# **Hydrogen Storage Materials**

## Influence of Transition Metals on Hydrogen Storage Properties of LaNi<sub>5</sub> Alloy

### Asheesh Kumar\*, Seemita Banerjee, Priyanka Ruz and V. Sudarsan

Chemistry Division, Bhabha Atomic Research Centre, Mumbai 400085, INDIA



#### ABSTRACT

LaNi<sub>4</sub>Fe alloy is found to have good hydrogen storage capacity among studied AB5 alloy at room temperature. Effect of partial substitution of Fe by Zr and V in LaNi<sub>4</sub>Fe alloy on its hydrogen storage properties has been investigated in detail. Alloys with composition LaNi<sub>4</sub>Zr<sub>0.5</sub>Fe<sub>0.5</sub> and LaNi<sub>4</sub>V<sub>0.5</sub>Fe<sub>0.5</sub> were prepared by arc melting method and the phase formation was confirmed by X-ray diffraction (XRD) technique. Hexagonal structure of the parent alloy is found to be retained even after substitution. Hydrogen absorption properties of these alloys as well as the kinetics involved in hydrogen absorption-desorption process were studied in detail using a Sievert's type set-up. LaNi<sub>4</sub>Zr<sub>0.5</sub>Fe<sub>0.5</sub> and LaNi<sub>4</sub>V<sub>0.5</sub>Fe<sub>0.5</sub> are found to absorb a maximum of 1.3 wt. % and 1.5 wt, % hydrogen respectively at room temperature. The substituted alloy shows improved kinetics than LaNi<sub>5</sub> alloy at room temperature.

KEYWORDS: Solid state electrolyte, NASICON, Li-ion solid state battery

#### Introduction

In recent years many hydrogen storage materials such as carbon nanotubes, porous metal-organic frameworks, complex hydrides, alanates, intermetallic compounds etc., have been explored extensively[1-2]. However, hydrides of alloys and intermetallic compounds continue to be the most promising materials for practical applications[3]. Among intermetallic compounds the AB5 type are well known for their excellent hydrogen storage properties like easy activation, fast kinetics, cyclic stability and moderate plateau pressure[4-5]. LaNi<sub>5</sub> is one of the extensively studied systems among AB5 alloys with a storage capacity of 1.5 wt%. This alloy absorbs hydrogen rapidly at room temperature without rigorous activation of surface at high pressure and temperature[6-7]. Besides hydrogen storage application, this alloy shows excellent catalytic properties.

Many researchers reported CO<sub>2</sub> methanation using LaNi<sub>5</sub> alloys. The ball-milling of LaNi<sub>5</sub> powder in a mixture of CO<sub>2</sub> and H<sub>2</sub> gases was found to successfully result in CH<sub>4</sub> generation[8]. LaNi<sub>5</sub> type alloys are commercially used as negative electrode in Ni-MH rechargeable batteries.

The hydrogen storage properties such as reversibility, desorption capacity, hydrogen storage capacity, and desorption temperature of the alloys can be further improved by changing their composition [9] or by elemental modification. The elemental modification by suitable substitution at La/Ni sites is expected to tune the hydrogen storage properties of LaNi<sub>5</sub> alloy. Researchers have tried partial substitution of elements like Ce, Zr, Mg, Co, Fe, Mn, Al, Cu and Sn in place of both elements and investigated the hydrogen storage properties in detail [10-11]. The partial substitution of Co, Fe, Al and Sn in place of Ni in this alloy is found to improve the hydrogen storage properties of the parent alloy. For example,

Sn substitution for Ni in LaNi<sub>5</sub> alloy enhances the long-term hydrogen storage stability, and the hydrogen storage capacity of the alloy reduced only 1.2 % in 1000 cycles[12]. It is inferred from the studies that hydrogen storage properties and cyclic stability improved significantly upon elemental modification [13].

Though it is reported that substitution of Fe for Ni is found to increase the storage capacity of LaNi<sub>4</sub>Fe to 2.2 wt%[14], several other studies reported storage capacities in the range of 1 to 1.25 wt.% at room temperature[15-16].

In general, hydrogen absorption capacity of LaNi<sub>4</sub>Fe alloy can be enhanced by the substitution of Fe with elements having higher electron affinity and bigger size than that of Ni. Substitution of bigger size element increases the c/a ratio of the hexagonal lattice, and larger value of c/a ratio decreases the diffusion path length of hydrogen atoms into the unit cell and reduces the micro strain.

With this background, in the present study elemental substitution of Fe in LaNi<sub>4</sub>Fe alloy has been carried out with bigger atomic size element such as Zr and V, with a view to improve the hydrogen storage properties of the alloy.

In the present manuscript effect of partial substitution of Fe by Zr and V in LaNi<sub>4</sub>Fe alloy on its hydrogen storage properties have been discussed. The alloys LaNi<sub>4</sub>Zr<sub>0.5</sub>Fe<sub>0.5</sub> and LaNi<sub>4</sub>V<sub>0.5</sub>Fe<sub>0.5</sub> were synthesized by arc melting of the constituent elements. The structure of the alloy and their hydrogen absorption properties have been studied in detail.

#### Experimental

The studied LaNi<sub>4</sub>Zr<sub>0.5</sub>Fe<sub>0.5</sub> and LaNi<sub>4</sub>V<sub>0.5</sub>Fe<sub>0.5</sub> alloys were prepared by arc melting high purity constituent elements in a water-cooled copper hearth under argon atmosphere. For achieving the homogeneity, the alloy button was turned over and re-melted 4 times. The crystal structure of the as-cast alloy was examined by X-ray diffraction (XRD) technique using

<sup>\*</sup>Author for Correspondence: Asheesh Kumar E-mail: asheeshk@barc.gov.in



Fig.1a: XRD pattern of  $LaNi_4V_{o_5}Fe_{o_5}$  alloy as cast and after hydrogenation.



Fig.1b: XRD pattern of LaNi $_4$ Zr $_{0.5}$ Fe $_{0.5}$  alloy, as cast and after hydrogenation.

monochromatic Cu Ka radiation. Hydrogen absorption and desorption studies were done using a Sievert's type set up described in our earlier studies[17].

The activation procedure involved heating of the alloy under vacuum  $(10^6 \text{ mbar})$  for 2 hours at 673 K. Pressurecomposition isotherms were studied at room temperature and up to a hydrogen pressure of 2 MPa. Kinetic study was done at room temperature and hydrogen pressure of 2 MPa after one absorption-desorption cycle. The amount of total hydrogen in the hydrides was estimated by monitoring change in the hydrogen pressure during the absorption process. The hydride sample was surface poisoned before being taken out. Hydrogen content of the saturated hydride sample was estimated by complete decomposition of a small amount of the hydride sample in a pre-calibrated evacuated quartz chamber described in our earlier studies [17].

#### **Results and Discussion**

#### **Crystal structure**

Fig.1 (a and b) show the XRD patterns of LaNi<sub>4</sub>Zr<sub>0.5</sub>Fe<sub>0.5</sub> and LaNi<sub>4</sub>V<sub>0.5</sub>Fe<sub>0.5</sub> alloys, before and after hydrogen absorption. The data confirmed that all the samples are single phase, and crystallized in the hexagonal CaCu<sub>5</sub> type structure, (space group P6/mmm), the same structure as of prototype LaNi<sub>5</sub>.



Fig.2: Crystallographic arrangements of LaNi $_{\rm 5}$  unit cell adopted from Ref [18].

The unit cell lattice parameters were obtained by least square fitting. The lattice parameters of both the alloys are given in Table 1. It can be seen that with the substitution of V in the alloy, the lattice parameters "a" and "c" as well as the cell volume increases. The observation is in line with the expectation as V (134 pm) has higher atomic size compared to both Ni (124 pm) and Fe (126 pm). The increase in the lattice parameter suggests that V preferentially gets substituted in the lattice position of Ni. It can also be observed that there is an increase in the c/a ratio of the hexagonal unit cell after V substitution.

In Fig. 2, the structure of LaNi, with two different layers of atoms is shown. The basal plane contains both La and Ni atoms at the 1a and 2c sites, respectively. The intermediate layer consists of only Ni atoms in 2c sites. After the substitution of V in the structure, there is an increase in the c/a ratio indicating that the substituent elements preferentially goes in the intermediate layer and replace Ni atoms in the structure. The situation is slightly different for Zr substitution. With Zr substitution, the c/a ratio remains almost same and it is obvious that in the latter system the basal or both available nickel crystallographic positions are involved in the substitution process. It is also clear from the XRD patterns of both the alloys that the peaks are similar in as cast and hydrogenated alloys with minor change in peak positions, which indicates that the hydrides are of the same structure as the parent alloy with change in lattice parameters.

During the formation of hydrides the hydrogen atoms go into the interstitial position of the alloy, increasing the lattice parameter slightly. The strain created during hydride formation leads to broadening in the X-ray diffraction peaks. As peak become broader merging take place, leading to removal of necks.

#### Hydrogen Absorption Study

The hydrogen absorption and desorption properties of the alloys were studied at room temperature using a Sievert's type set up. For the construction of pressure-composition isotherms at a temperature, certain pressure of hydrogen is introduced in the reaction chamber and the hydrogen absorption was monitored with pressure drop. After complete absorption at that dose pressure, same procedure was repeated until the equilibrium pressure reaches 20 atm.

S.N.	Alloy	a(Å)	c (Å)	Unit cell volume	c/a ratio	Rate of H <sub>2</sub> uptake (cc/g/min)	Hydrogen storage capacity (H/M)
1.	LaNi <sub>5</sub>	5.017	3.986	86.2	0.7945	22	6
2.	LaNi <sub>4</sub> Fe	5.049	4.015	88.02	0.7952	19	5.4[15]
4.	$\text{LaNi}_4\text{V}_{0.5}\text{Fe}_{0.5}$	5.052	4.022	8828	0.7961	28	6.5
5.	$LaNi_4V_{0.5}Fe_{0.5}$	5.049	4.014	8800	0.7950	23	5.9

Table 1: Hydrogen storage capacity, lattice parameter and unit cell volume of the studied alloy.



Fig.3: The pressure-composition isotherm of LaNi $_4$ Zr $_{0.5}$ Fe $_{0.5}$  and LaNi $_4$ V $_{0.5}$ Fe $_{0.5}$  alloys.

Fig.3 shows the room temperature pressure-composition isotherms of  $LaNi_4Zr_{0.5}Fe_{0.5}$  and  $LaNi_4V_{0.5}Fe_{0.5}$  alloys. As shown in Fig.3, alloys  $LaNi_4Zr_{0.5}Fe_{0.5}$  and  $LaNi_4V_{0.5}Fe_{0.5}$  are found to absorb maximum of 5.9 H/formula unit and 6.5 H/formula unit respectively at room temperature. The absorption in LaNi<sub>4</sub>Zr<sub>0.5</sub>Fe<sub>0.5</sub> is close to the hydrogen storage capacity of LaNi<sub>5</sub> alloy. In AB5 type alloy total 34 tetrahedral holes are available for hydrogen storage. But all the holes cannot be occupied simultaneously due to stability consideration. As per Switendic Criterion, minimum distance between two H atoms is 2.1 Å and this controls the hydrogen occupancy in holes. Hydrogen storage capacities of both the alloys are listed in Table 1. The probable cause for reduction in hydrogen storage capacity of the studied alloys may be unavailability of suitable interstitial site. Pressure composition isotherm studies show change in plateau pressure for both the alloys at room temperature. The plateau region, in the absorption isotherm of vanadium substituted alloy is found nearly flat and slightly above 1 bar pressure which actually suggest that at room temperature around 1 bar hydrogen pressure will be generated to from the alloy and at a particular temperature with small change in the equilibrium pressure hydrogen absorption and desorption can be carried out. On the other hand, Zr substitution in place of Fe increased the plateau pressure drastically and LaNi<sub>4</sub>Zr<sub>0.5</sub>Fe<sub>0.5</sub> alloy shows sloping plateau at higher pressure. Unlike the earlier case, the hydride LaNi<sub>4</sub>Zr<sub>0.5</sub>Fe<sub>0.5</sub>H<sub>5.9</sub> is quite unstable at room temperature and is not suitable for room temperature applications. Thus, from the above discussion it can be concluded that change in chemical composition of LaNi<sub>5</sub> alloy affect the thermodynamic stability of the alloy remarkably, which may or may not be beneficial for the practical application.

It is also expected that change in chemical composition would affect the kinetics of hydrogen absorption-desorption. The hydrogenation reaction of metal/alloy/intermetallic compound comprises following steps[19]

 $\blacksquare$  Physisorption of  $H_{\scriptscriptstyle 2}$  molecules on the surface of alloy/intermetallic compound.

Dissociation of H<sub>2</sub> molecules into H atoms.

Penetration of H atoms from surface into bulk followed by chemisorption.

- Diffusion of H atoms through the hydride layer.
- Hydride formation at the metal/hydride interface.

Among the above mentioned processes, the slowest one would govern the overall reaction kinetics, thus considered as rate determining step of the hydrogen absorption reaction. When the H atoms reach the interface (step 5) of metal/alloy/intermetallic compound ( $\alpha$  phase) and hydrides ( $\beta$  phase), a fast reaction happens leading to the formation of growing hydride layer.

#### $\alpha$ + H (in $\beta$ hydride phase) = $\beta$ (hydride).

The hydrogen desorption reaction follows the above mentioned steps in a reverse order. Extensive studies have been carried out on the hydrogenation-dehydrogenation kinetics of LaNi<sub>s</sub> alloy by different researchers[20-22]. The activation energy of hydrogen absorption-desorption of LaNi<sub>s</sub> alloy can be tuned by changing the reaction conditions as well as by chemical modifications. Some of the examples are listed in Table 2. It is

Table 2: Reported kinetic details of LaNi<sub>5</sub> alloy in different study.

Alloy	Operating condition	Kinetic model	Activation Energy	Ref.
LaNi <sub>5</sub>	25- 40°C	JMA 1 <sup>st</sup> order	30 (abs), 40 (des)	20
LaNi <sub>5</sub>	20- 50°C	Shrinking Core Model	19.65 (abs)	21
LaNi <sub>5</sub>	40- 70°C	JMA 1 <sup>st</sup> order	19.5(abs)	9
LaNi <sub>5</sub>	20- 40°C	Pressure dependent model	26.4(abs), 39.8(des)	22



Fig.4: The hydrogen absorption kinetics of  $LaNi_4Zr_{0.5}Fe_{0.5}$  and  $LaNi_4V_{0.5}Fe_{0.5}$  alloys.

found from the literature survey that different types of kinetic models have been used by researchers to describe the hydrogenation-dehydrogenation kinetics of  $LaNi_{\rm 5}$  alloy. These kinetic models are used to determine the rate constants of hydrogenation-dehydrogenation reactions from experimentally obtained kinetic data at different temperatures (T). Finally activation energy is obtained from the Arrhenius plot of rate constant vs (1/T).

Like the thermodynamic parameters, the derived activation energy plays an important role during the engineering design of metal-hydride systems for different applications. Hence in the present study, kinetics of hydrogen absorption for Zr and V substituted LaNi<sub>5</sub> alloys have also been investigated. The hydrogenation kinetics for LaNi<sub>4</sub>Zr<sub>0.5</sub>Fe<sub>0.5</sub> and LaNi<sub>4</sub>V<sub>0.5</sub>Fe<sub>0.5</sub> alloys have been studied after one absorption desorption cycle. The hydrogen absorption kinetics of both the alloys is shown in Fig.3. It is found that hydrogen absorption is fast and it reaches near saturation value very fast. There is no incubation period before absorption as clear from the figure.

The alloy LaNi<sub>4</sub>Zr<sub>0.5</sub>Fe<sub>0.5</sub> absorbs maximum 93% of its total hydrogen storage capacity within 5 minutes and LaNi<sub>4</sub>V<sub>0.5</sub>Fe<sub>0.5</sub> alloy absorbs 95% of total hydrogen absorption within same time period. As mentioned in Table 1 the rate of hydrogen absorption for V and Zr substituted alloy is faster than the parent alloy. Hence, it is inferred that hydrogen absorption kinetics of V substituted alloy is better than that of Zr substituted alloy.

#### Conclusions

Hydrogen absorption-desorption properties of LaNi<sub>4</sub>Zr<sub>0.5</sub>Fe<sub>0.5</sub> and LaNi<sub>4</sub>V<sub>0.5</sub>Fe<sub>0.5</sub> alloys have been studied. The maximum storage capacities of 1.3 and 1.5 wt. % are found for LaNi<sub>4</sub>Zr<sub>0.5</sub>Fe<sub>0.5</sub> and LaNi<sub>4</sub>V<sub>0.5</sub>Fe<sub>0.5</sub> alloys, respectively. The pressure composition isotherm studies show the change in plateau pressure for both the alloys at room temperature. The plateau region, in the absorption isotherm of vanadium substituted alloy is found nearly flat and slightly above 1 bar pressure, whereas, LaNi<sub>4</sub>Zr<sub>0.5</sub>Fe<sub>0.5</sub> alloy shows sloping plateau at higher pressure. Hydride of LaNi<sub>4</sub>V<sub>0.5</sub>Fe<sub>0.5</sub> alloy is more stable than LaNi<sub>4</sub>Zr<sub>0.5</sub>Fe<sub>0.5</sub> hydride under similar conditions. Hydrogen absorption kinetics of both (LaNi<sub>4</sub>V<sub>0.5</sub>Fe<sub>0.5</sub> and LaNi<sub>4</sub>Zr<sub>0.5</sub>Fe<sub>0.5</sub>) alloys are found to be faster than that of parent alloy. Crystal structure of the alloy remains unaffected with hydrogen

absorption and desorption. The LaNi $_4V_{0.5}Fe_{0.5}$  alloy may desorb hydrogen easily at ambient condition as plateau pressure of the alloy is above 1bar.

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