Crystallographic and thermodynamic study of La$_{0.55}$Y$_{0.45}$Ni$_5$–H$_2$, a candidate system for hydrogen buffer tanks

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Abstract

Electrical vehicles (EV) powered by a fuel cell will need a buffer tank to supply hydrogen especially for cold start and/or to overcome the delayed response time in the hydrogen supply system (reformer, dehydrogenation, etc.). To allow hydrogen supply at low temperature, the crystallographic and thermodynamic properties of the system La$_{0.55}$Y$_{0.45}$Ni$_5$–H$_2$ have been investigated. The pressure–composition–isotherm (PCI) curves have been carried out between 253 and 318 K. The compound La$_{0.55}$Y$_{0.45}$Ni$_5$ can deliver 5.4 H/f.u. (1.3 wt.%) under 0.35 MPa at 253 K. At room temperature, between 0.6 and 3.3 H/f.u., a well-defined plateau is observed in the PCI curve. However, for capacity values larger than 3.3 H/f.u., a step is observed followed by a sloppy domain. Investigation by neutron diffraction at various states of charge has allowed determination of the La$_{0.55}$Y$_{0.45}$Ni$_5$–D$_2$ phase diagram. The existence of an intermediate γ phase has been established. The crystal structures of the α, γ and β phases have been determined. The occurrence of the γ phase could significantly increase the cycle life of the hydride by decreasing the constraints which are generated during absorption/desorption cycling as previously observed in other LaNi$_5$-type systems.
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1. Introduction

The use of hydrogen as an energy carrier in automobiles is considered as a promising way to limit greenhouse gas emissions [1]. Fuel cells using hydrogen will release only water vapor into atmosphere. Metal hydrides can be used as hydrogen storage materials for supplying fuel cells. However, the kinetic properties of the metal hydride must be optimized to work at a temperature of about 338 K using the heat coming from the fuel cell. This implies a delay time to reach the working temperature, especially if the ambient temperature is very low. Thus, a buffer tank will be needed during the time necessary for start-up. For this application, the buffer tank has to supply 0.2 MPa of hydrogen at 253 K.

In our study, the storage properties of the pseudo-binary system La$_{1-x}$Y$_x$Ni$_5$ have been investigated. Both compounds

LaNi$_5$ and YNi$_5$ crystallise in the same hexagonal CaCu$_5$-type structure ($P6/mmm$ space group), and their equilibrium pressures are respectively 0.02 and 5 MPa at 253 K [2–4]. As the atomic radius of Y is smaller than that of La, substitution of La by Y leads to a linear reduction of the cell volume according to Vegard's law. Similarly, the corresponding hydrides show a linear relation between the logarithm of the equilibrium pressure and the cell volume. Considering these relations, a substitution rate of $x = 0.45$ was calculated to reach 0.2 MPa of hydrogen equilibrium pressure at 253 K. Hence the crystallographic and hydrogenation behaviour of La$_{0.55}$Y$_{0.45}$Ni$_5$ compound was characterized in this work.

2. Experimental details

La$_{0.55}$Y$_{0.45}$Ni$_5$ was prepared by induction melting of the pure elements (3N). Twelve grams of ingot were turned over and remelted five times to ensure homogeneity. The as-cast

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ingot was then annealed at 1223 K for 5 days and quenched to room temperature. Metallographic examination and elemental analysis by electron probe micro-analysis (EPMA Cameca SX100) were performed to check the homogeneity and stoichiometry of the alloy. The powder X-ray diffraction (XRD) experiment was obtained at room temperature on a Bruker D8advance Bragg Brentano diffractometer using Cu $K\alpha$ radiation. Pressure–composition–isotherm (PCI) curves were measured with a Sievert's type apparatus after five hydrogen absorption–desorption cycles. For powder neutron diffraction, about 8 g of crushed alloy were activated by five deuterium absorption–desorption cycles. Neutron diffraction patterns were recorded at room temperature on the 3T2 instrument ($\lambda = 1.225 \, \text{Å}^{-1}$) at the Laboratoire Léon Brillouin in Saclay. The sample holder was kept under controlled deuterium pressure during each measurement. All the patterns were refined with the Rietveld method using FULLPROF [5].

3. Results

The XRD of the intermetallic compound shows a single-phase pattern indexed with the $P6/mmm$ space group (CaCu$_5$-type structure). The composition determined by EPMA analysis, La$_{0.56(3)}$Y$_{0.42(3)}$Ni$_{5.02(1)}$, is close to the nominal composition with a slight over-stoichiometry on the Ni side. This slight over-stoichiometry can be explained by the replacement of La(Y) atoms by Ni dumbbells [6].

The PCT curves measured at 318, 298, 268 and 253 K are plotted in Fig. 1. One can notice the capacity reduction and the increase of the equilibrium pressure as a function of increasing temperature. The capacity reaches 6.3 H/f.u. at 253 K under 2 MPa, and only 5.1 H/f.u. at 318 K under 6.9 MPa. For the PCT curves at 298 K, a step is clearly observed above 3.5 H/f.u., followed by a sloppy domain.

Three neutron powder diffraction patterns, shown in Fig. 2, have been measured under controlled pressure to investigate the phase diagram of the La$_{0.55}$Y$_{0.45}$Ni$_5$–D$_2$ system at 298 K. The results of the Rietveld refinement of the neutron diffraction patterns are summarized in Table 1. All the phases are refined by a four-site structural model with the space group $P6/mmm$ [7].

The first pattern, D/f.u. = 1.6, was obtained in the middle of the first plateau. Two phases with CaCu$_5$-type structure are observed (Fig. 2). The first one is a low-deuterated compound corresponding to the α phase, La$_{0.54(1)}$Y$_{0.44(1)}$Ni$_{5.03(1)}$D$_{0.4(2)}$. The second one is an intermediate hydride, γ phase, between the α phase and the β hydride phase. The composition of this hydride phase is La$_{0.54(1)}$Y$_{0.44(1)}$Ni$_{5.03(1)}$D$_{3.3(3)}$.

The second pattern, D/f.u. = 4.1, was measured at a concentration in the sloppy domain. Two phases are observed: the intermediate γ phase, La$_{0.54(1)}$Y$_{0.44(1)}$Ni$_{5.03(1)}$D$_{3.3(3)}$, and a high-deuterated compound corresponding to the β phase, La$_{0.54(1)}$Y$_{0.44(1)}$Ni$_{5.03(1)}$D$_{4.9(3)}$.
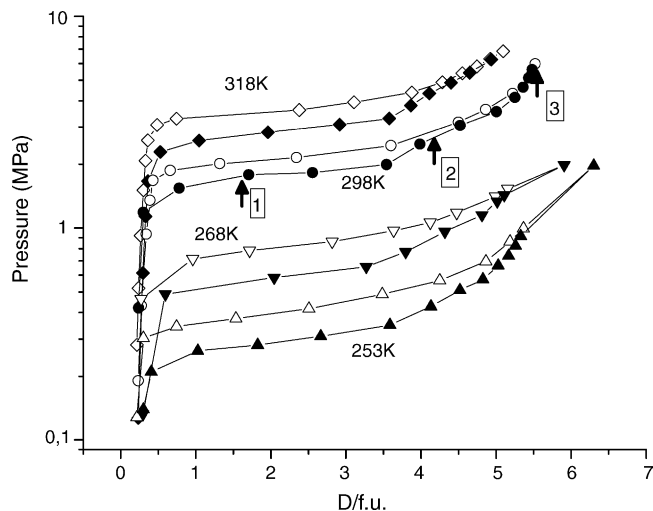

Fig. 1. PCT curves at 318, 298, 268 and 253 K for the La$_{0.55}$Y$_{0.45}$Ni$_5$D$_x$. Absorption and desorption curves are denoted by full and open symbols, respectively. Arrows correspond to the state of charge of the three samples that have been studied by neutron powder diffraction.

For the third measurement, D/f.u. = 5.5, the compound is fully charged with deuterium. Only the saturated β phase hydride phase is observed. Afterwards, this phase will be called β^+.

The evolution of the occupancy rate of the four deuterium sites in each phase is shown in Fig. 3. The occupancy rate of the $6m$ sites rises linearly with the overall concentration of deuterium to reach 31% for 5.5 D/f.u. The $12n$ sites are mainly occupied in the γ phase, but no additional filling is observed during the transition from γ to β phase. In the β branch, the $12n$ sites fill again and reach an occupancy rate of 21%. No filling of the $4h$ sites is observed in the γ phase, but 10% of them are occupied in the β phase. The $12o$ sites are linearly filled between α and β phases, but have a low occupancy rate of about 8%.
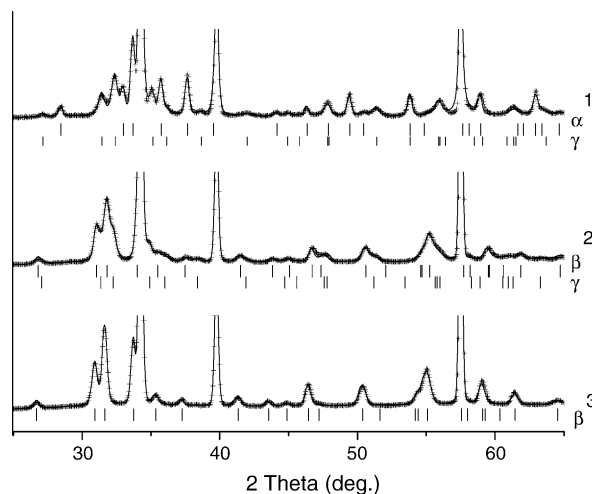

Fig. 2. Neutron powder diffraction patterns (observed (crosses), refined (full line)) of La$_{0.55}$Y$_{0.45}$Ni$_5$D$_x$ measured at the equilibrium pressures shown in Fig. 1.

Table 1
Evolution of the D site occupancy and cell parameters for the observed phases of $La_{0.55}Y_{0.45}Ni_5D_x$

	α	γ	β	β⁺
D $4h$ (1/3, 2x, 0.380)	0.04 (6)	0.00 (9)	0.38 (6)	0.44 (2)
D $6m$ (0.136, 2x, 1/2)	0.00 (8)	0.92 (18)	1.60 (10)	1.88 (6)
D $12n$ (0.485, 0, 0.091)	0.28 (11)	1.88 (22)	1.97 (9)	2.48 (5)
D $12o$ (0.212, 2x, 0.331)	0.00 (14)	0.46 (22)	0.95 (11)	0.71 (5)
a (Å)	4.976	5.225	5.280	5.296
c (Å)	3.987	4.070	4.185	4.216
V (Å³)	85.5	96.7	101.1	102.4
$\Delta V/V$ (%)	1.3	14.6	19.8	21.3
R_{wp}/R_{factor} (%)	11.5/9.89	11.6/15.7	12.8/21.8	7.96/8.50

For the γ phase, average parameters between the γ phase of the first and the second refinements are given (structure $P6/mmm$: (La,Y) 1a, Ni (2c,3g)).
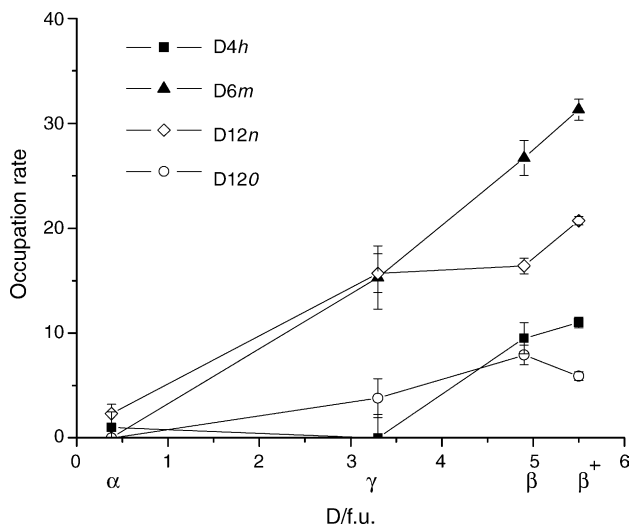

Fig. 3. Evolution of the occupancy rate of the four absorption sites as a function of the phase.

A schematic isotherm of the $La_{0.55}Y_{0.45}Ni_5D_x$ is proposed in Fig. 4, showing the γ phase and indicating the volume expansion for each phase.

4. Discussion

It is shown that an intermediate hydride phase exists between the α and β phases in the $La_{0.55}Y_{0.45}Ni_5$–H_2 system. To our knowledge, it is the first time that a γ hydride phase is observed in a rare-earth-substituted $LaNi_5$ compound. A similar intermediate γ phase appears in the $LaNi_5$–H_2 system after cycling at 353 K [8,9]. At this temperature, the equilibrium pressure of $LaNi_5$–H_2 system is about 1.2 MPa. For the $La_{0.55}Y_{0.45}Ni_5$–H_2 system, the γ phase is observed at 298 K with an equilibrium pressure of about 2 MPa. Thus, the appearance of this intermediate phase could be attributed to the additional constraints induced by hydrogen pressure and volume expansion during hydrogenation.

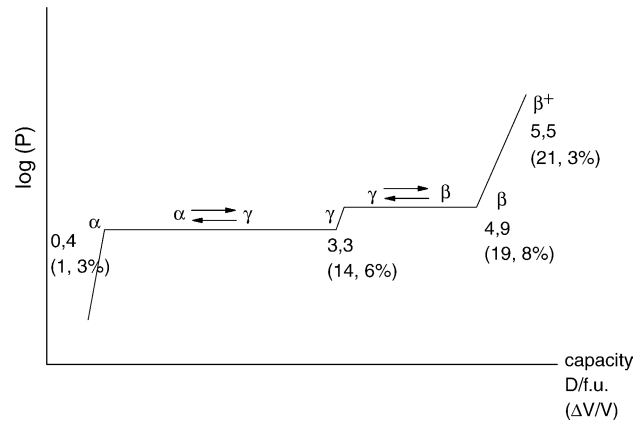The full hydrogenation of the $La_{0.55}Y_{0.45}Ni_5$ compound causes a large volume expansion, +21.3% between the α

Fig. 4. Schematic isotherm of the $La_{0.55}Y_{0.45}Ni_5$ alloy. The intermediate γ phase is observed and the volume expansion is indicated for each phase.

phase and the β phase. The presence of this γ phase with intermediate cell volume probably plays an important role in the strain distribution within the grain. It implies a two-step process in the discrete volume expansion (α→γ, γ→β) allowing the system to reduce the strains and to improve the cycle-life as previously proposed [10].

As reported in previous work on related AB_5 compounds [11,12], when increasing the capacity, a progressive filling of the deuterium sites is observed. The $12n$ and $6m$ sites are preferentially occupied, with 31 and 21% of sites filled, respectively. A partial filling of the $4h$ sites is only observed in the β hydride phase.

The equilibrium pressure of the $La_{0.55}Y_{0.45}Ni_5$ deuteride compound at 253 K is between 0.2 and 0.4 MPa. This pressure is appropriate for a cold start. First kinetic estimation shows that $La_{0.55}Y_{0.45}Ni_5$ absorbs 90% of its capacity in about 120 min at 253 K. Further investigations are in progress concerning the kinetic behaviour. A buffer tank containing this hydride will allow starting the fuel cell, even at low external temperature.

5. Conclusion

$La_{0.55}Y_{0.45}Ni_5H_x$ has an equilibrium hydrogen pressure of 0.2 MPa at 253 K. The presence of an intermediate γ phase deuteride, $La_{0.54(1)}Y_{0.44(1)}Ni_{5.03(1)}D_{3.3(3)}$, allows a reduction of the strains induced by a large volume expansion during absorption–desorption cycles. Consequently, the compound could be a potential candidate to fill a buffer tank in a fuel-cell car for delivering sufficient hydrogen during the cold start.

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