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New ternary intermetallic compounds belonging to the R–Y–Ni (R=La, Ce) system as negative electrodes for Ni–MH batteries

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Abstract

New ternary yttrium-based alloys with general formula $La_{1-x}Ce_xY_2Ni_9$ ($0 \leq x \leq 1$) have been synthesized and the influence of cerium substitution on the structural, thermodynamic and electrochemical properties is discussed. The hydrogen absorption–desorption properties are consistent with the application as negative electrode materials in alkaline medium. The electrochemical study shows promising results for $0 \leq x \leq 0.5$ compositions in terms of hydrogen storage applications.

Keywords: Hydrogen storage applications; Yttrium-based alloys; Ni–MH batteries

1. Introduction

Rare earth intermetallic compounds of AB_n-type (A, rare earth; B, transition metal; $2 \leq n \leq 5$) can store reversibly large quantities of hydrogen through solid–gas reactions to form intermetallic hydrides. This property has prompted their electrochemical application as negative electrode to replace cadmium in alkaline batteries of the type $NiOOH/Ni(OH)_2/KOH/AB_n/AB_nHx$ [1].

Two classes of binary or pseudo-binary alloys are currently being developed: 'AB_2' Laves-type alloys, and 'AB_5' multicomponent alloys. Practically, commercial negative electrodes are made of $MmNi_5$ substituted compounds. Use of mischmetal instead of lanthanum is for economical reasons, since this rare earth mixture is cheaper than lanthanum but it appears that the mischmetal composition, and particularly the cerium content, is also of great importance for cycle life [2]. On the transition metal sublattice, substitution by Mn, Al and Co has been found to offer the best compromise between high hydrogen capacity, good resistance to corrosion and cyclability [3].

In contrast, few works or phase diagrams are known for the ternary compositions. A recent investigation of the R–Mg–Ni system has revealed a new series of ternary alloys of general formula RMg_2Ni_9 (R=rare earth or Ca element) [4–7], which have been shown to correspond to an intergrowth of $MgNi_2$ and RNi_5 layers. However these new compounds are not adapted to the electrochemical application from the thermodynamic point of view.

The knowledge of the hydrogen storage properties of the binary compounds $LaNi_5$ and YNi_2 prompted us to focus our interest on the La–Y–Ni ternary system. The possible replacement of lanthanum by cerium has also been studied. In this work, we report the structural, thermodynamic and electrochemical features of new intermetallic compounds with general formula $La_{1-x}Ce_xY_2Ni_9$ ($x=0$; 0.25; 0.5 and 1).

2. Experimental

All the alloys were prepared by induction melting of the pure La, Ce, Y, and Ni elements in the $(1-x)$:x:2:9 atomic ratio ($x=0$; 0.25; 0.5; 1) followed by annealing at 750°C for 3 weeks to ensure good homogeneity.

The X-ray patterns were recorded with a Bragg–Brentano geometry, using flat plate samples and a Bruker D8 diffractometer, equipped with Cu Kα radiation and a back graphite monochromator. Conventional hydrogen gas PC isotherms were measured with a Sievert's type apparatus using calibrated and thermalized volumes.

Electrochemical measurements were conducted in KOH 7 N at room temperature and atmospheric pressure in a

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Table 1
Compositions of the main phase determined by electron probe microanalysis of expected stoichiometry $La_{1-x}Ce_xY_2Ni_9$

	x_{Ce}			
	0	0.25	0.5	1
La	1.06 (5)	0.81 (5)	0.536 (8)	–
Ce	–	0.250 (5)	0.520 (5)	1.040 (9)
Y	1.94 (5)	1.92 (6)	1.95 (2)	1.93 (5)
Ni	8.99 (2)	8.99 (3)	8.98 (2)	9.02 (4)

conventional three electrodes open air cell already described [8].

The composite anodic electrodes were prepared as described previously [8]. Electrochemical potential composition (EC) isotherms were obtained from open circuit voltage (OCV) measurements after current increments, and partially under intensiodynamic conditions at a very low current density (5 mA/g). The relation between equilibrium electrode potentials, E_{eq}, and hydrogen pressures, P_{eq}, is given by the Nernst equation [9]:

$$E_{eq}\ (\text{V versus Hg/HgO}) = -0.925 - 0.03 \log(P_{eq})$$

3. Results and discussion

3.1. Intermetallic composition

From metallographic examination, it is found that single phase compounds are obtained for $x = 0.25$; 0.5 and 1, whereas the compound with $x = 0$ exhibits small quantities of secondary phase. The composition of the main phase shown in Table 1 proves the stoichiometry '1–2–9' for all the compounds.

3.2. Structural properties

Detailed structural results determined from X-ray diffraction data are presented in another paper [10]. It is shown that $La_{1-x}Ce_xY_2Ni_9$ compounds crystallise in the *R-3m(166)* space group ($Z = 3$) related to the hexagonal $PuNi_3$ type.

A typical XRD pattern corresponding to the $x = 0.5$ composition is reported in Fig. 1. The analysis of the diffraction lines leads to the following cell parameters and volume: $a = 5.0052(1)$ Å; $c = 24.508(2)$ Å; $V = 531.73$ Å^3.

It is found that progressive replacement of lanthanum by cerium leads to a decrease of the *a* parameter (−1.3%), an increase of the *c* parameter (+0.15%) and a subsequent decrease of the unit cell volume (−2.4%) [10]. The Rietveld refinement reveals that La and Y atoms occupy two distinct sites (3*a* and 6*c*, respectively) for the compound with $x = 0$. Hence LaY_2Ni_9 is a ternary compound isostructural with $LaMg_2Ni_9$ [4]. However, as lanthanum is replaced by cerium, the distribution of rare earth and yttrium atoms among the two types of site evolves progressively towards a statistical one. As a matter of fact, the compound with $x = 1$ is correctly described as a pseudo binary compound of $NbBe_3$-type, which can be written as $(Ce_{0.33}Y_{0.66})Ni_3$ [10].

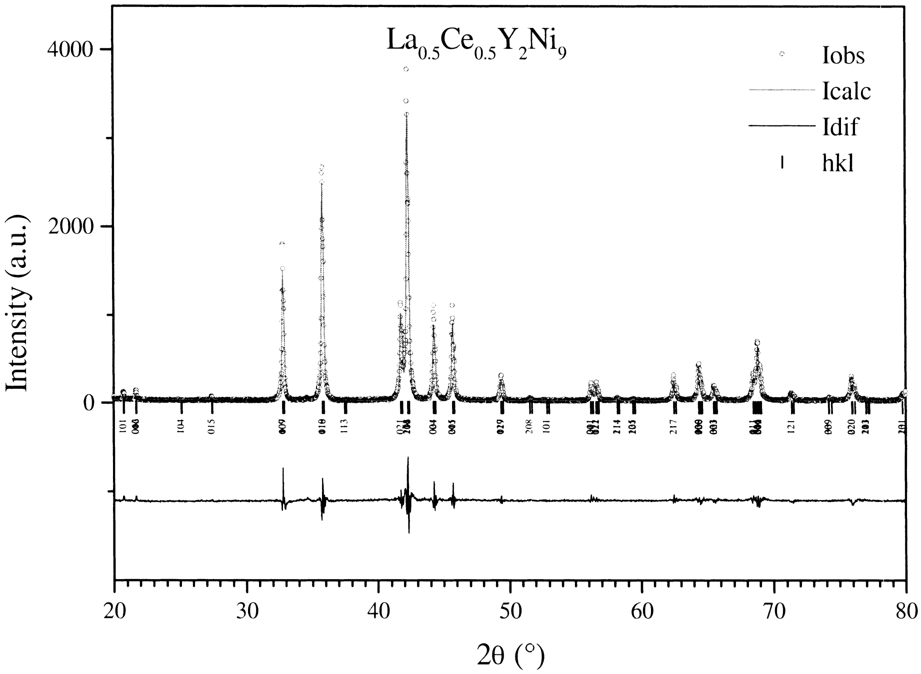

Fig. 1. X-ray diffraction pattern of $La_{0.5}Ce_{0.5}Y_2Ni_9$.

Table 2
Thermodynamic data at 25°C for LaY_2Ni_9 and CeY_2Ni_9 compounds

	Absorption pressure (bars)	Desorption pressure (bars)	Hydrogen capacity at 10 bars (H/mol)
LaY_2Ni_9	0.09	5×10^{-3}	12
CeY_2Ni_9	0.128	–	8

3.3. Thermodynamic properties

The hydrogen equilibrium pressures and capacities extracted from the P–C isotherm curves at 25°C are reported in Table 2 for LaY_2Ni_9 and CeY_2Ni_9. The lanthanum compound absorbs 12 H/mol under 10 bar of hydrogen gas and its plateau pressure is equal to 0.09 bar in absorption and 5×10^{-3} bar in desorption, which implies a large hysteresis.

The cerium compound absorbs 8 H/mol under 10 bar. The absorption pressure is higher than that of the lanthanum compound at 0.128 bar. Reversibility is very poor and only the hydrogen dissolved in the β phase can be desorbed.

The thermodynamic data of the lanthanum compound are very promising towards the electrochemical application, which requires good capacities in the 0.01–1-bar pressure range: the hydrogen capacity of 11 H/mol observed for LaY_2Ni_9 in normal conditions of temperature and pressure is as large as that reported for $LaNi_5$ (~1 H/metallic atom). For comparison, previous studies on isotype ternary compounds reported a capacity reduced to only 0.2 H/mol for $LaMg_2Ni_9$ [7] (at 3.3 bar, 25°C); 0.75 H/M for $CaMg_2Ni_9$ [5] (at 3.3 bar, 0°C) and 1 H/M for $Y_{0.5}Ca_{0.5}Mg_2Ni_9$ [6] (at 33 bar, −10°C).

Table 3
Electrochemical data at 25°C for $La_{1-x}Ce_xY_2Ni_9$ compounds

	Discharge capacity (in mAh/g)	Discharge capacity (in H/mol)	Discharge potential (in mV)
$x=0$	265	8.3	−881
$x=0.25$	230	7.5	−830
$x=0.5$	240	7.5	−830
$x=1$	200	6.25	−811

Current density 20 mA/g except for $x=0.25$ ($I=40$ mA/g).

3.4. Electrochemical study

The hydride electrode properties have been studied through constant current chronopotentiometric measurements. Detailed results are presented in another paper [11].

Fig. 2a reports the evolution of the equilibrium potential of the LaY_2Ni_9 electrode as a function of the hydrogen content in charge and discharge, and for comparison the solid–gas isotherm (Fig. 2b), where the measured equilibrium pressures have been converted to equivalent equilibrium potentials through the Nernst equation [9]. The correlation between the gas phase and the electrochemical isotherms is fairly good. The difference observed beyond 5 H/mol comes from the fact that electrochemical isotherms were obtained from intensiodynamic measurements (*C*/100 rate) in this composition range. The charge capacity of 11 H/mol corresponds to the solid–gas absorption capacity recovered at 1 bar. Conversely, the discharge is not quantitative as it involves a lower capacity of 8 H/mol, which probably comes from the relative stability of the hydride. However, the rechargeable capacity of 260 mAh/g remains still interesting.

The influence of the substitution on the discharge potentials and capacities is reported in Table 3. The

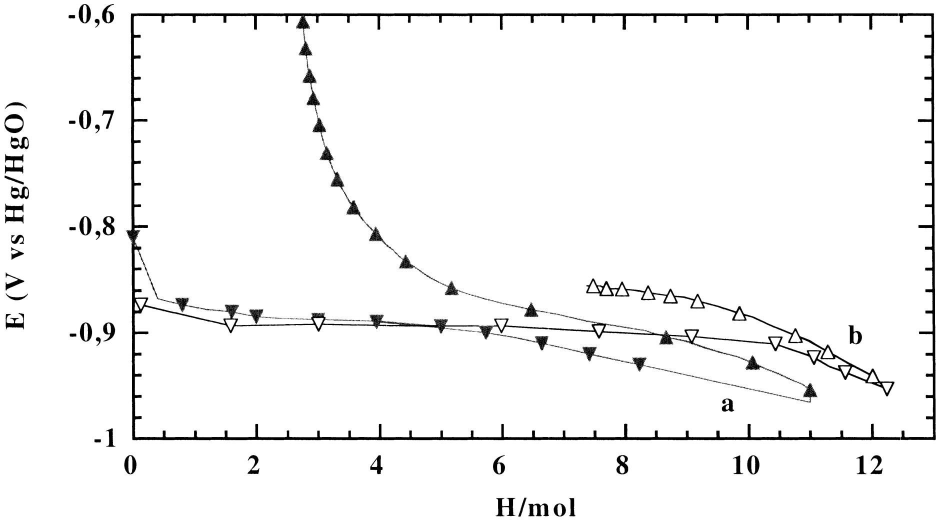

Fig. 2. Electrochemical (a) and solid–gas (b) isotherms at 25°C for LaY_2Ni_9.

LaY_2Ni_9 composition exhibits the highest discharge capacity of 265 mAh/g corresponding to 75% of the solid–gas capacity. Then, the capacity decreases as the Ce/La ratio increases to reach 200 mAh/g for CeY_2Ni_9, which corresponds to a 20% capacity loss between the two limit compositions. Such capacities are the highest among those reported for isotype ternary compounds. For example, an electrochemical discharge capacity of 166 mAh/g, involving only 40% of the solid–gas capacity (9 H/mol), has been reported for $CaMg_2Ni_9$ at a similar current density [5].

Fig. 3 illustrates the influence of the current density (5–150 mA/g range) on the discharge capacity and potential for the compounds with $x=0$ and $x=1$. It turns out that an increase of the current density involves an increase in the discharge potential and a decrease in the discharge capacity, but to a different extent for the two compounds. LaY_2Ni_9 exhibits a good rate capability as the capacity decay is of 5% when the *C* rate changes of one order of magnitude whereas the cerium compound is strongly affected by an increase in the current density (60% loss of capacity when *C* rate increases by a factor of 3).

Finally, the cycling properties at a sustained current density (80 mA/g) is illustrated in Fig. 4 for the different compounds. The La-rich compounds ($x \leq 0.5$) exhibit stabilized capacities between 150 and 230 mAh/g, whereas the CeY_2Ni_9 composition shows a reversible capacity lower than 70 mAh/g. Furthermore, for the $x=1$ composition, the activation period is not followed by a stabilization of capacity but rather by a continuous decrease, which occurs up to a constant value of ~2 H/mol. The use of a very low current density does not allow the improvement of the reversible capacity of the CeY_2Ni_9 alloy, as 30% of the capacity is lost from the second cycle. These results demonstrate the poor rechargeability of this composition. The value of the practical reversible discharge capacity (~2 H/mol) corresponds to the fraction of hydrogen which can be desorbed from the β phase through the solid–gas reaction.

Finally, two comments can be made concerning the cycling behavior of the La-rich compounds: (i) For LaY_2Ni_9 and $La_{0.75}Ce_{0.25}Y_2Ni_9$ compositions, a maximal capacity is reached after activation around the tenth cycle (215 and 190 mAh/g, respectively), then a low decrease is observed (15% capacity loss at the 30th cycle for both compounds). (ii) The maximal capacity reached for $La_{0.5}Ce_{0.5}Y_2Ni_9$ is lower (160 mAh/g) but remains stable at least over the first 30 cycles.

4. Conclusion

As a conclusion, this study reports the main structural, thermodynamic and electrochemical features of a new series of ternary alloys belonging to the $La_{1-x}Ce_xY_2Ni_9$ system. It has been shown that these properties were consistent with an application as negative electrode in alkaline medium, particularly for the $x \leq 0.5$ compositions. Typically, hydrogen capacities ranging from 7 to 11 H/mol are measured at ambient temperature and pressure, which corresponds to a practical specific capacity of 260

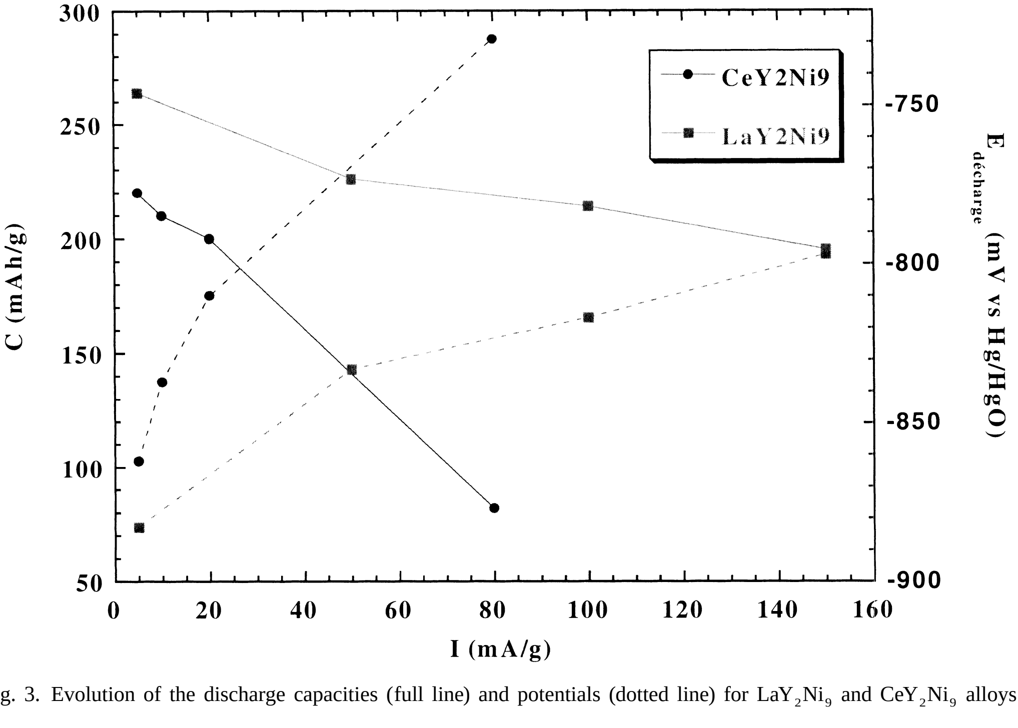

Fig. 3. Evolution of the discharge capacities (full line) and potentials (dotted line) for LaY_2Ni_9 and CeY_2Ni_9 alloys.

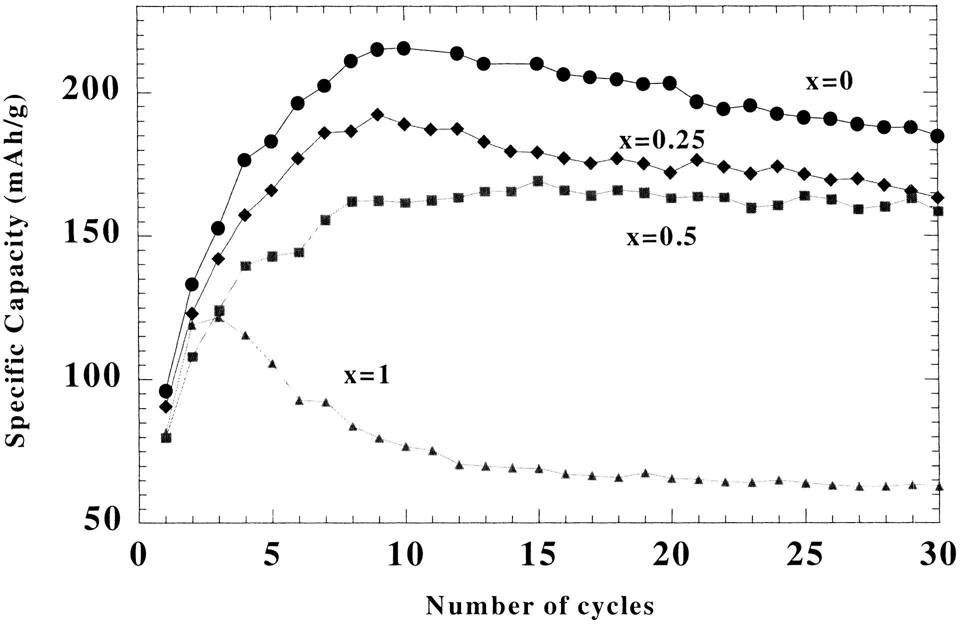

Fig. 4. Evolution of the specific capacity with the number of cycles for $La_{1-x}Ce_xY_2Ni_9$ alloys (*C* rate, 80 mA/g).

mAh/g for the best composition, the highest reported as yet for isotype ternary compounds. First electrochemical investigations have outlined the good reversibility and cycling behavior of the La-rich compositions. The peculiar behavior of the CeY_2Ni_9 compound is probably related to the pseudo-binary character of this alloy, which entails both a loss of capacity and reversibility. However, structural investigations on the hydride phases are in progress to ascertain these assumptions.

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