



# Electrochemical hydrogen storage properties of Ti<sub>1.4</sub>V<sub>0.6</sub>Ni alloy comprising quasicrystal coating with Cu



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## ABSTRACT

The Ti<sub>1.4</sub>V<sub>0.6</sub>Ni alloy ribbons are prepared by arc-melting and subsequently melt spinning technique. Different percentage compositions of *x* Cu (*x* = 1, 3, 5 and 10 wt%) are covered on the surface of the alloy particles utilizing electro-less plating method. The phase structures of the Ti<sub>1.4</sub>V<sub>0.6</sub>Ni alloy contain icosahedral quasicrystal phase (I-phase), fcc-Ti<sub>2</sub>Ni-type phase and bcc-V-based solid solution phase. With increasing *x* value, the maximum electrochemical hydrogen storage capacity reaches 260 mAh g<sup>-1</sup> when *x* = 10. After 100 cycles, 23% capacity retention rate is promoted by covering 10 wt% Cu on the alloy than the bare Ti<sub>1.4</sub>V<sub>0.6</sub>Ni. Cu offers well electrical conductivity and corrosion resistance, especially it also inhibits the dissolution of V from the alloys.

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## 1. Introduction

The discovery of quasicrystals with five-fold symmetry surprised the world of solid-state physics in 1982 and led to a paradigm shift in our understanding of the solid structure [1]. Since then, plenty of new quasicrystals have been developed and their functional properties have been well researched [2]. As one of the largest quasicrystal systems, Ti-based quasicrystals exhibit excellent hydrogen storage properties for the novel icosahedral structure and fascinate researchers to apply in the field of energy. Kelton and coworkers made a significant break-through on researching Ti<sub>41.5</sub>Zr<sub>41.5</sub>Ni<sub>17</sub> quasicrystal, a hydrogen concentration up to H/M = 3 at modest pressures (6.9–13.8 bar) as well as H/M = 1.9 by electrolytic loading were achieved [3–5]. However, a terrible electro-catalytic activity of Ti–Zr–Ni alloys in alkaline liquor lead to a rapid declined cycle life, such as ZrV<sub>2</sub> which has been extensively studied possessing a hydrogen uptake H/M = 3.8 but a poor electrochemical performance [6]. The researches on utilizing Ti<sub>45</sub>Zr<sub>35</sub>Ni<sub>17</sub>Cu<sub>3</sub> quasicrystal as the negative electrode in Ni–MH battery was reported by Liu et al. [7,8]. In their reports, the major factor

causing capacity declined was the pulverization of the alloys during charge–discharge cycles. Various amounts of nickel addition have been already attempted to promote the catalytic performance of the alloys, but it transformed the quasicrystal into other phases because that the Ti–Zr–Ni quasicrystals only formed within a narrow range of the component elements [9]. Recently, another promising quasicrystalline Ti–V–Ni alloys possessing high electrochemical activity have been researched [10–14].

Ti–V–Ni system alloys containing icosahedral quasicrystal were first discovered by Zhang et al. in 1985 [10], the relationships among crystal, non-crystal and quasicrystal were expounded in detail. For a potential hydrogen storage alloys possessing the same kinds of constituent elements with V-based solid solution alloys such as TiV<sub>3</sub>Ni<sub>0.56</sub>, the electrochemical properties of Ti<sub>1.4</sub>V<sub>0.6</sub>Ni quasicrystal were reported by Hu et al. [11,12], and a maximum discharge capacity reached 271.3 mAh g<sup>-1</sup> was obtained. The phase transition of (Ti<sub>1-x</sub>V<sub>x</sub>)<sub>2</sub>Ni (*x* = 0.0–0.3) had been discussed and with the amount of V increasing the discharge capacity of the alloys were increased. The effect of I-phase which improves the discharge capacity has been proved by comparing the alloy without I-phase (prepared by lower melt spinning speed at 20 m s<sup>-1</sup>) with the alloy contains I-phase (prepared by higher melt spinning speed at 34 m s<sup>-1</sup>) [15]. For further development, Liu et al. reported an excellent discharge capacity when mixed Ti<sub>1.4</sub>V<sub>0.6</sub>Ni with 40 wt% ZrV<sub>2</sub> [13]. Lin et al. prepared the Ti–V–Ni–Mg quasicrystal

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composite materials and presented that the improvement in the hydrogen storage characteristics may be ascribed to better hydrogen diffusion and anti-corrosion ability [14]. Although the electrochemical capacity of  $\text{Ti}_{1.4}\text{V}_{0.6}\text{Ni}$  ( $270 \text{ mAh g}^{-1}$ ) which possesses a lower cost for reducing the usage of expensive vanadium is closed to  $\text{TiV}_3\text{Ni}_{0.56}$  ( $320 \text{ mAh g}^{-1}$ ), the issue which needs to be addressed urgently is the fading rate of discharge capacity of the alloys. The reasons causing the capacity fade of Ti–V-based alloys were both the pulverization of the alloy particles and the dissolution of the main hydrogen absorbing elements (V and Ti) into the KOH solution [16]. It is well-known that V is an amphoteric substance which can dissolve in alkaline electrolyte, and increasing of the solution temperature would promote the dissolution [17]. However, the dissolution mechanism of V in  $\text{Ti}_{1.4}\text{V}_{0.6}\text{Ni}$  alloy should not be hastily speculated to be the same with the mode of V-based solid solution alloys and the two steps of V dissolution in KOH solution are first revealed in our work.

Usually, the corrosion-resistant properties of V can be strengthened by forming alloys with other elements which are stable under the alkaline condition [18], while the structure of quasicrystal is too impressionable to add new element or change the elementary composition. In response to solve the mentioned issues, we cover the  $\text{Ti}_{1.4}\text{V}_{0.6}\text{Ni}$  alloy with Cu utilizing an electro-less plating method [19]. Electro-less plating with metal element is a common method to prevent surface corrosion or act as catalyst. Cu is much more stable in alkaline solution and possessing a proper hydrogen evolution overpotential, it is also an optional element in industry for a lower cost and nontoxic. As early as 1987, Iwakura et al. had microencapsulated  $\text{LaNi}_{4.7}\text{Al}_{0.3}$  with porous thin film of Cu which improved the performances of the alloy electrode, then subsequently a cycle life of 742 times of the alloys coating Cu was tested by Lim et al. [20]. Feng et al. got a complete coverage of the alloy powders with 9 wt% Cu and significant improvements in exchange current density [21]. For getting a suitable coating content of Cu, which has a stable capacity and also maintains a higher content of active substances, different amounts (1, 3, 5 and 10 wt%) of Cu coating are carried out in our present work.

In this work, we cover  $\text{Ti}_{1.4}\text{V}_{0.6}\text{Ni}$  alloy powders with Cu element which is used as the negative electrode materials of a simulated Ni–MH secondary cell utilizing an electro-less plating method and the discharge stability performance of the alloy is researched systematically.

## 2. Experimental

### 2.1. Synthesis

The elements of Ti, V and Ni (>99.9 wt%) are used as starting materials, and  $\text{Ti}_{1.4}\text{V}_{0.6}\text{Ni}$  alloy ingots are prepared by arc melting under argon atmosphere. The alloy ribbons are produced by melting the pieces and spinning onto a Cu wheel rotating at  $34 \text{ m s}^{-1}$ .

$\text{Ti}_{1.4}\text{V}_{0.6}\text{Ni}$  powders are prepared by mechanical pulverization into a particle size less than 200 meshes. 5 g alloy powders are immersed in 15 mL deionized water, and then 200  $\mu\text{L}$  40 wt% HF is added in water with intensively stirring for 1 min. The treated powders are washed with deionized water by centrifuging for three times and dried in a vacuum oven for 2 h at  $60^\circ\text{C}$ . These prepared alloy precursors are immersed in 15 mL deionized water, different volumes of 1.25–12.5 mL  $\text{CuSO}_4$  solution with  $\text{Cu}^{2+}$  of  $4 \text{ g L}^{-1}$  are mixed in the solution under stirring for 5 min, respectively. The mass ratio of Cu in  $\text{Ti}_{1.4}\text{V}_{0.6}\text{Ni}$  are 1%, 3%, 5% and 10%, then the products are washed with deionized water and subsequently dried under vacuum for 2 h at  $60^\circ\text{C}$ .

### 2.2. Characterization

Surface morphology of modified  $\text{Ti}_{1.4}\text{V}_{0.6}\text{Ni}$  is examined by using a scanning electron microscope (SEM). Crystal structures of the modified powders are identified by X-ray diffraction (XRD) with a Cu K $\alpha$ . The dissolved elements in alkaline electrolyte are determined by inductively coupled plasma spectrometry (ICP). Thin foils for transmission electron microscopy (TEM) and high-resolution electron microscopy (HRTEM) are prepared from these ribbons by ion-beam milling at  $-168^\circ\text{C}$  which is maintained by a liquid nitrogen cooling system. Selected-area electron diffraction (SAED) patterns and local compositional information are obtained to study the phase microstructures.

### 2.3. Electrochemical measurement

After mixing 0.2 g alloy particles with carbonyl nickel powder in a weight ratio of 1:5, the mixture is pressed under 20 MPa pressure into a small pellet of 10 mm diameter and 1.5 mm consolidated thick.

A conventional three-electrode system immersing in 6 M KOH solution include a Hg/HgO electrode as the reference electrode, a commercial sintered  $\text{Ni}(\text{OH})_2$  electrode as the counter, and the alloy electrode as the work electrode. The working electrode are fully charged at a current density of  $60 \text{ mA g}^{-1}$  for 6 h, and then discharged at  $60 \text{ mA g}^{-1}$  to 1.0 V. Electrochemical impedance spectroscopy (EIS) analysis is taken at a 50% depth of discharge (DOD), which is measured with an Auto lab PGSTAT 302.

A simulated cell is constructed with a wafer negative and wrapped in a non-woven Nylon separator, which are clamped together using two  $\text{Ni}(\text{OH})_2$  anodes of a much larger capacity than the negative, then the sandwich simulated cell is immersed in a polyethylene container with 50 mL 6 M KOH solution. The cells are fully charged at  $60 \text{ mA g}^{-1}$  for 6 h, then be discharged to 1.0 V at  $60 \text{ mA g}^{-1}$  after resting for 5 min for cycling test, and discharged at

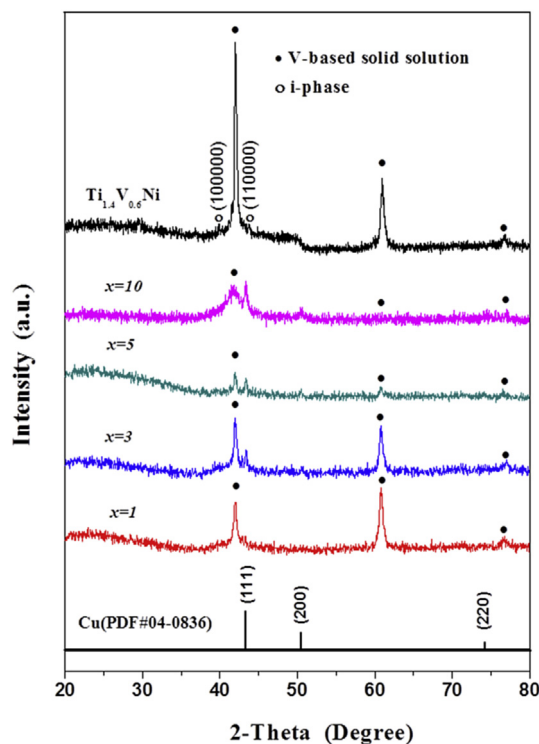


Fig. 1. XRD patterns of the  $\text{Ti}_{1.4}\text{V}_{0.6}\text{Ni} + x\text{Cu}$  alloys.

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