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Thermal desorption of H_2, H^- and electron by temperature-programmed heating of saline hydrides in vacuum

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Abstract

To clarify the thermochemical and thermionic properties of saline hydrides, a small amount (ca. 1 mg) of powdery NaH or LiH deposited on a molybdenum ribbon was heated up to ca. 1000 K either stepwise at ca. 10 K intervals or continuously at a constant rate (ca. 2–20 K/s) in vacuum (ca. 10^{-4} Pa), and the desorption rates of H_2, electron (e^-) and/or H^- were measured mass spectrometrically as a function of the sample temperature (T), the introduced hydrogen gas pressure (P_H) or the time (t) after a change in T or P_H. Theoretical analysis of the data thus achieved yields the following results: (1) In the temperature-programmed desorption spectra observed with NaH, both e^- and H^- showed a single peak at ca. 800 K while a broad peak of H_2 appeared around ca. 750 K. (2) The activation energies (E^- and E^0) for the desorption of H^- and H_2 from NaH were 172 ± 18 and 61 ± 7 kJ/mol, respectively, whilst the work function (ϕ) of NaH at those temperatures corresponding to the leading edge of an electron desorption peak was 261 ± 19 kJ/mol. (3) In the case of LiH, E^-, E^0 and ϕ were 940 ± 89, 97 ± 12 and 747 ± 41 kJ/mol, respectively. (4) By the thermal dissociation such as LiH(solid) $\rightarrow$ Li(solid) + H_2(gas)/2, ϕ was decreased by 20 kJ/mol or much more depending upon t or T, but the active spots (mainly Li) thus produced was destroyed by admission of H_2 up to ca. 10^{-1} Pa. (5) The deactivation (Li + $H_2/2 \rightarrow$ LiH) depending upon both T and P_H was readily recovered (reactivated) after stopping the admission. (6) Our new method of monitoring e^- was very convenient and useful for studying the thermal decomposition of saline hydrides. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Saline hydride; Thermal negative hydride ion desorption; Thermal electron emission; Hydrogen gas liberation

1. Introduction

In our previous work [1–3], powdery saline hydride (LiH, CaH_2 or SrH_2) deposited on a molybdenum ribbon was heated stepwise in vacuum, and the currents (I^- and J^-) of H^- and electron (e^-) desorbed thermally from each hydride were measured simultaneously as a function of sample temperature (T). Theoretical analysis of the data thus obtained yielded the desorption energy (E^-) of H^- and the work function (ϕ) of each hydride kept at high temperatures ranging from ca. 700 to 800 K, where both I^- and J^- were reproducible to within ±10% at any temperature. Namely, E^- and ϕ were, respectively, 536 and 318 kJ/mol for LiH, 728 and 492 kJ/mol for CaH_2, and 937 and 702 kJ/mol for SrH_2. By the above method, however, neither E^- nor ϕ could be determined with NaH because NaH was thermally so unstable that both Arrhenius and Richardson plots could not be obtained.

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In other words, reproducible currents of I^- and J^- were not obtained in the temperature range (ca. 700–800 K) suitable for the above plots because much more than half of the powder of NaH was desorbed from the ribbon before reaching the suitable temperature range.

In order to conquer the above difficulty found with NaH and also to obtain further information about the thermochemical and thermionic properties of saline hydrides, the desorption rates of not only H^- and e^- but also H_2 desorbed from NaH or LiH were measured as a function of sample temperature (T), which was increased either stepwise at ca. 10 K intervals or continuously at a constant rate using a temperature programming system. For this purpose, the present work employed two special apparatus including a 180° deflection- or quadruple-type mass spectrometer, which was connected to a microcomputer system.

This paper summarizes (1) the experimental data on the dependence of I^- and J^- upon T and upon the introduced H_2 pressure (P_H) and also upon the time (t) after a change in T or P_H; (2) the analytical results obtained from temperature-programmed desorption spectra of H^-, e^- and H_2; and (3) the relation between the degree of thermal liberation of H_2 and the desorption current of H^- or e^-.

2. Experimental

A schematic diagram of our main apparatus is shown in Fig. 1. Here, R is the molybdenum ribbon (ca. 0.1 cm wide, ca. 3 cm long and ca. 0.0025 cm thick) and has a small box (ca. 0.1 cm wide,ca. 0.2 cm long and 0.05 cm high) at the center of R. A powdery sample (S, ca. 1 mg) of NaH or LiH deposited in the box was heated up to ca. 1000 K either stepwise at ca. 10 K intervals every ca. 20 min or continuously at a constant rate (β) using a temperature-programmed heating system. The sample temperature (T) was monitored with an alumel–chromel thermocouple (A) spot-welded onto the bottom of the box. The total negative current (J^-) almost entirely owing to thermal electron (e^-) was extracted by the voltage of V_0 (usually 90 V) and collected with the first slit plate (P_1). The acceleration voltage (V_a) for focusing H^- desorbed from the sample on R was 550 V in this mass spectrometer, where the ion path radius was 2.5 cm and the analyzing magnetic field was 1350 gauss. The current (I^-) of H^- collected with a Faraday cup (C) was measured with a femtoampere meter. The residual gas pressure (P) was monitored with an ionization type vacuum gauge (IG), which made it possible to measure the amount of neutral gases (mainly H_2) desorbed from the heated sample under study.

Our another apparatus is shown in Fig. 2, where J^- and P are essentially the same as those in Fig. 1. QMS is a quadruple type mass spectrometer by which the positive ion current (I^+) of H_2^+ produced by electron impact of desorbed H_2, was measured to determine the desorption rate of H_2 liberated from the sample on R. The energy and current of bombarding electrons were ca. 3×10^3 kJ/mol and ca. 40 μA, respectively. This apparatus also was evacuated with an oil diffusion pump with a liquid nitrogen trap, and the vacuum was usually at ca. 1×10^{-4} Pa.

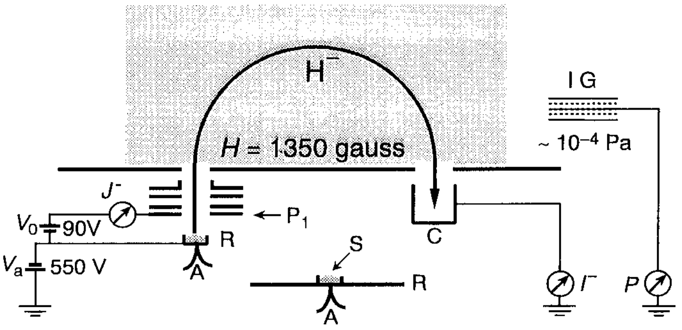

Fig. 1. Schematic diagram of our main apparatus to measure the desorption rates of H^-, e^- and neutral gases from a sample (S) on a molybdenum ribbon (R).

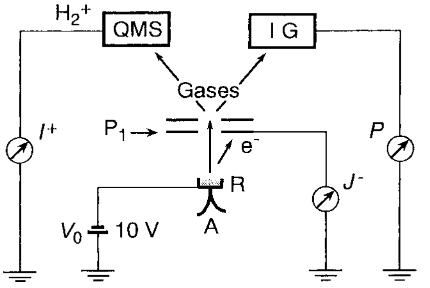

Fig. 2. Sketch of our simple system to determine the thermal desorption rates of e^-, H_2 and neutral gases from a sample (NaH or LiH) on a molybdenum ribbon (R).

In this way, the desorption rates of H_2, e^- and/or H^- were measured as a function of the sample temperature (T), the introduced hydrogen gas pressure (P_H) or the time (t) after a change in T or P_H.

3. Results and discussion

3.1. Stepwise heating

Firstly, the temperature (T) of a fresh powder sample was gradually increased stepwise at ca. 10 K intervals, and the electron current (J^-) was measured to examine the thermal stability of the sample. Usually at ca. 640 K, J^- from LiH became strong (ca. 10^{-10} A) enough to be detectable by our system. When T is kept constant at 674 K after increasing from 650 K at the time (t) of $t = 0$, for example, J^- increases monotonically from 1.4 to 25 nA at $t \approx 5$ h after passing a minimum at $t \approx 1$ min, as shown by curve (1) in Fig. 3a. Curve (2) is obtained by the increase from 694 to 710 K at $t = 0$. The value of J^- is generally given by Richardson's equation:

$$J^- = AST^2 \exp\left[-\frac{\phi}{RT}\right]. \tag{1}$$

Here, A is the Richardson constant, S the emitting surface area, ϕ the work function and R the gas constant. Therefore, the change in work function ($\Delta\phi$) is evaluated from

$$\Delta\phi = RT \ln J_0/J_t, \tag{2}$$

where J_0 is the minimum current at $t \approx 0$, and J_t is a value at a given time. As shown by curves (1') and (2') in Fig. 3b, $\Delta\phi$ decreases by ca. 19 and 4 kJ/mol, respectively, at $t \geq 5$ h. These results suggest that a part of the sample is thermally decomposed like LiH(solid) → Li(solid) + H_2(gas)/2 and hence that those active spots (composed mainly of Li) having a low work function are produced by the "activation reaction". In order to check this suggestion, the effect of hydrogen gas upon ϕ at constant T was examined, thereby yielding Fig. 4. Introduction of H_2 at $t = 0$ after aging (activation) of LiH for 6 h at 710 K (see Fig. 3) causes the work function increase up to ca. 20 kJ/mol depending upon the hydrogen gas pressure (P_H). This increase due to deactivation (Li + H_2/2 → LiH), however, is reduced to ~0 (reactivation) soon after stopping the introduction at $t = 40$ min.

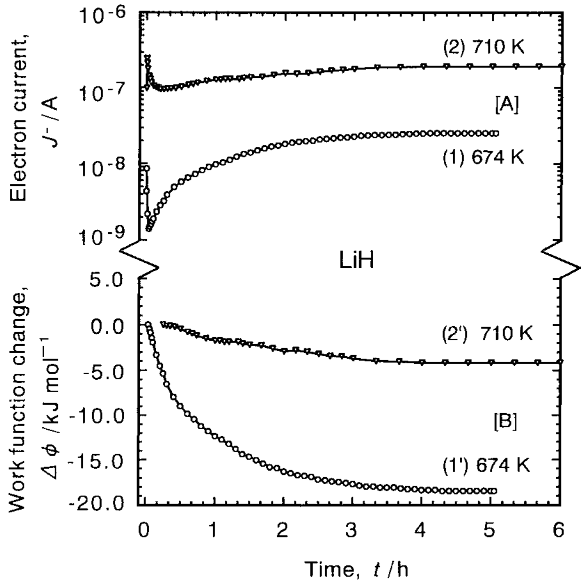

Fig. 3. Time variation of (a) the electron current and (b) the work function change of LiH kept at a constant temperature of 674 or 710 K.

In order to study the above activation/deactivation reactions from a different point of view, J^- was measured as a function of P_H and also $\Delta\phi$ was evaluated similarly as above, thereby yielding Fig. 5. The value of $\Delta\phi$ begins to increase sharply at $P_H \approx 5 \times 10^{-3}$ Pa, which indicates that the desorption rate (D_H) of H_2 from the sample kept at 674 K is virtually the same as the adsorption rate (A_H) of the introduced hydrogen upon the sample. These rates are evaluated from Eq. (3), which is based on Knudsen's

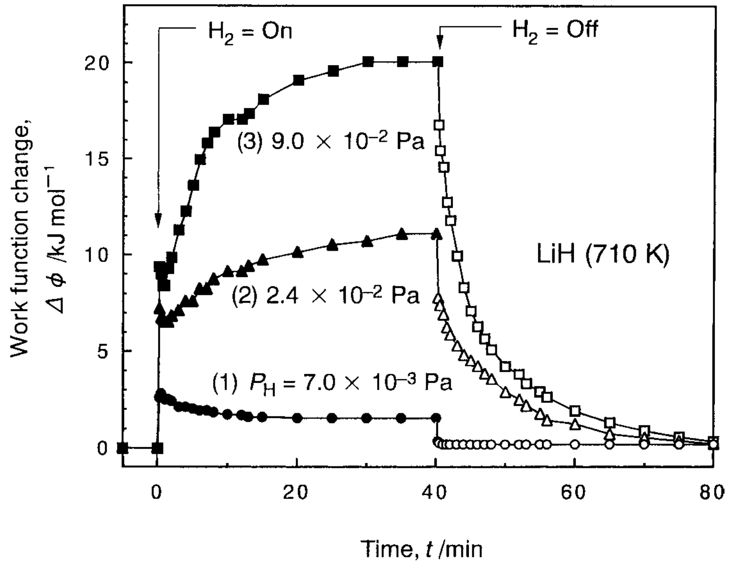

Fig. 4. Time variation of the work function increase by admission of H_2 at $t = 0$ and the work function decrease after stopping the admission at $t = 40$ min. Here, LiH is kept at 710 K.

formula,

$$D_H = A_H = \frac{10N_AP_HS}{\sqrt{2\pi MRT}} \approx 4 \times 10^{16}\,\text{molecules/cm}^2\,\text{s}. \qquad (3)$$

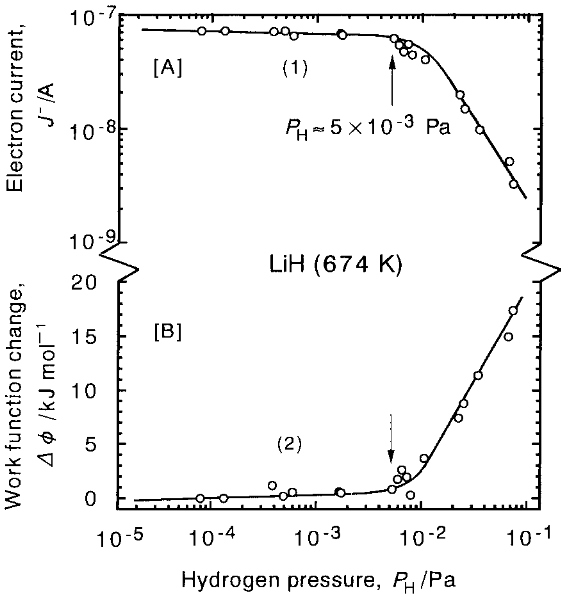

Fig. 5. Hydrogen gas pressure vs. (a) the electron current and (b) the work function change observed with LiH kept at 674 K.

Here, N_A is the Avogadro's number, P_H the pressure of H_2 in Pa, S the desorbing surface area of the sample, and M the molecular weight of H_2. In this way, the measurement of J^- as a function of P_H makes it possible to determine D_H without direct measurement of both the desorbing H_2 itself and the desorbing surface area of the powdery sample. In other words, thermal electron current can be used as a useful probe for the study of thermal decomposition of the sample under study.

3.2. Temperature-programmed heating

Secondly, T was increased at a constant rate ($\beta \approx 2$–20 K/s) up to ca. 1000 K, thus yielding characteristic spectra of temperature-programmed desorption (TPD). In Fig. 6, both pattern and peak position are virtually the same between [A] and [B], thereby indicating that the total desorption gases detected as a pressure change by IG are mainly due to the hydrogen gas liberated from the sample under study. A broad peak of H_2 appears at ca. 750 K while the peaks of e^- and H^- appear at ca. 800 K. The difference in peak temperature indicates that the strong emissions of e^- and H^- occur after the activation of $LiH \rightarrow Li + H_2$ proceeds to some extent, as may be understood readily from the results described in

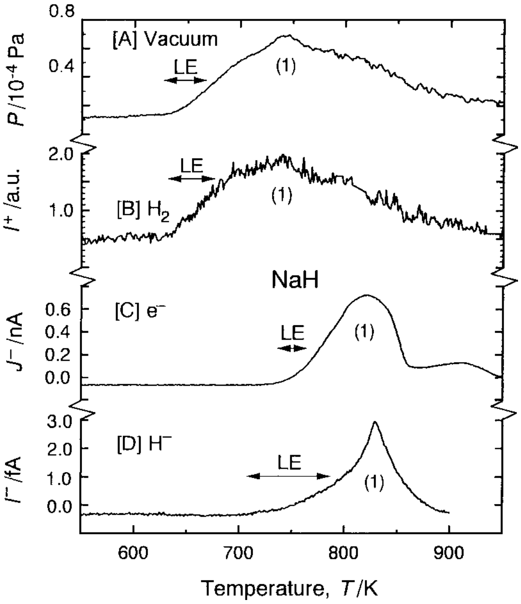

Fig. 6. Typical example of the temperature-programmed desorption spectra observed with NaH at the heating rate of 9.6 K/s. Here, LE shows the temperature range of a leading edge.

Section 3.1. A small peak of e^- at ca. 900 K (see Fig. 6) originates from a partly contaminated surface of Mo. Without sample deposition, it is usually at ca. 1000 K that J^- becomes strong (ca. 0.1 nA) enough to be detected by the present system. In the case of LiH (see Fig. 7), H_2 shows two peaks at ca. 650 and 900 K. On the other hand, each of H^- and e^- shows a single peak around ca. 900 K, which is higher by ca. 100 K compared with the case of NaH.

Employment of the leading edge (LE) analysis method [4] makes it possible to determine the activation energy (E) for the desorption of H_2 or H^- on the basis of

$$\frac{d(\ln I^{\pm})}{d(1/T)} = -\frac{E}{R}. \qquad (4)$$

With respect to e^-, on the other hand, we employ Eq. (5) according to Eq. (1).

$$\frac{d(\ln J^-/T^2)}{d(1/T)} = -\frac{\phi}{R}. \qquad (5)$$

From the slope of each line exemplified in Figs. 8 and 9, the activation energies for the desorption of H_2, H^- and e^- were determined according to Eq. (4) or Eq. (5), thus yielding the results summarized in Table 1.

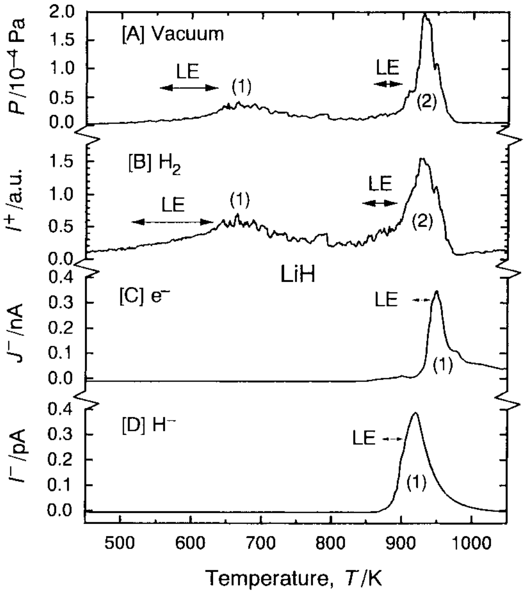

Fig. 7. TPD spectra obtained with LiH at $\beta = 2.8$ K/s.

By using thermochemical tables [5], the energy (E_H) necessary for the reaction (activation) of NaH(solid) → Na(solid) + H_2(gas)/2 is evaluated to be 57 kJ/mol, to which our value (61 ± 7 kJ/mol) is very

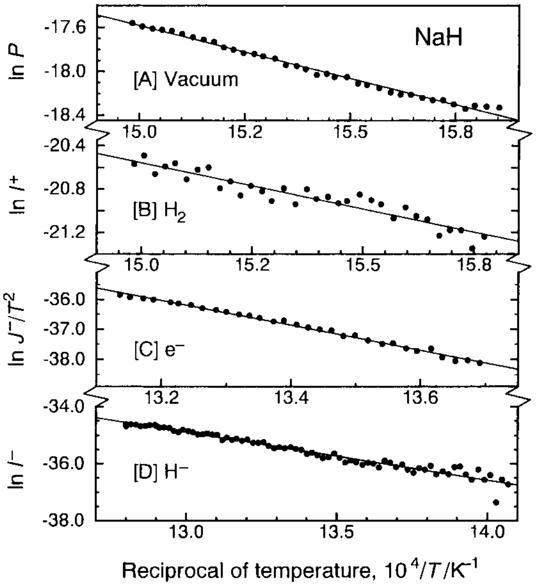

Fig. 8. Reciprocal temperature at a leading edge region (LE, see Fig. 6) vs. the desorption rate of (a) total gases, (b) H_2, (c) e^- and (d) H^-. The heating rate of NaH is 9.6 K/s.

Table 1
Summary of the activation energy (E) and frequency factor (ν) determined with total gases, H_2, e^- and H^- desorbed from NaH or LiH by temperature-programmed heating[a]

Sample	Desorbate	Peak	E (kJ mol^{-1})	ν (s^{-1})	T_L (K)	L_H (%)
NaH	Gases	(1)	61 ± 7	$10^{6.7 \pm 03}$	630–670	4
	H_2	(1)	61 ± 7	$10^{6.8 \pm 0.3}$	630–670	4
	e^-	(1)	261 ± 19	$10^{20.3 \pm 0.3}$	730–760	50
	H^-	(1)	172 ± 18	$10^{14.0 \pm 0.3}$	710–780	27
LiH	Gases	(1)	49 ± 4	$10^{6.1 \pm 0.3}$	510–610	5
		(2)	91 ± 10	$10^{7.7 \pm 0.3}$	850–890	45
	H_2	(1)	50 ± 2	$10^{6.3 \pm 0.1}$	510–610	5
		(2)	97 ± 12	$10^{8.1 \pm 0.3}$	840–890	45
	e^-	(1)	747 ± 41	$10^{45.5 \pm 0.3}$	920–950	90
	H^-	(1)	940 ± 89	$10^{58.0 \pm 0.3}$	870–900	80

[a] Here, T_L is the temperature range (see LE with ↔ in Figs. 6 and 7) adopted for leading edge analysis and L_H is the percentage of H_2 liberated during the time until the maximum temperature in T_L.

close. In the case of LiH, our value (91 ± 10 or 97 ± 12 kJ/mol) determined from the edge of each main peak (2) exemplified in Fig. 7a or b is nearly the same with $E_H = 94$ kJ/mol evaluated for LiH(solid) → Li(solid) + H_2(gas)/2 using thermochemical data [5]. These results suggest that the present method is almost free from systematic errors although the reproducibility is very poor. On the other hand, the value of 49 or 50 kJ/mol found with the edge of each low peak (1) is much smaller than E_H, thereby suggesting it necessary to consider another mechanism different from that for peak (2).

The activation energy (E^-) for the desorption of H^- and the work function (ϕ) of NaH are determined to be 172 and 261 kJ/mol, respectively, while E^- and ϕ of LiH are 940 and 747 kJ/mol, respectively. To the best our knowledge, no data on these values have yet been published by any other group of workers.

The frequency factor (ν) for each desorption is evaluated [6] from

$$\ln\left(\frac{T_P^2}{\beta}\right) = \left(\frac{E}{RT_P}\right) - \ln\left(\frac{\nu R}{E}\right), \qquad (6)$$

where T_p is the peak appearance temperature in TPD spectra exemplified in Figs. 6 and 7.

All the data given in Table 1 are accompanied with the standard deviations of up to about ±10%, which are much larger than those found in usual experiments. The poor reproducibility in our experiment is mainly due to the condition that the sample powder itself is directly deposited on the heater (R), thereby making it very difficult to produce the same condition (sample layer thickness, desorbing surface area, etc.) in repeated runs.

With respect to NaH, the percentage (L_H) of liberated H_2 and the current (I^-) of H^- are shown as a function of T in Fig. 10. At the maximum temperature (ca. 780 K in T_L, see Table 1) of the leading edge (LE) of curve (2), L_H is about 30% and hence the progress in 30% of the activation reaction (NaH → Na + H_2/2) yields $E^- = 172$ kJ/mol. With an increase in T, I^-

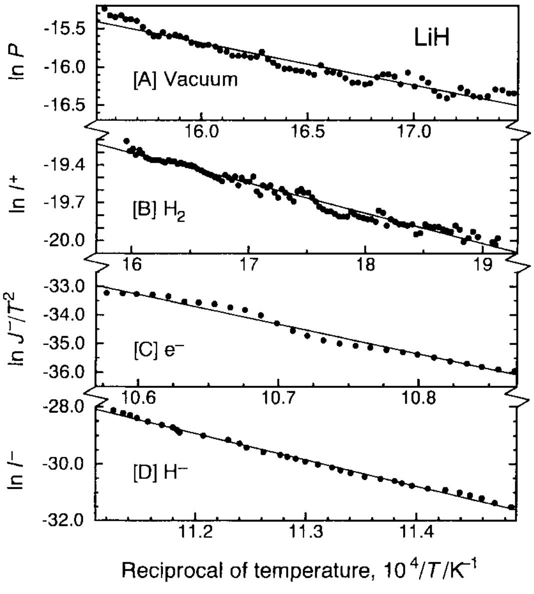

Fig. 9. Reciprocal temperature dependence of the four signals observed with LiH at $\beta = 2.8$ K/s. With respect to the leading edge region, see Fig. 7.

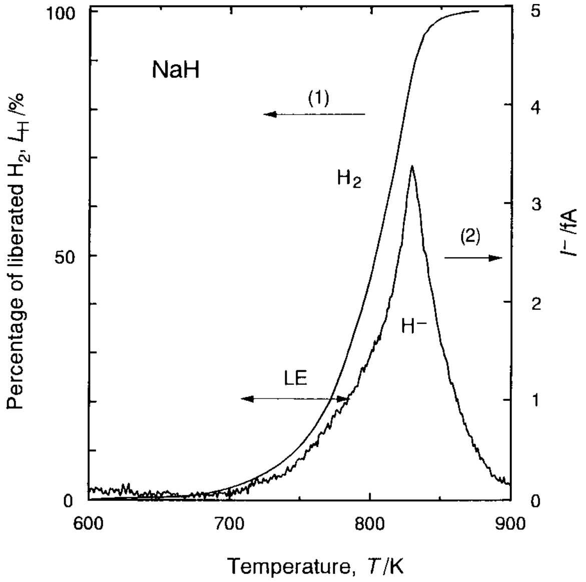

Fig. 10. Temperature dependence of (1) the percentage of the hydrogen liberated from NaH and (2) the current of H^- desorbed from the sample activated by heating ($\beta = 9.6$ K/s) to high temperatures above ca. 700 K.

increases up to the maximum at 825 K, where L_H is as large as 90%. Also J^- has the same tendency, as may readily be understood from Fig. 6c and Fig. 7c. It should be noted that ϕ depends upon both L_H and T and also that E^- depends upon ϕ [1].

4. Conclusion

The experimental data and analytical results summarized above lead to the conclusions as follows: (1) Thermal electron current can be employed as a convenient and useful probe to study the thermal decomposition of saline hydrides. (2) Measurement of electron emission current as a function of introduced hydrogen gas pressure makes it possible to determine the rate of hydrogen desorption from heated saline hydride. (3) Temperature-programmed heating of saline hydride enables us to determine the activation energies and frequency factors of those desorbates of H_2, H^- and e^-.

However, much work is necessary to obtain more reproducible data and also to clarify the fine mechanism of the change in work function.

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