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# Electrochemical study of the reversible hydrogen storage in CeTi<sub>2</sub>Cr<sub>4</sub>Ni<sub>5</sub>-based metal hydride alloys

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## ABSTRACT

A novel PuNi<sub>3</sub>-type intermetallic compound CeTi<sub>2</sub>Ni<sub>5</sub>Cr<sub>4</sub> is elaborated by mechanical alloying and investigated as a negative electrode material for nickel-metal hydride (Ni-MH) batteries. The synthesis reaction is performed from pure AB<sub>5</sub>-type CeNi<sub>5</sub> and AB<sub>2</sub>-type TiCr<sub>2</sub> intermetallic precursors. The crystallographic parameters of prepared compounds are calculated by the Rietveld refinement of X-ray diffraction (XRD) patterns for powders ball-milled between 2 and 20 h. The highest content of CeTi<sub>2</sub>Ni<sub>5</sub>Cr<sub>4</sub> phase is 51 wt.% in powder elaborated after 8 h of milling time. The reversible hydrogenation of CeTi<sub>2</sub>Ni<sub>5</sub>Cr<sub>4</sub>-based electrodes is characterized electrochemically in the presence of alkaline electrolyte at room temperature. The maximum discharge capacity is 205 mAh g<sup>-1</sup> and the average capacity retention is 84% upon 30 charge/discharge cycles, demonstrating the suitable electrochemical behavior of CeTi<sub>2</sub>Ni<sub>5</sub>Cr<sub>4</sub>. Competitive hydrogen diffusion rates are also obtained in the range of (1.9–10.5) 10<sup>-10</sup> cm<sup>2</sup> s<sup>-1</sup>.

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## Introduction

Ni-MH batteries have progressively replaced the Nickel Cadmium accumulators in low-weight electronic devices because of their longer life cycling, higher energy capacity and lower environmental toxicity [1–3]. Among a series of intermetallic compounds, the AB<sub>3</sub>-type alloys have shown promising performances as negative electrodes for Ni-MH batteries. They reversibly absorb a large amount of hydrogen and may lead to a maximum discharge capacity of 400 mAh g<sup>-1</sup> [4–8]. Comparatively to commonly used AB<sub>5</sub>-type alloys, the AB<sub>3</sub>-type ones are distinguished by their longer electrochemical stability in highly alkaline media and faster charge/discharge kinetics [9–11]. The AB<sub>3</sub>-type compounds belong to a PuNi<sub>3</sub>-

type structure ones and their crystal structure may be described as a stacking of CaCu<sub>5</sub> and MgZn<sub>2</sub> structures [9–11]. The AB<sub>3</sub>-type alloys may be synthesized by: (i) reacting a specific amount of AB<sub>2</sub> with AB<sub>5</sub> intermetallic compounds, or (ii) reacting the chemical elements in the corresponding stoichiometric ratio [9]. In the first case (i), the AB<sub>3</sub> type structure is prepared following this reaction schema:



In the present work, the formation of the AB<sub>3</sub> phase is based on Eq. (1) and will be performed by mechanical alloying. This technique is commonly used to elaborate fine micro-structured powders and, in some extents, alloys from non-miscible elements [11]. Among the AB<sub>5</sub>-type hydride alloys studied in the literature, CeNi<sub>5</sub> was largely applied for devices

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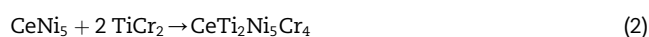
operating at high pressures and showed a hydrogen absorption capacity of 6 H/u.f, cyclic durability and a high resistance against impurities [12–17]. However, the hydrogen absorption kinetic in CeNi<sub>5</sub> is very low at ambient conditions since the pressure of its hydride is significantly elevated (60 MPa) [14,15]. On the other hand, among AB<sub>2</sub>-type hydride alloys, TiCr<sub>2</sub> is a promising candidate since it reversibly absorbs an amount of hydrogen of 2.4 wt.% H [18–22]. Bououdina et al. reported that TiCr<sub>2</sub> crystallizes in the hexagonal C<sub>14</sub> type at low temperatures, from 1123 K to 1423 K, and C<sub>15</sub> at high temperature of 1550 K [23]. The hydrogenation of TiCr<sub>2</sub> leads to two non-stoichiometric hydride phases TiCr<sub>1.9</sub>–H<sub>2.5</sub> and TiCr<sub>1.9</sub>–H<sub>3.5</sub> with plateau pressures of 0.2 and 30 atm at –78 °C, respectively [22].

The scope of the present work is the elaboration of a novel AB<sub>3</sub>-type alloy CeTi<sub>2</sub>Cr<sub>4</sub>Ni<sub>5</sub> by mechanical alloying from CeNi<sub>5</sub> and TiCr<sub>2</sub>. These precursors present distinct hydrogenation plateau pressures and, for this reason, we aim to prepare a new material with intermediate hydrogenation behavior. The reversible absorption of hydrogen will be investigated electrochemically at room temperature. The crystal structure of CeTi<sub>2</sub>Cr<sub>4</sub>Ni<sub>5</sub> will be characterized by X-ray diffraction. The chronopotentiometry, cyclic voltammetry and chronoamperometry techniques will be carried out in order to investigate the electrochemical hydrogenation properties.

## Experimental section

### Elaboration of the hydride alloys

CeNi<sub>5</sub> and TiCr<sub>2</sub> precursors were prepared by ultra high frequency (UHF) induction melting from pure elements (Ce 99.9%, Ni 99.9%, Ti 99.99% and Cr 99.99%) placed into a water cooled copper crucible under argon atmosphere. The melting step was repeated five times and alloys were inverted between each melting to ensure a good homogeneity. The chemical composition of the as-prepared precursors was determined by energy dispersive X-ray (EDX) technique with an environmental scanning electron microscope (ESEM) type FEI Quanta 200. The crystallographic characterization of elaborated powders was carried out with a (θ–2θ) Panalytical XPERT PRO MPD diffractometer using Cu Kα radiation (λ = 0.15406 nm). The XRD patterns were refined by the Fullproof program based on the Rietveld method [24–26]. CeTi<sub>2</sub>Cr<sub>4</sub>Ni<sub>5</sub> was synthesized by mechanical alloying (MA) from CeNi<sub>5</sub> and TiCr<sub>2</sub> following this reaction:



The mixture of CeNi<sub>5</sub> (0.588 g) and TiCr<sub>2</sub> (0.412 g) was sealed, inside a glove box, into a stainless steel vial of 50 cm<sup>3</sup> in volume. The alloying was carried out by 5 stainless steel balls with 12 mm in diameter and 6.98 g in mass. The mechanical alloying (MA) process was realized at room temperature using a Retch PM400 planetary ball mill operating at disc and vial rotation speeds equal to 320 and 640 rpm, respectively. These conditions correspond to an injected shock power of 6.175 W g<sup>-1</sup>. The ball milling durations were varied from 2 to 20 h. The powder morphology of the different samples was

characterized with environmental scanning electron microscopy (ESEM-FEI Quanta 200).

### Preparation of the electrode

The alloy ingots were mechanically grounded and sieved to less than 63 μm in a glove box under an argon atmosphere. The “Latex” technology has been used for the preparation of the electrode [27]: 90% of the active material was mixed with 5% of polytetrafluoroethylen (PTFE) and 5% of carbon black. Two square pieces of 0.5 cm<sup>2</sup> of this Latex are cutted and pressed on each side of a nickel grid [28]. The electrochemical measurements were investigated with a VMP Biologic potentiostat/galvanostat in a conventional three-electrodes cell. The Hg/HgO electrode immersed in 1 M KOH solution was employed as a reference electrode and the counter electrode was formed by Ni oxyhydroxide (Ni(OH)<sub>2</sub>). The electrolyte solution consisted in a 1 M KOH aqueous solution, which was bubbled by argon gas during each measurement.

### Electrochemical measurements

The discharge capacity of the electrode was determined galvanostatically by charging at C/3 until reaching a potential of –1.1 V, and discharging at D/6 until reaching a potential of –0.6 V. The cyclic voltammetry was performed after the activation of the negative electrode during 30 charge/discharge cycles with scan rates varying between 10 and 50 μV s<sup>-1</sup>. The chronoamperometry was carried out after 30 charge/discharge cycles and consists, in a first step, of a fully charging of the electrode and, subsequently, a discharging at a constant potential of –0.6 V.

## Results and discussion

### SEM and EDX characterizations

Fig. 1 shows the SEM photomicrographs of TiCr<sub>2</sub> and CeNi<sub>5</sub> performed in secondaries electron mode, together with their EDX micro-analyses performed in two regions for each sample. For as-prepared precursors, both surface morphologies are flat, composed by superposed platelets and typical of alloys elaborated by UHF melting technique (Fig. 1a,b). The prevailing grey regions correspond to the CeNi<sub>5</sub> and TiCr<sub>2</sub> phases, while the few white spots are assigned to other phases with higher electronic densities. The EDX results confirm that compositions of TiCr<sub>2</sub> and CeNi<sub>5</sub> are x = B/A = 2/1 and 5/1, respectively, in agreement with the expected stoichiometries.

### Structural characterizations

Fig. 2 shows the XRD patterns of TiCr<sub>2</sub>, CeNi<sub>5</sub> and the mechanically alloyed powders as a function of the alloying duration. The XRD patterns of the TiCr<sub>2</sub> and CeNi<sub>5</sub> precursors show well-defined peaks corresponding to a long-range crystalline order. The XRD pattern of TiCr<sub>2</sub> is indexed in the hexagonal structure with P6<sub>3</sub>/mmc space group with unit cell parameters “a” and “c” equal to 4.9155(6) Å and 7.8910(1) Å, respectively. The XRD pattern of CeNi<sub>5</sub> is indexed in the

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