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# Electrochemical hydrogen storage in $(Ti_{1-x}V_x)_2Ni$ ($x = 0.05–0.3$) alloys comprising icosahedral quasicrystalline phase

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ABSTRACT

For $(Ti_{1-x}V_x)_2Ni$ ($x = 0.05$, 0.1, 0.15, 0.2 and 0.3) ribbons, synthesized by arc-melting and subsequent melt-spinning techniques, an icosahedral quasicrystalline phase was present, either in the amorphous matrix or together with the stable $Ti_2Ni$-type phase. With increasing $x$ values, the maximum discharge capacity of the alloy electrodes increased until reached 271.3 mAh/g when $x = 0.3$. The cycling capacity retention rates for these electrodes were approximately 80% after a preliminary test of 30 consecutive cycles of charging and discharging. $Ti_{1.7}V_{0.3}Ni$ alloy electrode displayed the best high-rate discharge ability of 82.7% at the discharge current density of 240 mA/g.

## 1. Introduction

An efficient and safe hydrogen storage medium is a vital issue in realizing the hydrogen economy [1]. Titanium (Ti)-based icosahedral phase (i-phase) alloys exhibit much higher density of favorable interstitial sites for hydrogen absorption compared with normal crystals and large chemical affinities between the constituent chemical elements and hydrogen. Furthermore, they possess low cost. Consequently, in recent years, much attention has been attracted to develop Ti-based i-phase alloys as promising materials that are capable of reversibly storing relatively large amounts of hydrogen, either through absorbing gaseous hydrogen at certain pressure and temperature or by an electrochemical process to form a metal hydride [2,3]. Majzoub et al. achieved hydrogen concentration up to $H/M = 1.9$ in the $Ti_{45}Zr_{38}Ni_{17}$ i-phase by electrolytic loading [4]. Kelton and coworkers have revealed a relatively flat plateau for hydrogenated $Ti_{41.5}Zr_{41.5}Ni_{17}$ quasicrystals at modest pressures (6.9–13.8 bar) that extends to hydrogen concentrations of $H/M = 3$, exceeding 4 wt.%, making a significant breakthrough in overcoming the obstacle of low hydrogen equilibrium vapor pressures for Ti–Zr–Ni quasicrystals [5,6]. Liu et al. have synthesized icosahedral quasicrystalline $Ti_{45}Zr_{35}Ni_{17}Cu_3$ alloy and focused their investigation on the kinetic and electrochemical properties [7].

Surprisingly, hydrogen storage in other Ti-based i-phase materials, which frequently occur in rapidly quenched Ti-TM (TM = transition-metal) alloys, such as Ti–V–Ni [8], Ti–Mn [9], Ti–Cr–Si [10], etc., have scarcely received attention. This is probably because the atomic arrangement is less well ordered with respect to that of an ideal quasicrystal as evidenced by the appearance of arcs of diffuse scattering in the transmission electron microscope (TEM) diffraction patterns [9]. Another possible reason is that these i-phases were realized to be metastable phases with respect to the corresponding crystalline approximant [11]. Though they are less well investigated, early studies by Viano et al. have demonstrated that melt-spun icosahedral Ti–Mn can absorb hydrogen from gas phase [12]. That Ti–Cr–Si–O quasicrystal can absorb only small quantities of hydrogen is presumably due to blocking by the interstitial oxygen that is essential for the quasicrystal formation [10,13]. Up to now there has been rare research on the electrochemical characteristics for this class of Ti-based quasicrystals as negative electrode materials of Ni-metal hydride battery. Thus that we selected Ti–V–Ni system for study is meaningful.

## 2. Experimental

Alloy ingots of composition $(Ti_{1-x}V_x)_2Ni$ ($x = 0$, 0.05, 0.1, 0.15, 0.2 and 0.3) were prepared by arc melting in a water cooled copper hearth under a high purity argon atmosphere. These ingots were subsequently crushed, and the pieces were melt-spun onto a copper wheel rotating at 34 m/s to produce rib-

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bons of this material. The average cross-section of the ribbons was 2–3 mm by 30–40 $\mu$m.

Negative electrodes were constructed through mixing as-prepared alloy powders (250–400 mesh) with carbonyl nickel powders in a weight ratio of 1:5. The powder mixture was pressed under 15 MPa pressure into a small pellet of 10 mm in diameter and 1.5 mm consolidated thick. The electrochemical characteristics of the electrodes were measured by using a sintered $Ni(OH)_2/NiOOH$ counter electrode and a Hg/HgO reference electrode in 6 M KOH solution ranging from 303 K to 343 K. Except for specific indication, the electrodes were charged at a current density of 60 mA/g for 6 h and then discharged at a current density of 30 mA/g to −0.6 V (vs. Hg/HgO) after resting for 5 min. The high-rate discharge ability HRD (%), defined as $C_n/C_{30}$, where $C_n$ and $C_{30}$ are the maximum discharge capacities at discharge current densities of $n = 60$, 120, 180, 240 and 30 mA/g, respectively, is measured. On the basis of equation $CR(\%) = (1 - 2C_2/(C_1 + C_3))$, when $C_1$, $C_2$ and $C_3$, that is the maximum discharge capacities after activation, after the open-circuit condition for 24 h and of the charge/discharge cycle immediately after the measurement of $C_2$, respectively, are measured, then charge retention CR (%) is obtained, which enables us to quantitatively evaluate the self-discharge characteristic of a battery.

The phase of the as-obtained ribbons was determined by XRD. The electrochemical impedance spectroscopy (EIS) analysis was taken at the 50% depth of discharge (DOD) using a Solartron 1287 Potentiostat/Galvanostat and a Solartron 1255B frequency response analyzer with Z-PLOT software for WINDOWS. In this work potentiostatic discharge technique was selected to estimate the hydrogen diffusion coefficient through a given electrode. After being fully charged followed by 30 min open-circuit lay-aside, the test electrodes were discharged with +500 mV potential-step for 3600 s on the EG&G PARC Model 273 Potentiostatic/Galvanostat.

## 3. Results and discussion

### 3.1. Phase structure

Fig. 1 shows XRD patterns of as-synthesized $(Ti_{1-x}V_x)_2Ni$ ($x = 0$, 0.05, 0.1, 0.15, 0.2 and 0.3) alloys. From Fig. 1(A), an amorphous phase was formed without V element addition. In spectrums (B) and (C), all the diffraction peaks could be indexed to the $Ti_2Ni$-type face centered cubic (fcc) phase (Fd3m), which was first proposed as the appropriate crystal approximant for some Ti-based i-phases, while the electron diffraction pattern (EDP) along fivefold direction for the $Ti_{1.8}V_{0.2}Ni$ ribbons demonstrated the presence of the i-phase. This inconsistence of analysis might arise not only from too little amount of i-phase that could not be detected by XRD, but also from the dangers of using only conventional X-ray powder diffraction to characterize these alloy ribbons that have already been put forward [14]. Previous calculations have shown that powder patterns from high-order approximants which formed with local icosahedral symmetry closely resemble those from the true i-phase [15]. Furthermore, the conclusion that under the same rapid solidification condition compared with $Ti_2Ni$ alloy, V element addition accelerated the crystallization of $Ti_2Ni$ fcc phase could be drawn. It could be observed that i-phase coexisted with $Ti_2Ni$-type and amorphous phase appeared in both Fig. 1(D) and (E). The peaks indexed to i-phase used the scheme first proposed by Bancel et al. [16]. Here the icosahedral glass model was recommended as very promising to describe the structure of metastable quasicrystals, since it could incorporate the icosahedral subunits of the crystalline approximant and could also explain the broad diffraction peaks observed experimentally [11]. In comparison, the XRD pattern of $Ti_{1.4}V_{0.6}Ni$ (Fig. 1(E)) coincided well with that of Fig. 1(D) and (E), except for peaks that can be indexed as NiTi with a simple cubic structure.

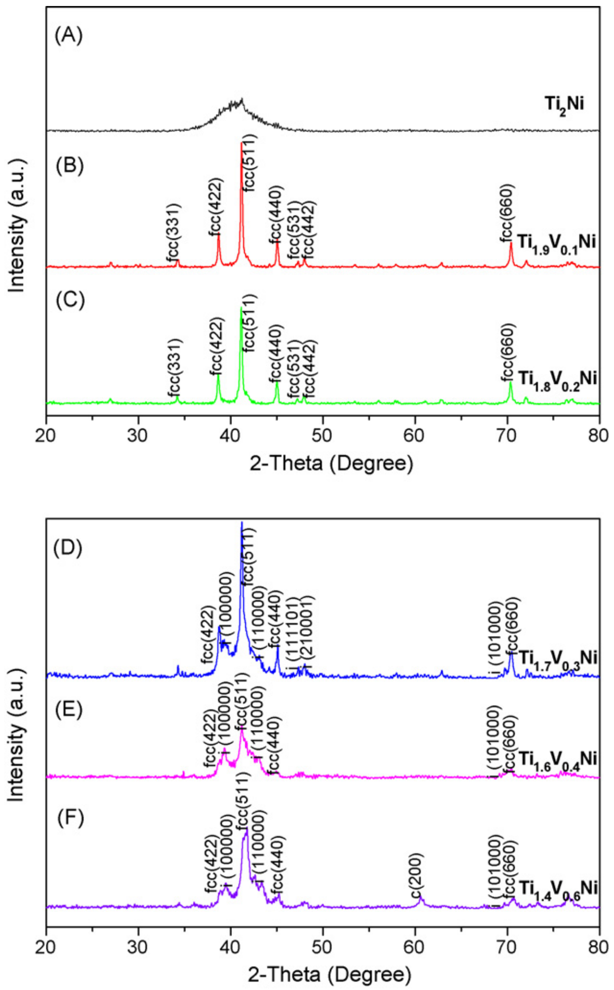

**Fig. 1.** X-ray diffraction patterns of the as-synthesized $(Ti_{1-x}V_x)_2Ni$ ($x = 0.0$–0.3) ribbons: fcc, $Ti_2Ni$-type fcc phase; i, i-phase; c, NiTi simple cubic phase.

### 3.2. Discharge capacity and cycling stability

Discharge capacities of five as-prepared $(Ti_{1-x}V_x)_2Ni$ ($x = 0.05$, 0.1, 0.15, 0.2 and 0.3) samples electrodes were summarized in Table 1. It could be seen that the maximum discharge capacity of the alloy electrodes increased from 233.1 mAh/g to 271.3 mAh/g with increasing $x$ values at a discharge current density of 30 mA/g. The enhanced discharge capability of the samples probably contributed to the increased proportion of V substituted for Ti in $Ti_2Ni$-type fcc lattice and quasilattice structure. Although V displays a high affinity for hydride formation, V hydrides may also be decomposed very easily. It is reported that the energy barrier for H desorption from a free V surface is only 0.04 eV [17]. Subsequently, the atomic hydrogen transferred to the interstitial location near Ti atoms, forming hydride around the V site. V was regarded as an “atomic hydrogen pump”, which facilitated atomic hydrogen transportation [18]. The hydrogen atoms combined with V first dissociated and released, which forced the atomic hydrogen transfer to V.

The cycle life performance of these electrodes is shown in Fig. 2. All the alloy electrodes could be activated at two charging/discharging cycles, which indicated their excellent activation property. The capacity decay was relatively serious for the initial two cycles after activation due to the corrosion of V in the electrolyte. From the fifth cycle, the slower deterioration of cycle stability could be explained by the existence of Ti, where a quite porous Ti oxide film restrained the fast corrosion of V in the elec-