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Structure of nanoconfined LiBH_4 from first principles ^{11}B NMR chemical shifts calculations

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ABSTRACT

Nanoconfinement of metal borohydrides is a promising route for improvement of their kinetic and thermodynamic properties related to hydrogen storage. Since the atomic-scale properties of nanoconfined LiBH_4 remain under debate we propose a model of such a structure. Within extensive density functional theory calculations we consider continuous transformation of the lithium borohydride equilibrium structures from 3-dimensional to 1-dimensional. Such structures consist of single linear chains, linear ribbons and 3-dimensional chains, and together with the low temperature bulk phase they reproduce ^{11}B NMR spectra observed in LiBH_4 confined in porous carbon. The present model suggest that nanoconfined LiBH_4 consists of a dense bulk-like region and loosely distributed chains and ribbons of Li-BH_4 . Even with the low effective density of loosely distributed LiBH_4 they occupy region with thickness as small as a quarter of a pore diameter.

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Introduction

Metal borohydrides have been extensively studied as promising hydrogen storage candidates over the last 10 years [1,2]. Within this class of materials lithium borohydride (LiBH_4) has high theoretical gravimetric and volumetric hydrogen density [3]; however, the kinetics and thermodynamics of hydrogen release/load are still far from meeting practical requirements for hydrogen storage applications [4,5]. Recently, a strong alternation of thermodynamics, de(re)hydrogenation kinetics and cycling capacity of metal borohydrides nanoconfined in porous scaffolds gained attention, (see e.g. Refs. [6,7] and references therein). LiBH_4 confined in nanoporous carbon scaffold has different kinetics, dynamical properties or reaction pathway when compared to the bulk material.

At the nano-scale increased mass transport rates through shorter diffusion pathways and the reduced correlation lengths of the collective phenomena facilitate hydrogen transport and alter phase transformations in LiBH_4 [8–10]. In particular enhanced anion and cation mobilities were reported for LiBH_4 confined in carbon areogels with the pore size of 13–25 nm even at temperatures below orthorhombic–hexagonal phase transition in the bulk [8]. LiBH_4 confined in nanoporous carbon with pore sizes smaller than 3 nm shows no sign of structural phase transition, and exhibits greater anion mobility and reduced activation energy when compared to the bulk at temperatures below 350 K, while the vibrational spectra are similar to those in the bulk [9]. The lack of the long range order in LiBH_4 confined in 4 nm pores in nanoporous carbon together with rapid translational and rotational motion of BH_4^- anions were also reported [10].

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The nanoconfinement affects the reaction pathway of LiBH_4 decomposition, suppressing diborane release [11].

The lack of detailed insight into properties of nanoconfined borohydrides is related to experimental difficulties: the techniques like X-ray diffraction (XRD) or neutron scattering are not always applicable to systems with reduced length-scales. The local methods, such as solid state NMR, quasielastic neutron scattering (QENS), are used [9,10,12] to provide indirect information about structural properties. For the bulk systems theoretical calculations can serve as a support for interpretation of the experimental data [13–15], yet such a support is difficult for nanoconfined structures due to the lack of appropriate experimental reference systems.

Below we report density functional theory (DFT) calculations of the observable NMR ^{11}B and ^1H chemical shifts in nanoconfined lithium borohydride. By identifying structural features of LiBH_4 related to the positions of the ^{11}B chemical shifts we propose a model for nanoconfined LiBH_4 . This system consists of solid-like centers and quasi-linear chains and open structures of Li-BH_4 . The combination of these structures has the experiential fingerprint of ^{11}B chemical shift measured by solid state NMR. The model is in accordance with the suggestion of negative pressures in nanoconfinement by Remhof et al. [9] as well as with the model with a dense core proposed by Liu et al. [10]. The enhanced ionic mobility is an intrinsic feature of the model.

Computational details

The first principles studies were carried out within DFT [16], implemented in the QuantumEspresso package [17], employing a plane-wave basis set for the one-electron wave-functions and periodic boundary conditions. The plane-wave basis set extends up to energy cutoff of 110 Ry. For the exchange-correlation functional Perdew, Burke, and Ernzerhof (PBE) [18] parametrization is used in the generalized-gradient approximation (GGA). The valance-electrons core interactions were described by the projector-augmented-wave (PAW) formalism [19]. The gauge including projector-augmented-waves (GIPAW) [20,21] approach, extending Blöchl's PAW method to the ab-initio calculation of the NMR tensors through the reconstruction of the all-electron wave-functions in the core region, was used to yield the chemical shielding tensor $\sigma(\mathbf{r})$ at the nuclear position \mathbf{r} of ^1H and ^{11}B in a variety of nanostructured LiBH_4 , see below. The isotropic chemical shift δ_{iso} was obtained from isotropic shielding $\sigma_{\text{iso}} = \text{Tr}[\sigma/3]$ employing the relationship $\delta_{\text{iso}} = -(\sigma_{\text{iso}} - \sigma_{\text{ref}})$, where σ_{ref} is the isotropic shielding of the reference material. As references the calculated ^1H and ^{11}B isotropic shielding of C_6H_6 at 7.36 ppm [22] and BPO_4 at -3.60 ppm [23], were used respectively.

The ^{11}B NMR spectra were simulated using the QUADFIT program [24] at 128.38 MHz with the theoretical chemical shifts and quadrupolar coupling constant C_q , and the asymmetry parameter η . The quadrupolar interaction parameters were determined from the traceless electric field gradient tensor (EFG), taking into account the local electric field at the position \mathbf{r} as obtained from the charge density $n(\mathbf{r})$ [25]. The relationships among EFG, C_q , and η are expressed as

$C_q = eQV_{zz}h^{-1}$ and $\eta = (V_{xx} - V_{yy})V_{zz}^{-1}$, where e is the electron charge and h denotes the Planck constant. The convention $|V_{zz}| > |V_{yy}| > |V_{xx}|$ and the ^{11}B quadrupole moment Q of 40.59 mb were used [26]. A Gaussian broadening was applied to each spectral component to ensure the best comparison with the experimental line shape.

The model structures of nanoconfined LiBH_4

LiBH_4 confined in pores of sizes from 2 nm to 5 nm, consists of 600–10,000 formula units (f.u.) per pore. This is still a prohibitively large size for direct accurate calculations on DFT level. On the other hand, it is too small for structural studies with scattering methods. It is well established that kinetic and thermodynamic properties are altered via nanoconfinement [8–10]. The origin of this change could be attributed to the lattice strains induced by different thermal expansion of the carbon matrix and LiBH_4 [9]. Liu et al. [10] proposed nanoconfined LiBH_4 consisting of two regions: the interior with bulk-like properties and the outer interface with enhanced translational and reorientational ion mobility. Enhanced ion mobility cannot be attributed to the interaction with the matrix, as this interaction is weak [27]. Moreover, a fraction of ions appears as immobile [9]. The lattice strains might contribute to enhanced rotational diffusion of BH_4 anions; however, it is unlikely that enhanced cation mobility results from the strains [9].

LiBH_4 has low surface energy: for (010), (101), (100), (011) facets it is below 0.115 J/m^2 [28]. The formation enthalpy of small clusters with 12 to 4 formula units is only 0.17 eV – 0.36 eV per formula unit larger than the formation enthalpy of the low temperature bulk structure [28]. Such smallest stable clusters consist of either linear ($N = 3\dots5$), double ($N = 6\dots10$) rings or closed isocahedral shape ($N = 12$) [28,29]. Larger clusters do not possess a well defined structure.

One of the common features of the nanoconfined LiBH_4 is the modification of the solid state NMR characteristics for ^{11}B and ^1H . The chemical shift of ^{11}B located at $\delta^{11}\text{B} = -41.3$ ppm in the bulk is low frequency shifted in the nanoconfined LiBH_4 , similar shift is observed for hydrogen [10,12]. Additionally, the measured spectra are significantly broader than those in the bulk [10,12]. We have shown previously that the ^{11}B chemical shift for small cluster can be located at $\delta^{11}\text{B} = -51$ ppm for the smallest rings, and this shift is attributed to the lower coordination number for ions [29].

Here, we propose the model that explores structural features of LiBH_4 clusters. The scheme of the model is depicted in Fig. 1. The idea beyond the model is to explore the properties of linear chain-like structures of LiBH_4 that undergo continuous transformation from 3-dimensional to linear chains. This transformation is done by elongation/contraction of the chain-like structures and calculation of the equilibrium geometry for each unit length of the chain. The elongation of the linear chains accounts for structural and electronic features that underline shielding of boron nucleus in NMR experiments. Additionally, for the reference we consider the structures of LiBH_4 clusters consisting of $N = 3\dots12$ formula units [28]. In the nanoconfined LiBH_4 the size or shape distribution of clusters is unknown thus the present approach allows exploration of the variety of local Li-BH_4 geometries that are

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