Hydrogen diffusion in NaH as derived from isotope exchange experiments

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(Received 4 February 2009; accepted 25 February 2009; published online 17 March 2009)

We report on hydrogen-deuterium-exchange experiments on NaH probed by thermogravimetry. From the measurements a diffusion parameter of deuterium in NaH of $D=1.1 \times 10^{-17} \text{ m}^2/\text{s}$ at 523 K is derived. The activation energy of tracer diffusion of D in NaH is found to be 1.0 eV. The results are hints for a diffusion process mediated by neutral hydrogen vacancies. © 2009 American Institute of Physics. [DOI: 10.1063/1.3103277]

Because of its apparent simplicity, diffusion of hydrogen in solids can be regarded as a general model system for diffusion. Apart from basic research, hydrogen might play an important role as an energy carrier in a sustainable energy concept. On the search for a high capacity hydrogen storage material,¹ complex hydrides, e.g., NaAlH_4 , receive increasing attention. Starting materials in the sorption cycle are NaH and Al. Surprisingly, the diffusion parameters of hydrogen in NaH are still unknown, as are the underlying mechanisms. Recent studies brought to the fore that hydrogen can be exchanged by deuterium in NaH at relatively low temperatures, which corresponds to a fast hydrogen diffusion in this material.^{2–4} Recently published density-functional theory (DFT) calculations pinpointed the importance of hydrogen vacancies in the solid to allow for this fast diffusion.⁴ We make use of the HD-exchange reaction probed by thermogravimetry to measure the deuterium tracer diffusion coefficient in NaH. The results are in very good agreement with the DFT calculations of Singh and Eijt⁴ and are thus hints for a diffusion process mediated by neutral hydrogen vacancies.

NaH powder was provided by Fluka (Switzerland). We would like to emphasize the fact that we are investigating as received powders without additional treatment (such as ball milling, etc.). The surface of such chemically prepared powders is oxidized as measured by x-ray photoelectron spectroscopy (to be published), but had been demonstrated by HD-scrambling experiments to be dissociatively active.³ HD can only be formed from the gases H_2 and D_2 after both are split and chemisorbed on a surface. The HD desorption rate as shown for temperatures of more 80 °C is thus indication of a high hydrogen dissociation ability (Fig. 1). On hydrides, chemisorbed hydrogen forming HD can also originate from the underlying bulk material. For that, a significant diffusion from the bulk to the surface has to occur, which is found at slightly higher temperatures. The surface process is the precursor of the bulk diffusion process. Indeed the bulk HD-exchange as probed by thermogravimetry is observed at higher temperatures (see Fig. 1).

When deuterium is applied to a hydride, the hydrogen in it can be exchanged by deuterium. In this paper we make use of the HD-exchange to investigate the transport of hydrogen in NaH.⁵ A magnetic suspension balance (Rubotherm, Germany) is used to measure the weight change in NaH in a deuterium atmosphere, respectively, up to a temperature of

750 K. To avoid any contaminations, the balance is built in an Ar-glove box. Figure 2 shows a typical measurement of a sample of NaH in a finite and closed volume filled with deuterium. The measured signal in such an experiment is the weight gain of 1 a.u. per exchanged hydrogen ($m_{\text{H}}=1 \text{ a.u.}$, $m_{\text{D}}=2 \text{ a.u.}$). From this, it is straightforward to determine the amount of deuterium diffusing into the particle. Using classical diffusion theory, the total amount of deuterium entering a sphere with radius a is given by⁶

FIG. 1. (Color online) Top: Temperature programmed hydrogen deuterium exchange as measured by mass spectrometry (a), taken from Ref. 3 and measured gravimetrically (b). The surface activity is probed by measuring the concentration of H_2 , D_2 , and HD during heating of NaH in a gas stream containing initially Ar+4% D_2 +1% H_2 at 1 bar. The as measured spectra are shifted (but not normalized) to zero signal at $t=0$. The surface exchange is measured at a constant heating rate of $\beta=30 \text{ K/min}$, the bulk exchange at various rates β in 11 bars of D_2 . Bottom (c): Kissinger plot of the bulk HD-exchange in NaH.

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FIG. 2. Fractional uptake of deuterium in NaH as measured gravimetrically at 250 °C and an applied deuterium pressure of 11 bars.

$$\frac{m(t)}{m_\infty} = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} e^{-n^2 \pi^2 D/a^2}. \quad (1)$$

$m(t)/m_\infty$ is the fractional uptake, D the diffusion coefficient. This equation is based on the assumption that the surface concentration is in equilibrium with the gas phase and that the composition of the gas does not change. This is not the case, as the limited volume V with initially 100% of deuterium is hydrogen enriched. This is demonstrated by purging the pressure vessel with pure deuterium (see Fig. 2). The curves show an asymptotic behavior toward a constant weight, which corresponds to an equality between the hydrogen/deuterium ratio in the equilibrated bulk and gas phase, respectively. With purging, the gas atmosphere is changed back to pure deuterium restarting the diffusion process. A mathematical solution for this problem exists as⁶

$$\frac{m(t)}{m_\infty} = 1 - \sum_{n=1}^{\infty} \frac{6\alpha(\alpha+1)e^{-q_n^2 t D/a^2}}{9 + 9\alpha + q_n^2 \alpha^2}, \quad (2)$$

where the q_n s are the nonzero roots of

$$\tan q_n = \frac{3q_n}{3 + \alpha q_n^2}. \quad (3)$$

The parameter α is expressed in terms of the final uptake by the sphere by the relation

$$\frac{m_\infty}{Vc_0} = \frac{1}{1 + \alpha}. \quad (4)$$

c_0 is the initial surface concentration. The model neglects a thermodynamic driving force originating from an isotope effect of the thermodynamic properties.⁷ The normalized uptake curves from Fig. 2 are fitted to Eq. (2). The best fit reveals $D/a^2 = (1 \pm 0.2) \times 10^{-3} \text{ min}^{-1}$ (Fig. 3).

To estimate the geometry parameter a , the surface area of the particles is extracted from nitrogen adsorption isotherms at 77 K measured with a Sieverts apparatus BELSORP-max (BEL, Japan). The negligible hysteresis indicates that there is no significant chemisorption and/or reaction of nitrogen with NaH as expected for oxygen on NaH,⁸ i.e., the curves show a physisorption behavior and can thus be fitted using Brunauer–Emmett–Teller- (BET)-model isotherms.⁹ The fit reveals an averaged surface area of the

FIG. 3. (Color online) Normalized uptake curves (from Fig. 2) and fits with Eq. (2). The best fit reveals $D/a^2 = (1 \pm 0.2) \times 10^{-3} \text{ min}^{-1}$.

particles of $A/m = 1.18 \text{ m}^2/\text{g}$. Assuming ideally spherically shaped particles, the corresponding particle radius a is

$$a = \frac{4}{3\rho A/m}, \quad (5)$$

where $\rho = 1.363 \text{ g cm}^{-3}$ is the density of NaH.¹⁰ With this an averaged diffusion path of $a = 0.83 \text{ }\mu\text{m}$ is obtained, from which a diffusion parameter of $D_{\text{NaH}}(T = 523 \text{ K}) = 1.1 \times 10^{-17} \text{ m}^2/\text{s}$ is calculated. The value is in a very good agreement with the theoretically derived diffusion parameter of $D_{\text{NaH}}^{\text{DFT}}(T = 420 \text{ K}) = 6.3 \times 10^{-19} \text{ m}^2/\text{s}$ giving $D_{\text{NaH}}^{\text{DFT}}(T = 523 \text{ K}) = 1.0 \times 10^{-16} \text{ m}^2/\text{s}$ using an Arrhenius law with $E_{\text{diff}} = 0.94 \text{ eV}$.⁴ Possible sources of errors are a nonspherical shape of the particles and a finite size distribution of them. Furthermore, it should be noted that the self-diffusion can differ from the corresponding intrinsic diffusion coefficient as deduced, e.g., by transport measurements (Ref. 6, p. 212). Since hydrogen deuterium exchange is an interchange of labeled and unlabeled molecules, which are chemically nearly identical (except $m_D = 2m_H$), there is no bulk flow and the true mobility with respect to stationary solution is measured. Nevertheless, the diffusion coefficient D so deduced will generally differ from the corresponding chemical diffusion coefficient D_i . One important difference originates from the intrinsically different diffusion coefficient of hydrogen and deuterium, which is in first order $D_H = \sqrt{2}D_D$, if changes in the activation energy due to quantum effects (zero point energies) are neglected (see Refs. 11 and 12). Second, the self-diffusion coefficient differs from D_i , independently of the used measurement method (e.g., tracer diffusion experiments or quasielastic neutron scattering). The relationship between the diffusion coefficients D_i and D is given by the so-called Haven ratio including correlation and thermodynamic factors.¹² In most cases, though, changes in the activation energy of diffusion are small.¹²

To derive the activation energy experimentally, we use nonisothermal HD-exchange experiments. In experiments with a constant heating rate β , the determination of a temperature $T_{1/2}$ after a certain proportion of the reaction [here $m(t)/m_\infty = 1/2$] can be related to the activation energy of diffusion E_{diff} using the Kissinger–Akahira–Sunose (KAS) method¹³

$$\ln\left(\frac{\beta}{T_{1/2}^2}\right) = -\frac{E_{\text{diff}}}{kT_{1/2}} + C, \quad (6)$$

where C is a not further defined constant. The great advantage of this method is its model independency. Errors from geometry uncertainties, etc., do not enter Eq. (6). Figure 1 shows temperature programmed hydrogen deuterium exchange in NaH at various constant heating rates. From this, the peak temperatures $T_{1/2}$ are determined. $T_{1/2}^2/\beta$ is plotted as a function of the reciprocal temperature in the bottom panel of Fig. 1, a so-called Kissinger plot. From the slope an activation energy of diffusion of $E_{\text{diff}} = (1.0 \pm 0.1)$ eV is derived. For diffusion in stoichiometric hydrides, the probability of finding a vacant site is as important as the barrier height E_{diff} . In ionic crystals, charge fluctuations can accompany vacancies, e.g., a hydrogen vacancy can be charged neutral, i.e., V_{H}^0 , or positively, respectively, negatively charged (V_{H}^+ , V_{H}^-). DFT calculations of hydrogen diffusion in NaH give diffusion barrier heights of 0.94, 0.57, and 1.17 eV for V_{H}^0 , V_{H}^+ , and V_{H}^- vacancies, respectively.⁴ The value of 1.0 eV and the absolute value of the diffusion parameter are in excellent agreement with the calculated values of hydrogen diffusion via V_{H}^0 vacancies and thus a corroboration of this model.

In conclusion, we have demonstrated the use of HD-exchange experiments to derive the diffusion parameters of deuterium in NaH. The measurements confirm recent DFT calculations and thereby the hypothesis of hydrogen diffusion mediated by charge neutral hydrogen vacancies in NaH.

This work was financially supported by the European Commission [Contract Nos. MRTN-CT-2006-032474 (Hydrogen) and MRTN-CT-2006-032474 (COSY)].

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