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ABSORPTION AND DESORPTION RATES OF H2 AND D2 FOR LANI5, LAC05, --ETC(U)
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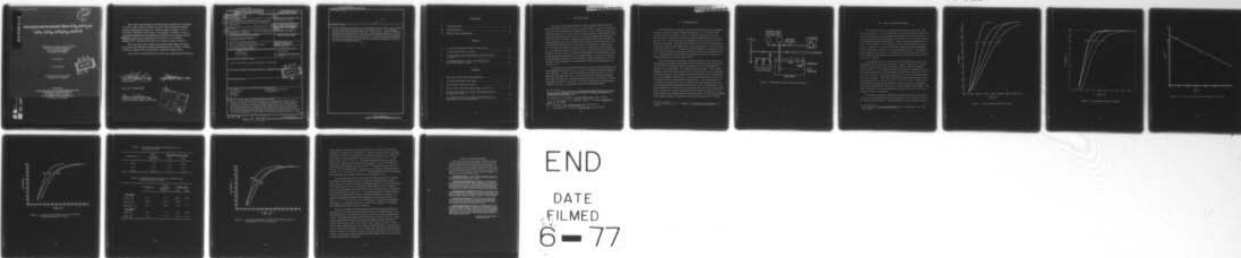
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Absorption and Desorption Rates of H₂ and D₂ for LaNi₅, LaCo₅, LaNi₂Co₃, and FeTi

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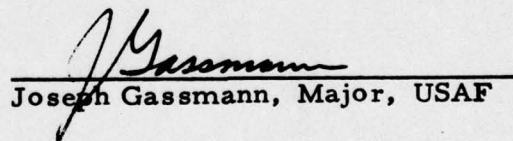
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This report has been reviewed by the Information Office (IO) and is releasable to the National Technical Information Service (NTIS). At NTIS, it will be available to the general public, including foreign nations.

This technical report has been reviewed and is approved for publication.


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19. KEY WORDS (Continued)

20. ABSTRACT (Continued)

rate law indicated that the rate-controlling step was hydrogen atom diffusion through an adherent hydride layer to the alloy surface. The activation energy for desorption from LaNi_5 was $4.5 (\pm) 0.5$ kcal. Even at 0.4°C , the H_2 absorption and desorption rates were sufficient that batteries could be charged and discharged in less than 30 min. Rates for D_2 were also determined and found to be lower than for H_2 . The use of LaCo_5 and LaNi_2Co_5 permitted even lower pressures than those needed with LaNi_5 for H_2 storage in Ni- H_2 satellite batteries.

PLUS OR MINUS

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I. INTRODUCTION

Because Ni-H₂ storage batteries can have higher energy densities¹ and longer lifetimes than the Ni-Cd and Ag-Zn batteries now used in spacecraft, it would be desirable to eliminate most of the problems encountered with Ni-H₂ batteries: H₂ pressures as high as 500 psi, which demand heavy cell walls; large volume for storing H₂; and rather rapid self discharge.² It was shown by van Vucht, Kuijpers, and Bruning³ that LaNi₅ can absorb large quantities of H₂ at pressures below 65 psi, where the cell walls need not be heavier than those for Ni-Cd cells, self discharge is slower, and 1 cm³ of LaNi₅ hydride holds about twice as much H₂ as 1 cm³ of liquid H₂. For the use of LaNi₅ storage of H₂ to be practical for Ni-H₂ batteries, however, the rates of H₂ desorption and absorption should be rapid enough to permit battery discharging and charging within a 1 hr period. Because of the practical importance of these kinetics, measurements were made of the rates of H₂ absorption and desorption by LaNi₅ at temperatures from zero to 32°C.

It was shown by Kuijpers⁴ that hydrides of LaCo₅ and LaCo₃Ni₂ reach their equilibrium pressures at even lower pressures than those required to form LaNi₅H₆. Because this would allow even lower pressures in Ni-H₂ batteries, H₂ absorption rates were also measured for these two alloys. Because FeTi alloy also absorbs large amounts of H₂ as FeTiH₂,⁵ FeTiH₂ desorption rates were measured. In order to enhance our understanding of these new alloys, D₂ absorption rates were also determined.

¹R. W. Easter, Proceedings of the Ninth Intersociety Energy Conversion Engineering Conference, American Society of Mechanical Engineers, New York (1974), pp. 888-895.

²J. Giner and J. D. Dunlop, J. Electrochem. Soc. **122**, 4 (1975).

³J. H. N. van Vucht, F. A. Kuijpers, and H. C. Bruning, Philips Res. Rep. **25**, 133 (1970).

⁴F. A. Kuijpers, Ber. Bunsen Gesel. **76**, 1220 (1972).

⁵J. J. Reilly and R. H. Wiswall, Inorg. Chem. **13**, 218 (1974).

II. EXPERIMENTAL

The LaNi_5 (Ronson Metals Corporation purified grade) was activated by using a process similar to that used by Kuijpers.⁴ 9.94 g of freshly crushed LaNi_5 was placed in a 300 cm^3 stainless steel pressure bomb, the vessel was evacuated, and then the alloy was exposed to 40 atm hydrogen for 18 hr. This procedure was repeated two times before the activation was successful. After this first activation, the bomb was transferred to the rate measurement system (Fig. 1) and immersed in a water bath controlled to within $\pm 0.1^\circ \text{C}$. The alloy was then subjected to a cycling sequence of 20 successive steps of hydrogen absorption followed by hydrogen desorption. This cycling sequence decreased the particle size and resulted in a constant surface area for the alloy powder.⁶

The absorption and desorption rates of hydrogen were measured by monitoring the variation of hydrogen pressure above the alloy as a function of time with a Uni-measure pressure transducer that was connected to a Moseley x-t recorder (Fig. 1). Duplicate runs were made. The average deviation of the pressure from the mean of the duplicate runs was typically less than 6 percent. The hydrogen used for absorption runs was contained in a 1-liter stainless steel vessel. For measuring absorption, this vessel was opened to the evacuated alloy-sample vessel. After absorption was completed, the desorption rate was measured by permitting the hydrogen to desorb from the hydrided alloy into several 1-liter vacuum flasks. The same procedures were also used in measuring the absorption and desorption rates of deuterium. Rate measurements were made for LaCo_5 , LaNi_2Co_3 (both donated by the Philips Research Laboratories), and FeTi alloy (donated by Brookhaven National Laboratory) with the procedures used for LaNi_5 .

⁶H. H. van Mal and K. H. J. Buschow, J. Less-Common Metals **35**, 65 (1974).

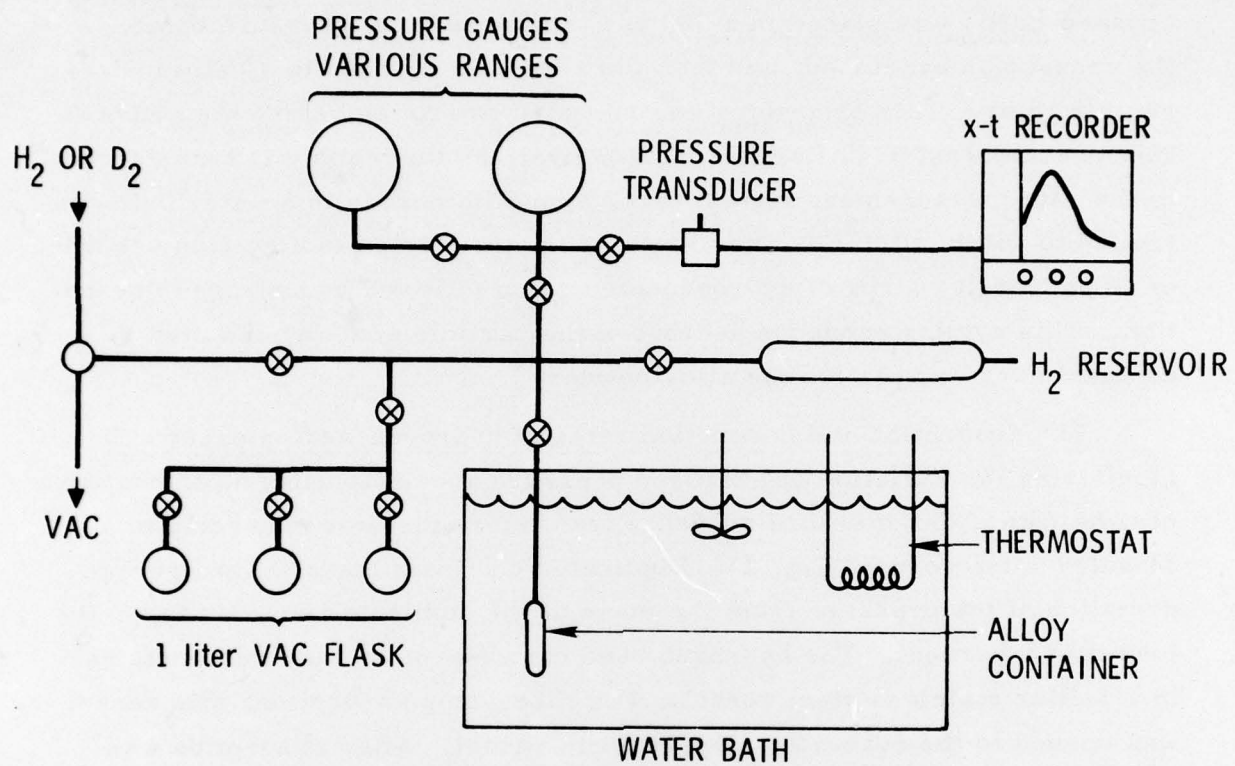


Figure 1. Schematic of Rate Measuring Apparatus

III. RESULTS AND DISCUSSION

The results for the H_2 desorption and absorption rates with $LaNi_5$ are shown in Figs. 2 and 3, respectively. The abscissa is the square root of time because it was consistently noted that the amount of H_2 desorbed and absorbed had a linear dependence on the square root of time up to about 60 percent desorption and absorption. Such a square-root dependence on time is not uncommon for the reaction of alloys with hydrogen⁷ and other gases. It is known to occur when the rate-controlling step is diffusion of H-atoms through an adherent, crack-free hydride layer.⁷ If the hydride layer, however, has cracks or is nonadherent, the amount of H_2 absorbed or desorbed will be proportional to the time of contact rather than to the square root of time.

It is apparent in Fig. 2 that the rate of desorption decreased as the temperature of the alloy was decreased. Figure 4 shows the T^{-1} dependence for the log of the slope of the linear section of the H_2 desorption curves in Fig. 2. The activation energy for diffusion of hydrogen atoms in the $LaNi_5$ hydride layer was calculated from the slope of the line in Fig. 4 to be 4.5 ± 0.5 kcal. The times required for 95 and 98 percent desorption are given in Table 1. The time required for 98 percent desorption of the H_2 decreased from 25 min at $0.4^\circ C$ to 2.6 min at $32.0^\circ C$. These desorption times are sufficiently rapid that it would be practical to discharge Ni- H_2 batteries within 30 min if such a rapid discharge were needed. The times required for 95 percent desorption of H_2 at 0.4° and $32.0^\circ C$ were 16 and 2.2 min, respectively.

The times required for 98 percent absorption by $LaNi_5$ (Fig. 3) of the H_2 at an initial pressure of 140 psi ranged from 4.5 min at $22.0^\circ C$ to 1.7 min at $0.4^\circ C$ (Table 2). These times are short enough to permit

⁷G. G. Libowitz, Binary Metal Hydrides, W. A. Benjamin, Inc., New York (1965).

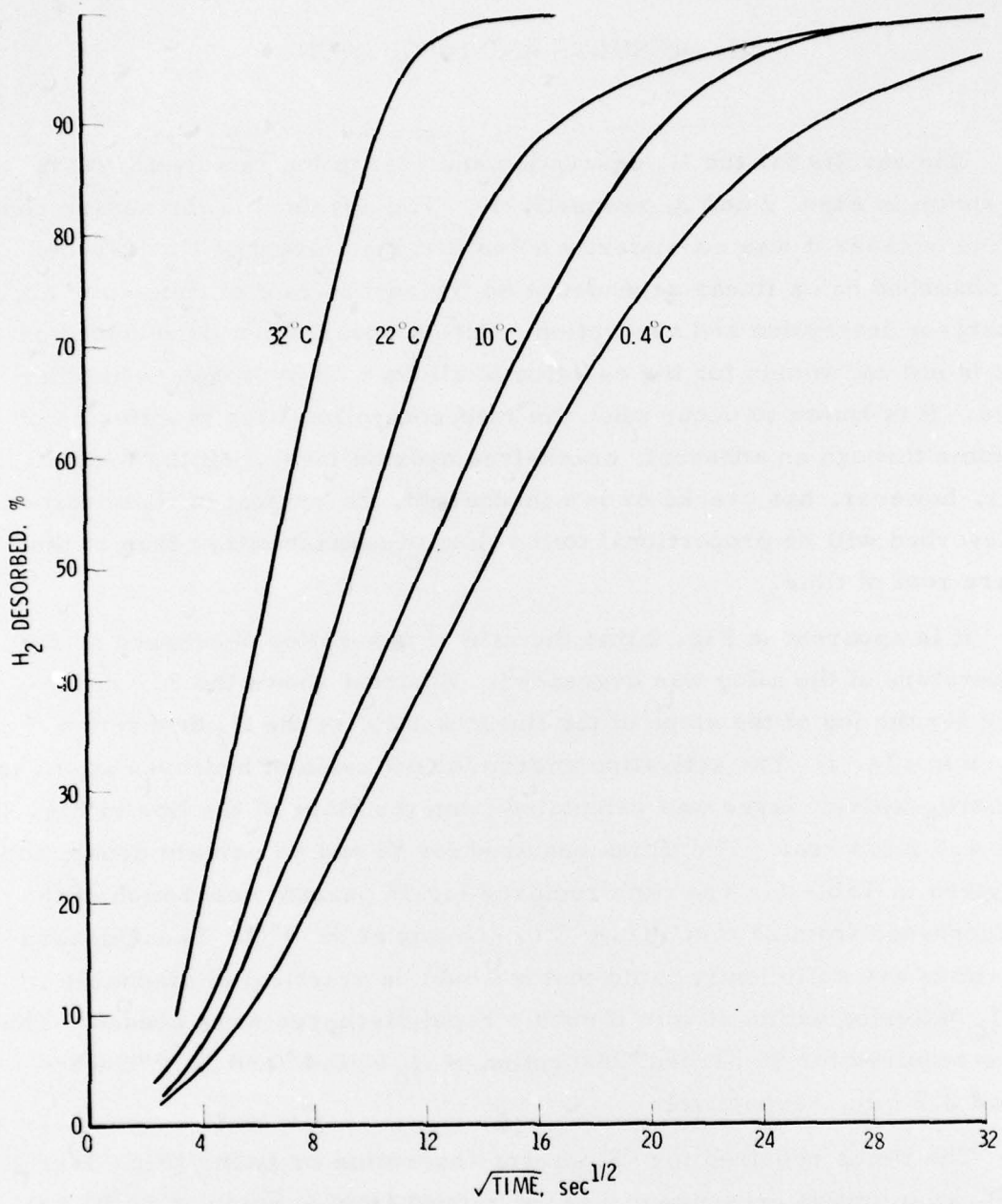


Figure 2. H₂ Desorption Rates from LaNi₅

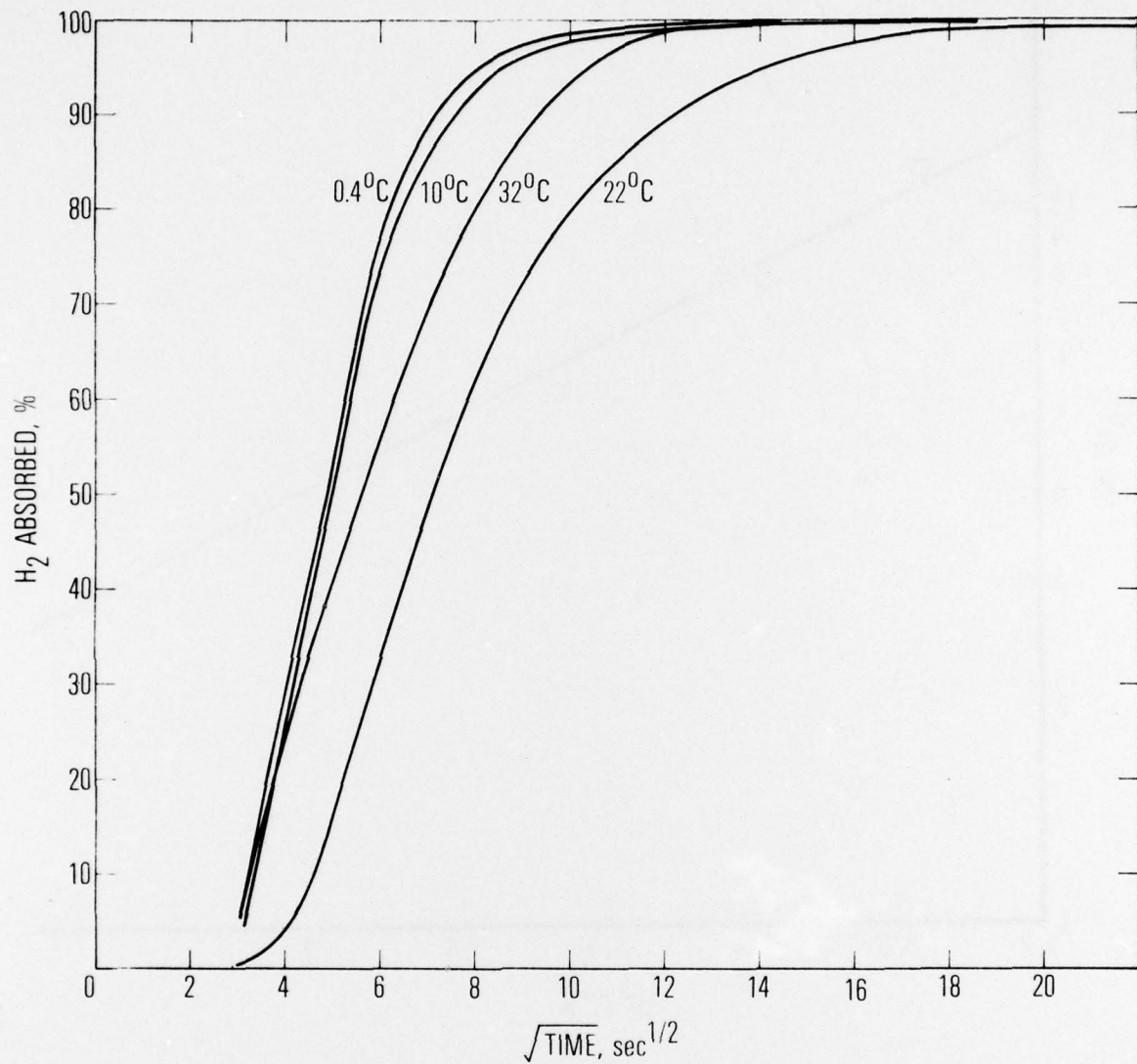


Figure 3. H₂ Absorption Rates for LaNi₅

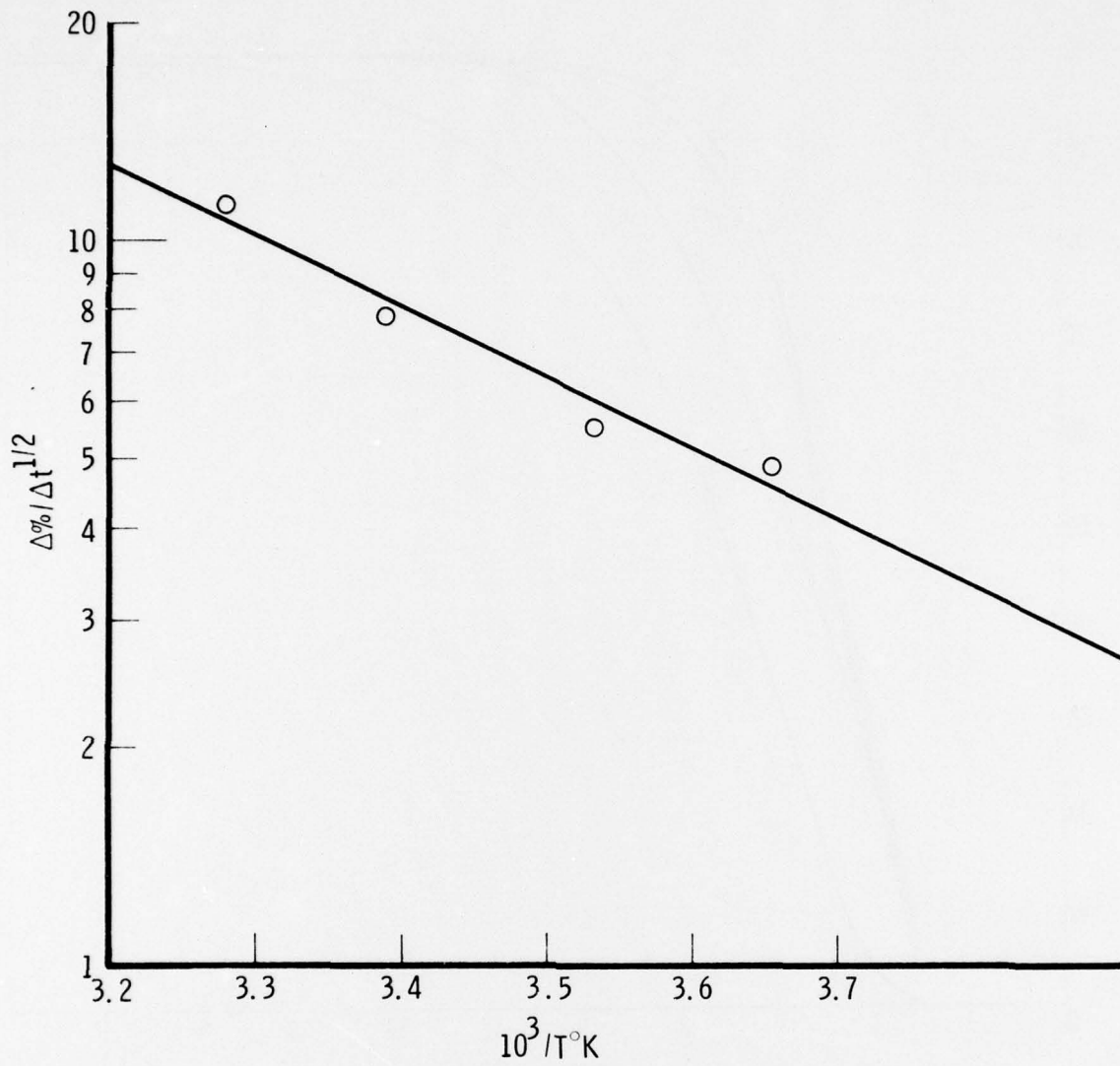


Figure 4. Log of LaNi₅ Alloy Desorption Rates vs $10^3/T^\circ\text{K}$

Table 1. H₂ and D₂ Desorption Rates for LaNi₅ Alloy

Temperature, °C	Slope ($\Delta\%/ \Delta t^{1/2}$), sec ^{-1/2}	Desorption Time, min		Deuterium Slope ($\Delta\%/ \Delta t^{1/2}$), sec ^{-1/2}
		95%	98%	
32.0	11.4	2.2	2.6	11.1
22.0	7.9	7.0	10.4	7.5
10.0	5.6	8.8	11.7	
0.4	4.9	15.7	24.8	

Table 2. H₂ Absorption Rates for LaNi₅, with Initial Reservoir Pressure of 140 psi

Temperature, °C	Slope, sec ^{-1/2}	Absorption Time, min	
		95%	98%
32.0	15.5 ^a	1.9	2.2
22.0	16.7	3.3	4.5
10.0	24.0	1.3	1.9
0.4	24.0	1.2	1.7

^aThe slope for D₂ absorption was 9.0 at 32.0°C.

convenient absorption by LaNi_5 of H_2 generated during the charging of Ni- H_2 batteries. The linear portion of each absorption curve in Fig. 3 does not extend to much above 60 percent H_2 absorbed. This nonlinearity is expected to arise because, as the hydride layer becomes thicker, the surface area of the unreacted LaNi_5 becomes smaller. The rate of absorption depends on the LaNi_5 surface area, which decreases because the alloy is replaced by the hydride layer.

Inasmuch as the Ni- H_2 cell wall thickness required to withstand the H_2 pressure would be even less at an initial H_2 pressure of 70 psi than at the 140 psi of Fig. 3, absorption rate measurements were made with an initial pressure of 70 psi for three temperatures (Fig. 5). The times required for 98 percent absorption by LaNi_5 at 10.0 to 32.0°C are shown in Table 3. The increase in absorption times and decrease in slope with increased temperature can be attributed to the increase of the equilibrium pressure of the hydride at the higher temperatures.³ In this case the faster diffusion rates at the higher temperatures are not sufficient to outweigh the effect of the increase in equilibrium pressure. Nevertheless, the absorption times are short enough to permit discharge of the Ni- H_2 battery in less than 30 min.

In Fig. 6, the absorption rates at 22.0°C are compared for initial H_2 pressures of 50, 70, and 140 psi. Even at an initial pressure of 50 psi, the rate of H_2 absorption by LaNi_5 was high enough to permit 98 percent discharge of a Ni- H_2 battery in about the same time required as with initial H_2 pressure of 70 psi.

Because the transition equilibrium pressures for LaCo_5 and LaNi_2Co_3 ⁴ are considerably lower than for LaNi_5 , lower H_2 pressures could be used in the Ni- H_2 cells than are required for LaNi_5 storage of H_2 . In Table 4, data are given for the absorption times and slopes for these cobalt-containing alloys at initial H_2 pressures of 30 psi. Only 7.3 min were required for 98 percent absorption of H_2 on LaNi_2Co_3 at 25.7°C. For LaCo_5 , 40 min

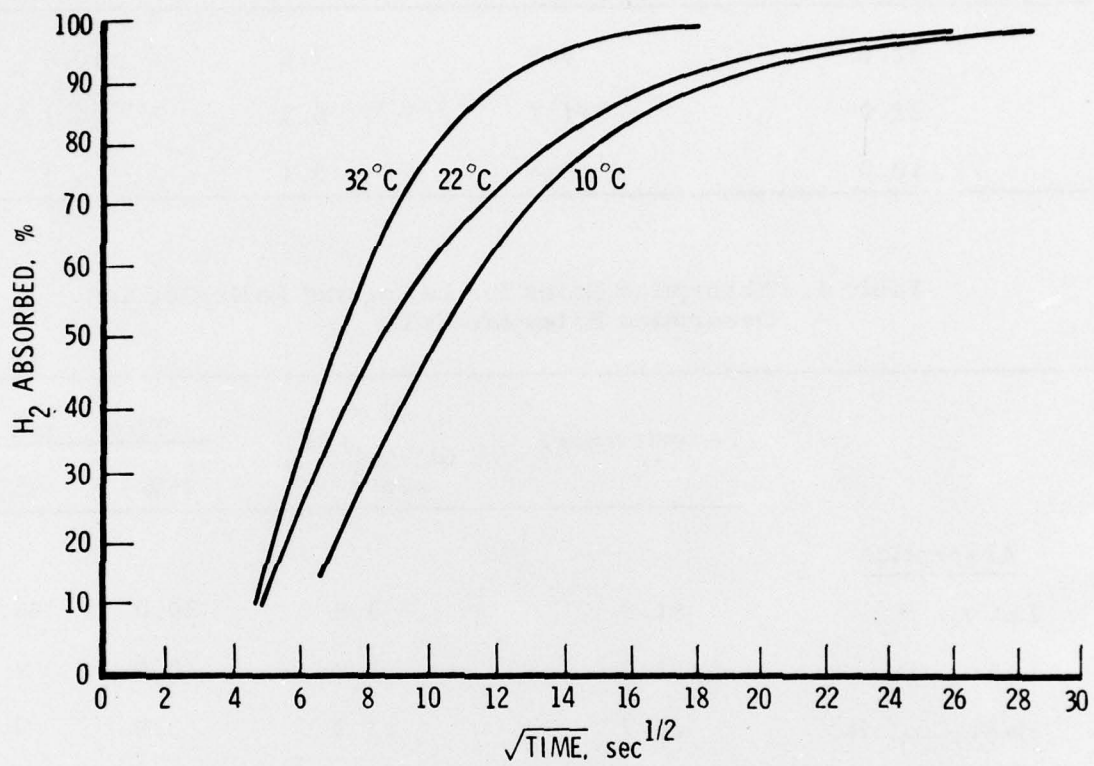


Figure 5. H₂ Absorption Rates for LaNi₅ with Initial Reservoir Pressure of 70 psi

Table 3. H₂ Absorption Rates with Initial Reservoir Pressure of 70 psi

Temperature, °C	Slope ($\Delta\%/ \Delta t^{1/2}$), sec ^{-1/2}	Absorption Time, min	
		95%	98%
32.0	9.9	7.6	10.9
22.0	11.1	6.7	9.1
10.0	15.4	3.1	4.1

Table 4. Absorption Rates for LaCo₅ and LaNi₂Co₃ and Desorption Rates for FeTi

	Temperature, °C	Slope ($\Delta\%/ \Delta t^{1/2}$), sec ^{-1/2}	Time, min	
			95%	98%
<u>Absorption</u>				
LaCo ₅ , H ₂	51.0	3.8	20.0	40.0
LaCo ₅ , D ₂	51.0	3.2	40.0	-
LaNi ₂ Co ₃ , H ₂	25.7	13.3	3.8	7.3
<u>Desorption</u>				
FeTi, N ₂	10.1	7.2	6.8	10.4
FeTi, H ₂	0.4	5.9	13.1	22.1

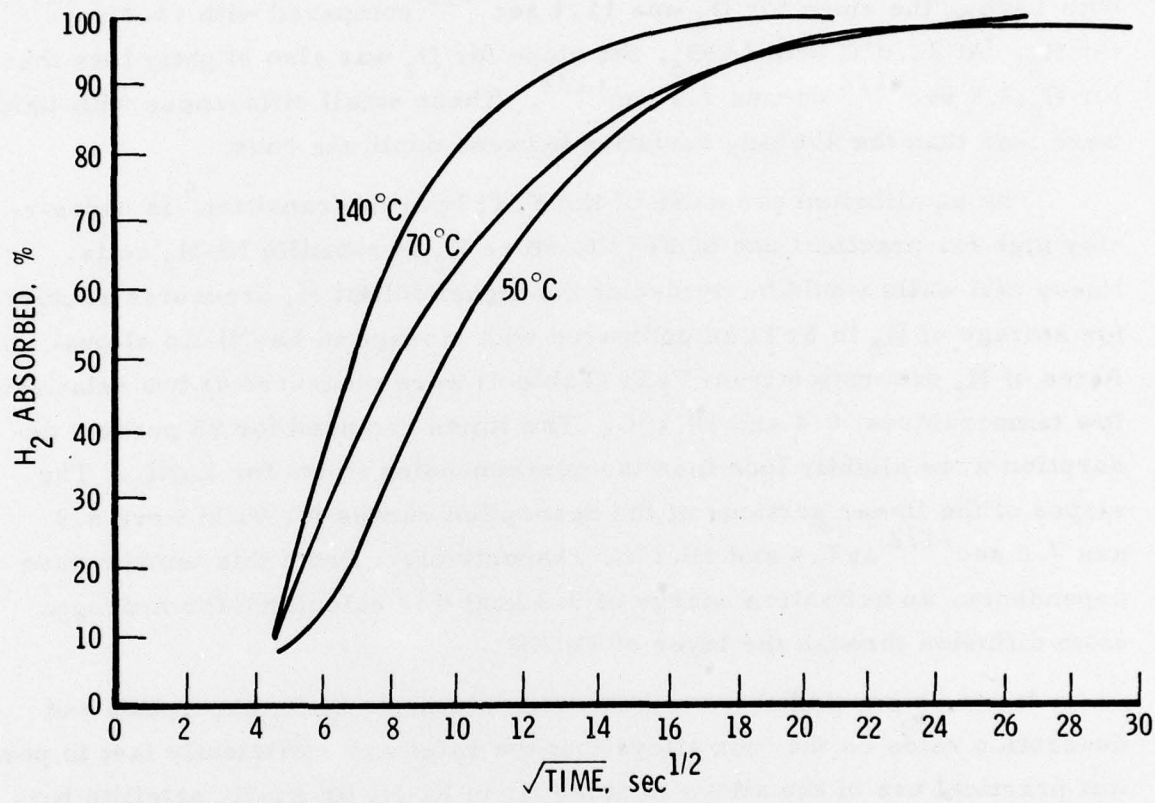


Figure 6. H₂ Absorption Rates for LaNi₅ with Initial Reservoir Pressures of 50, 70, and 140 psi

were required for 98 percent H_2 absorption and 20 min for 95 percent H_2 absorption. Deuterium is absorbed on $LaCo_5$ more slowly than hydrogen (Table 4); 40 min were required for 95 percent absorption of D_2 . The slope of the linear portion of the absorption curve for D_2 was $3.2 \text{ sec}^{-1/2}$ compared with $3.8 \text{ sec}^{-1/2}$ for H_2 . A smaller difference between D_2 and H_2 kinetics was observed with $LaNi_5$ than with $LaCo_5$. At 32.0°C (Table 1) with $LaNi_5$, the slope for D_2 was $11.1 \text{ sec}^{-1/2}$ compared with $11.4 \text{ sec}^{-1/2}$ for H_2 . At 22.0°C with $LaNi_5$, the slope for D_2 was also slightly less than for H_2 : $7.5 \text{ sec}^{-1/2}$ versus $7.9 \text{ sec}^{-1/2}$. These small differences with $LaNi_5$ were less than the average deviation between duplicate runs.

The equilibrium pressure of the FeTi hydride transition⁵ is undesirably high for practical use of FeTi to store H_2 in satellite Ni- H_2 cells. Heavy cell walls would be needed at the higher initial H_2 pressures required for storage of H_2 in FeTi as compared with storage in La-Ni-Co alloys. Rates of H_2 desorption from FeTi (Table 4) were measured at two relatively low temperatures; 0.4 and 10.1°C . The times required for 98 percent desorption were slightly less than the corresponding times for $LaNi_5$. The slopes of the linear portions of the desorption curves for FeTi were 5.9 and $7.2 \text{ sec}^{-1/2}$ at 0.4 and 10.1°C , respectively. From this temperature dependence, an activation energy of 3.3 kcal was calculated for hydrogen atom diffusion through the layer of $FeTiH_2$.

It can be concluded from these measurements of H_2 absorption and desorption rates on the four alloys that the rates are sufficiently fast to permit practical use of the alloys to store H_2 in Ni- H_2 or Ag- H_2 satellite batteries. The relatively high transition pressures for FeTi, however, make it less desirable than $LaNi_5$ in providing a weight savings by the use of lighter walls for the cells. On the other hand, $LaNi_5$ may be less advantageous than $LaNi_2Co_3$ because its higher transition pressures would require the use of heavier cell walls. It is recommended, therefore, that investigation be carried out to compare $LaNi_5$, $LaNi_2Co_3$, and other La-Ni-Co alloys in order to determine which would provide the highest battery energy density and the longest battery lifetimes.

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