

Motion of point defects and monitoring of chemical reactions in sodium aluminium hydride

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Abstract

Anelastic spectroscopy experiments (elastic modulus and energy dissipation) were carried out for the first time with Ti-doped and undoped NaAlH₄. We found that the various decomposition reactions taking place in the alanates are most sensitively monitored by the dynamic Young modulus variations. We also found that, during one of the decomposition reactions occurring at higher temperature, a new point-defect complex is formed, very likely involving hydrogen, which has fast dynamics and gives rise to a thermally activated relaxation process at 70 K in the kHz range, with an activation energy of 0.126 eV. The occurrence of this process suggests that any model concerned with the decomposition mechanism should take into account the hydrogen mobility in the crystal lattice.

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1. Introduction

Sodium aluminium complex hydrides have considerably high hydrogen capacities, but their potential use as hydrogen storage materials became more realistic when it was found [1] that small additions of Ti to NaAlH₄ greatly improves the kinetics of the hydrogen discharging reaction as well as the subsequent re-hydrogenation. Further kinetic enhancement was subsequently attained by varying the doping methods [2–5]. The actual hydrogen cycling capacity of Ti-doped NaAlH₄, under conditions that are relevant to practical operation of a PEM fuel cell, has been found to be 3.4–4.0 wt.% [6].

We report the first elastic modulus and energy dissipation study of NaAlH₄ during its dehydrogenation reactions. We show that the formation and evolution of different phases are very sensitively monitored by the modulus variations, and that a species having a very high mobility, likely a point

defect complex containing hydrogen, is formed during one of the decomposition reactions.

2. Experimental

Sodium aluminium hydride was obtained from Albermarle Corp. The aluminium metal was removed from the raw hydride via Soxhlet extraction with dry, oxygen-free tetrahydrofuran (THF) under a nitrogen atmosphere using the standard Schlenk technique. The final purification was accomplished through recrystallization from THF/pentane. The doping was performed by the mechanical milling method [2,3,7] in which the hydride was combined with 2 mol% TiF₃ (Aldrich, purity 99%) and ball-milled under an argon atmosphere in a stainless steel bowl using a Fritsch 6 planetary mill at 400 rpm and a grinding ball-to-powder ratio of 35:1. In order to obtain samples from the alanate powder for the anelastic spectroscopy measurements, the alanate was mixed with pure KBr, finely ground and pressed in dies having

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rectangular form and dimensions of 40 mm × 6 mm. After this procedure, in which KBr has the role of compactant, solid prismatic bars were obtained with thickness varying, according to the amount of material used, from 0.7 to 1.3 mm. This method, introduced by us, was fruitfully used in a study on organic molecules [8], and opened new perspectives to the anelastic spectroscopy, as it allows measurements to be conducted to systems which are not available as solid samples. Two bars doped with 2% Ti, Ti2-1 and Ti2-2, and two undoped bars, U-2 and U-3, were prepared for the present study. Some bars made of pure KBr were also prepared for comparison. As the alanate powder reacts with oxygen, all the operations were accomplished in flowing nitrogen atmosphere.

The complex dynamic elastic modulus, $E(\omega, T) = E'(\omega, T) + iE''(\omega, T)$, was measured as a function of temperature by suspending the prepared samples on their nodal lines and electrostatically exciting their first and third flexural modes, whose frequencies, $\omega_i/2\pi$ s are in the ratio 1:5.4. The real part of the elastic modulus, or dynamic Young's modulus, can be obtained from the vibration frequency by means of the relationship: $E'_i(\omega, T) = \alpha_i \rho \omega_i^2$, where ρ is the density and α_i are geometrical factors. As ρ usually varies much less than ω as a function of T , the temperature dependence of E' is practically due to the variation of ω^2 . The elastic energy dissipation coefficient, or the reciprocal of the mechanical quality factor, [9] is $Q^{-1}(\omega, T) = E''/E'$, where $E = E' + iE''$ is the stiffness elastic constant. The loss coefficient Q^{-1} was measured from the decay of the free oscillations or from the width of the resonance peak.

3. Results and discussion

Fig. 1 displays the vibration frequency f of sample Ti2-2 during thermal cyclings at progressively increasing temperatures. On heating the sample from room temperature (RT) to 322 K, f decreases as usually expected and Q^{-1} increases (result not shown), whilst on cooling back to room temperature both the f and Q^{-1} curves form a hysteresis loop which, however, practically close at RT. Also a previous cycle at 316 K displayed similar features. When the maximum temperatures of the cycles were increased to 343 and 368 K, the frequency curves did not close (and so did dissipation) and the modulus softened irreversibly of 2 and 6.6%, respectively, indicating the occurrence of a permanent modification in the material; simultaneously, moderate gas evolution out of the sample was monitored by the Pirani gauge. Indeed, the modulus measurements are very sensitive to detect phase transformations or to monitor the evolution of chemical reactions, as the presence or the formation of different phase particles strongly affect the mechanical properties. Fig. 1 reports, for reference, also the f heating and cooling curves of a KBr sample along a cycle up to 436 K, where is seen that this compound does not show any modification upon cycling up to this temperature.

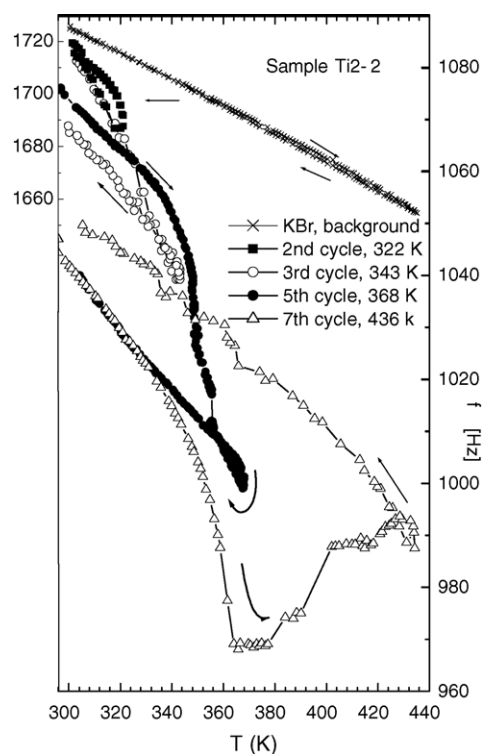
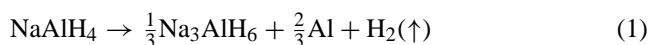


Fig. 1. Temperature dependence of the elastic energy dissipation and frequency of Ti-doped NaAlH₄ during thermal cycles up to 436 K.

The cycle of Ti2-2 up to 436 K behaved qualitatively differently with respect to the previous ones. The monotonic modulus decrease on heating was followed by a steep lowering starting at 340 K, and at about 365 K the modulus inverted its trend and slow hardening was measured up to the maximum temperature reached; simultaneously, the dissipation displayed a marked scattering indicating instability; on cooling back to room temperature the f curve was constantly above the cooling one and the sample remained hardened.

The present data show that the modulus variations arise upon heating. Permanent modifications are apparent when the samples reassume their initial temperature after thermal cycling, and are closely connected with the evolution of the decomposition reactions occurring in the alanates. Strong support for this assertion is also provided by the comparison of the thermal cycles in the Ti doped and in the undoped samples (results not shown in the figures). Indeed, it is clearly seen that the irreversibility behaviour of the elastic modulus displayed by the latter samples is shifted to higher temperatures, because the chemical reactions are correspondingly shifted, as is known from literature.

After cycling sample Ti2-2 to 343 or 368 K the value of the modulus is not recovered (Fig. 1). It is known that the first decomposition reaction occurring at the lowest temperatures is:



labelled here as the 114–316 formula unit transformation. Therefore, we ascribe the permanent modifications of the

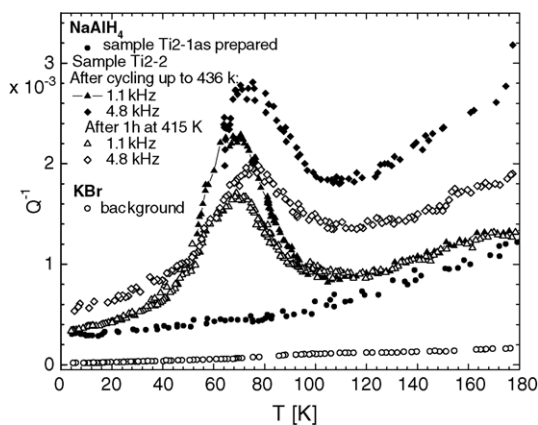
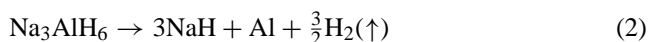


Fig. 2. Low temperature dependence of the elastic energy loss function of: $\text{NaAlH}_4\text{-Ti}2\%$, sample Ti2-1 as prepared (\bullet). $\text{NaAlH}_4\text{-Ti}2\%$, sample Ti2-2 after cycling up to 436 K: (\blacktriangle) 1.1 kHz; (\blacklozenge) 4.8 kHz. $\text{NaAlH}_4\text{-Ti}2\%$, sample Ti2-2 after subsequent ageing of 1 h at 415 K: (\triangle) 1.1 kHz; (\diamond) 4.8 kHz. KBr as prepared (\circ).

modulus and its softening, after cycling up to 343 and 368 K to the evolution of reaction (1).

We also observed that, after heating to a temperature not exceeding that of the previous cycle, the modulus and dissipation heating curves are retraced on cooling; this constitutes strong indication that the chemical reaction does not proceed appreciably in this case.

In the 7th cycle (Fig. 1) the sample was heated to 436 K, and it is known [10] that at this temperature the 316 product from reaction (1) is transformed to NaH, according to equation:



Therefore, the marked instability and the modulus hardening measured during cycling to 436 K is clearly linked to the evolution of decomposition (2). We point out that the phenomena observed in sample Ti2-2 are strictly due to intrinsic properties of the alanates, and are not due to KBr, whose modulus and dissipation curves are reproducible on heating and cooling. Fig. 2 displays the coefficient of elastic energy dissipation, from room temperature to 4 K of the Ti-doped sample Ti2-1 after preparation, which shows a monotonic decrease with decreasing temperature without any visible process. The dissipation of a pure KBr sample, to be considered as the background dissipation, is also drawn in Fig. 2. After cycling to 436 K, the low temperature measurement was repeated at two different frequencies, and the result is also shown in Fig. 2. Surprisingly, a well developed peak appeared at about 70 K which shifts to higher temperature at the higher frequency, indicating that the peak is caused by a thermally activated relaxation process. The peak is caused by a species which was absent before the T.T. at 436 K; this entity is very mobile, as it performs about 5×10^3 jumps/s at 70 K, corresponding to a relaxation rate of about 10^{11} s^{-1} at room temperature.

To check that the peak is due to a mechanism originating from the sodium aluminium hydride, rather than the compactant with which it is mixed, we prepared pure KBr prismatic bars and submitted them to several hydrogen charging treatments, in H_2 and in plasma atmospheres. In all cases the dissipation assumed values comparable with the background.

The analysis of the peak in terms of a Debye process indicated that the experimental curve is remarkably broader than a single Debye process. This means either that the relaxing complexes are strongly interacting, or that they perform different types of jumps having close relaxation rates; this fact implies a distribution of the activation energy, E , and of the pre-exponential factor, τ_0 , of the Arrhenius relaxation time. The best fit to the data, performed with Gaussian distributions of E and τ_0 , gave the following mean values for the relaxation parameters and the respective widths:

$$E = 0.126 \text{ eV} \quad \sigma(E) = 0.022 \text{ eV}$$

$$\tau_0 = 7 \times 10^{-14} \text{ s} \quad \sigma(\tau_0) = 3 \times 10^{-15} \text{ s}$$

Important information is obtained from the prefactor; in fact, its value is typical of point defect relaxation, and thus may provide the key to the interpretation of the nature of the relaxing entity. Preliminarily, we suggest that, in view of the fast dynamics of the mobile species causing the peak, as well as of the observation of H_2 outgassing during the reactions, hydrogen is very likely involved in the point-defect complex causing the detected relaxation.

To ascribe the peak to a possible physical mechanism, we consider that the peak cannot be ascribed to the products of reaction (1), like Na_3AlH_6 or aggregated Al, as it manifests itself only after the onset of reaction (2). Rather, the peak mechanism should involve one of the possible point-defects or point defect complexes produced by the decomposition reaction (2), and they may be: (i) a stoichiometry defect of Na_3AlH_6 . Indeed, if one or more of the six H atoms are missing, jumping is possible for the remaining H atoms, and in other words H vacancy dynamics may take place; (ii) the relaxation of H in the NaH compound produced by the decomposition reaction (2); (iii) the reorientation of H around Ti, or a Ti–Al complex, or a vacancy which acts as an attracting cluster for H after the transformation at 150 °C.

The present results clearly indicate that new models involving the H mobility should be considered to understand the catalytically enhanced kinetics.

4. Conclusions

The complex elastic modulus in alanates have been measured for the first time. The dynamic Young modulus clearly reflects the evolution of the decomposition reactions as a function of temperature and time. Moreover, the elastic

energy dissipation of the Ti-doped sample after a thermal treatment up to 436 K, revealed the presence of a thermally activated relaxation process due to the fast dynamics of a point-defect cluster, very likely involving hydrogen. The present data suggest that the hydrogen mobility and trapping, and stoichiometry defects should be taken into account, especially when considering models aiming at interpreting the decomposition reactions and kinetics in alanates.

Our study would not have been possible without the application of our new method of obtaining solid samples from alanate powders. Indeed, it opened new perspectives to anelastic spectroscopy, as it allows elastic modulus and dissipation measurements to be extended to all compounds which cannot be obtained in bulk form.

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