey, A., Minella, C. B., Fechler, N., Antonietti, M., Grafe, H. J., Schultz, L., et al. (2016). Improved hydrogen storage properties of LiBH4 via nanoconfinement in micro-and mesoporous aerogel-like carbon. Int. J. Hydr. Energy. 41, 5540–5548. doi: 10.1016/j.ijhydene.2016.01.163

Yu, X. B., Wu, Z., Chen, Q. R., Li, Z. L., Wang, B. C., and Huang, T. S. (2007). Improved hydrogen storage properties of LiBH4 destabilized by carbon. Appl. Phys. Lett. 90, 034106. doi: 10.1063/1.2432240

Xu, X. H., Zhang, L., Zhao, Y. R., Zhao, Y., Wang, Y. J., and Jiao, L. F. (2018). Dehydrogenation and rehydrogenation of 0.62LiBH4/SBA-15 nanocomposites prepared by melt infiltration under hydrogen pressure: synthesis and hydrogen sorption properties. J. Phys. Chem. C. 114, 6163–6168. doi: 10.1021/acs.jpcc.0c03216

Xu, X. H., Zang, L., Zhao, Y. R., Zhao, Y., Wang, Y. J., and Jiao, L. F. (2018). Entanglement of N-doped graphene in resorcinol-formaldehyde: Effect over nanoconfined LiBH4 for hydrogen storage. Carbon. 147, 284–294. doi: 10.1016/carbon.2019.02.090

Yin, L., Heere, M., Vasquez, L. C., Paterakis, C., Sorby, M. H., Hauback, B. C., et al. (2018). Dehydrogenation and rehydrogenation of a 0.62LiBH4·0.38NaBH4 mixture with nano-sized Ni. Int. J. Hydr. Energy. 43, 16782–16792. doi: 10.1016/j.ijhydene.2018.04.211

Liu, Y., Yeere, M., Vasquez, L. C., Paterakis, C., Sorby, M. H., Hauback, B. C., et al. (2018). Dehydrogenation and rehydrogenation of a 0.62LiBH4·0.38NaBH4 mixture with nano-sized Ni. Int. J. Hydr. Energy. 43, 16782–16792. doi: 10.1016/j.ijhydene.2018.04.211

Lowell, S., Shields, J. E., Thomas, M. A., and Thommes, M. (2004). Characterization of Porous Solids and Powders: Surface Area, Pore Size and Density. Dordrecht: Springer.

Azad, A. K. (2018). Hydrogen production, storage, transportation and key challenges with applications: a review. Energ. Convers. Manage. 165, 662–627. doi: 10.1016/j.enconman.2018.03.088

Meng, X., Wan, C., Wang, Y., and Ju, X. (2018). Porous Ni@C derived from bimetal metal-organic frameworks and its application for improving LiBH4 dehydrogenation. J. Alloy Compd. 735, 1637–1647. doi: 10.1016/j.jallcom.2017.11.197

Ntigou, O., Adelhelm, P., Beale, A. M., de Jong, K. P., and de Jong, P. E. (2010a). LiBH4/SBA-15 nanocomposites prepared by melt infiltration under hydrogen pressure: synthesis and hydrogen sorption properties. J. Phys. Chem. C. 114, 6163–6168. doi: 10.1021/acs.jpcc.0c03216

Ntigou, O., Verkuijlen, M. H., Zheng, Q., Kragten, J., Bentum, P. J. M., Bitter, J. H., et al. (2011). The role of Ni in increasing the reversibility of the hydrogen release from nanoconfined LiBH4. Faraday Discuss. 151, 47–58. doi: 10.1039/C0FD00002K

Orimo, S., Nakamori, Y., Kitahara, G., Miwa, K., Ohba, N., Towata, S., et al. (2005). Dehydrogenating and rehydrogenating reactions of LiBH4. J. Alloys Compd. 404, 427–430. doi: 10.1016/j.jallcom.2004.10.091

Shao, J., Xiao, X., Fan, X., Huang, X., Zhai, B., Li, S., et al. (2015). Enhanced hydrogen storage capacity and reversibility of LiBH4 nanoconfined in the densified zeolite-templated carbon with high mechanical stability. Nano Energy 15, 244–255. doi: 10.1016/j.nanoen.2015.04.023

Sun, W. W., Li, S. F., Mao, J. F., Guo, Z. P., Liu, H. K., Dou, S. X., et al. (2011). Nanoconfinment of lithium borohydride in Cu-MOFs towards low temperature dehydrogenation. Dalton Trans. 40, 5673–5676. doi: 10.1039/c0dt01727b

Zhang, Y., Liu, Y., Yang, Y., Li, Y., Hu, J., Gao, M., et al. (2018). Superior hydrogenation features of NaAlH4/Fe3Co(OH)2 composite. J. Mater. Res. Bull. 97, 544–552. doi: 10.1016/j.materresbull.2017.09.037
Zhang, Y., Zhang, W. S., Wang, A. Q., Sun, L. X., Fan, M. Q., Chu, H. L., et al. (2007). LiBH$_4$ nanoparticles supported by disordered mesoporous carbon: Hydrogen storage performances and destabilization mechanisms. *Inter. J. Hydr. Energy* 32, 3976–3980. doi: 10.1016/j.ijhydene.2007.04.010

Zhao, Y. P., Jiao, L. F., Liu, Y. C., Guo, L. J., Li, L., Liu, H. Q., et al. (2014). A synergistic effect between nanoconfinement of carbon aerogels and catalysis of CoNiB nanoparticles on dehydrogenation of LiBH$_4$. *Inter. J. Hydr. Energy* 39, 917–926. doi: 10.1016/j.ijhydene.2013.10.137

Züttel, A., Rentsch, S., Fischer, P., Wenger, P., Sudan, P., Mauron, P.h., et al. (2003). Hydrogen storage properties of LiBH$_4$. *J. Alloy Compd.* 356, 515–520. doi: 10.1016/s0925-8388(02)01253-7

**Conflict of Interest:** The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

Copyright © 2020 Chen, Li, Zhang, Liu, Wang, Li, Si and Zhang. This is an open-access article distributed under the terms of the Creative Commons Attribution License (CC BY). The use, distribution or reproduction in other forums is permitted, provided the original author(s) and the copyright owner(s) are credited and that the original publication in this journal is cited, in accordance with accepted academic practice. No use, distribution or reproduction is permitted which does not comply with these terms.