



# Effect of LiH on electrochemical hydrogen storage properties of $Ti_{55}V_{10}Ni_{35}$ quasicrystal



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## ABSTRACT

The electrochemical hydrogen storage properties and mechanisms of the  $Ti_{55}V_{10}Ni_{35}$  quasicrystal +  $xLiH$  ( $x = 3, 6$  and  $9$  wt.%) system are investigated and discussed in this paper. A composite material in the  $Ti_{55}V_{10}Ni_{35}$  quasicrystal and system has been synthesized moderately by means of mechanical milling under an argon atmosphere, which can avoid reaction of releasing of hydrogen during the process of milling. The results indicate that the addition of LiH significantly improves the electrochemical characteristics of composite material. The maximum discharge capacity increases from  $220.1$  mAh/g to  $292.3$  mAh/g on  $Ti_{55}V_{10}Ni_{35} + 6$  wt.% LiH, and the cycling stability is also enhanced too. In addition, the high rate dischargeability (HRD) is ameliorated remarkably, and the value of HRD value at  $240$  mA/g rises by  $78.1\%$ – $87.8\%$  for  $Ti_{55}V_{10}Ni_{35} + 6$  wt.% LiH alloy electrodes. The improvement of characteristics of the electrochemical hydrogen storage characteristics may be attributed to LiH, which has excellent electrochemical activity.

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## 1. Introduction

Hydrogen is an extremely promising candidate as the new generation of energy carrier, which can slow down the pace of the global warming and reduce the using of finite fossil fuel on the energy field. The development of safe hydrogen storage technology with a high energy density is one of the key requisites for the wide spreading usage of hydrogen mobile applications widely [1]. And the progress of high-performance hydrogen storage systems has become a social necessity for realizing a future economy of hydrogen [2,3]. Hydrogen storage capabilities of metal hydrides, especially lighter metallic elements, have been widely investigated [4]. So, tremendous efforts have been devoted to the development of light-weight, high hydrogen content chemicals for on-board hydrogen storage application in the past two decades.

By contrast, hydrogen storage in the interstitial sites of solid materials is relatively safe and potentially less capitalized cost. Furthermore, Ti-based icosahedral (I) quasicrystal phase, which has

a new type of translational long-range order and displays non-crystallographic rotational symmetry, possess more tetrahedral interstitial sites than normal crystal lattices [5]. As one of hydrogen storage materials as well as anodic materials for nickel/metal hydride (Ni/MH) secondary batteries, the I-phase alloys are attractive due to hydrogen atoms can enter into the interstitial sites favorably. Akito Takasaki reported that electrochemical hydrogenation/dehydrogenation properties of  $Ti_{45}Zr_{38}Ni_{17}$ -I-phase electrodes and that at room temperature, the maximum discharge capacity of the I-phase electrodes, at room temperature, was  $23.9$  mA h/g at a current density of  $15$  mA/g. Compared with the theoretical charge capacity of the  $Ti_{45}Zr_{38}Ni_{17}$  I-phase electrode, which is estimated to be  $795$  mAh/g [6], hydrogen in the I-phase quasi-lattice may not be removed easily. Liu et al. had prepared  $Ti_{45}Zr_{35}Ni_{17}Cu_3$  single I-phase alloy powder and investigated the hydriding/dehydriding characteristics. The results show that I-phase exhibits high discharge capacity and excellent high-rate discharge ability at relatively high temperature. However, the discharge capacity and cycling stability at room temperature are not satisfying [7]. We also reported electrochemical performance, discharge capacity and cycling stability of TiVNi-Quasicrystal composite materials [8].

Lithium hydride (LiH), an important compound which containing  $Li^+$ , has been studied as hydrogen storage material [9]. As

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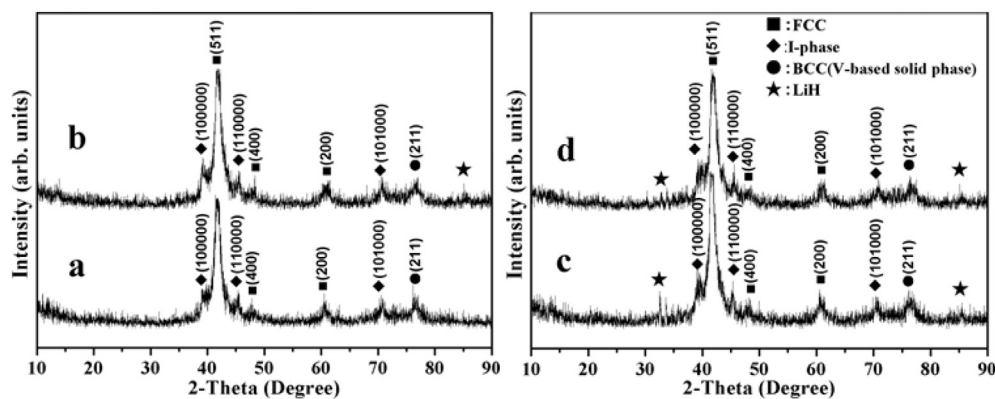


Fig. 1. XRD patterns of the  $Ti_{55}V_{10}Ni_{35}$  (a) alloy and composite materials corresponding to  $x = 3$  wt.% (b),  $x = 6$  wt.% (c) and  $x = 9$  wt.% (d).

we all known, LiH is the simplest neutral heteronuclear molecule with a stable ground state, which has drawn enormous attentions from theoreticians and experimentalists. Lithium hydride (LiH) is a potentially useful material for hydrogen storage, because it contains exceedingly high gravimetric density of hydrogen (12.7 wt.%). Pan et al. reported that  $Mg(NH_2)_2-2LiH$  composite system effectively improved the kinetics effectively, and lowering the reaction temperature [10].

In the present study, we report on the structure and the hydrogen storage properties of the new  $Ti_{55}V_{10}Ni_{35}-LiH$  system.

## 2. Materials and method

$Ti_{55}V_{10}Ni_{35}$  ingot was prepared by arc-melting method on the water-cooled copper hearth under the condition of purified argon atmosphere. To homogenous chemical compositions, ingots were melted and then were turned over at least three times. From the mother alloy ingot, ribbons were prepared by a single roller melt-spinning technique at the wheel speed of 34 m/s under argon atmosphere. Afterwards, the ribbons were crushed into alloy powders mechanically with the range of 200–400 mesh. As starting materials, LiH (98purity) were purchased from Aldrich, and the  $Ti_{55}V_{10}Ni_{35} + x LiH$  ( $x = 3, 6$  and  $9$  wt.%) were prepared by ball-milling. And ball-milling was carried out in a vibratory ball-miller under the vibration frequency of 25 Hz and amplitude of 2.5 mm for 20 min in an argon atmosphere. The stainless steel vial and

stainless balls were utilized, and the ball to powder mass ratio was 10:1. Lithium hydride powder can ignite sharply in moist air, for it could react with water vapor, oxygen and carbon dioxide. Therefore, the whole operation process must be carried out inside the argon atmosphere glove box. During this experiment, the concentration of moisture and oxygen in the glove box were controlled to be less than 5 ppm. With the step size of  $0.04^\circ$  from  $20^\circ$  to  $80^\circ$  ( $2\theta$ ), XRD measurements were conducted by using an ARL X-ray diffractometer with Cu K $\alpha$  radiation at 40 kV and 40 mA. Furthermore, the surface morphology of samples was characterized by JSM-5610LV scanning electron microscope (SEM). During the SEM test, first, the sample was adhered on the conductive stage, which was spread flat. Further, the sample was sprayed by gold treatment under the vacuum condition, which can enhance its electrical conductivity. Finally, the sample in the stage was placed into the sample chamber for the scan test.

The metal-hydride electrodes were prepared by pressing the mixture, which includes the 0.15 g of alloy powders and 0.75 g of nickel powders, into sheet with 10 mm in diameter under a pressure of 15 MPa. Then, the charge and discharge testing was conducted in a half cell consisting of a metal hydride electrode, a  $Ni(OH)_2/NiOOH$  counter electrode, and a Hg/HgO reference electrode in a 6 M KOH solution by utilizing the DC-5 testing equipment at 303 K. Next, the electrodes were charged on the condition at 60 mA/g for 6 h allowing to rest for 5 min, and then discharged at 30 mA/g of the cut-off potential of -0.6 V versus the Hg/HgO reference electrode. In order to evaluate high-rate discharge ability, discharge capacities at different discharge current densities were measured. Then the relative percentage of the high rate of discharge ability, HRD% was defined as  $C_n \times 100/C_{30}$ , the  $C_n$  ( $n = 60, 90, 120, 180$  and  $240$ ).

## 3. Results and discussion

### 3.1. Phase structure

Fig. 1 shows the XRD patterns of  $Ti_{55}V_{10}Ni_{35}$  mixed with different amounts of LiH additive (3, 6 and 9 wt.%) by the means of ball-milling. From Fig. 1(a), it can be seen that the pure LiH sample is composed of I-phase, face centered cubic (FCC) phase with  $Ti_2Ni$ -type structure in space group R-3m, V-based solid solution phase with body centered cubic (BCC) structure in space group Im3m. In the terms of  $Ti_{55}V_{10}Ni_{35}$  mixed with LiH composites, the I-phase, FCC and BCC initial phases are still observed, displays the similar features to the pure LiH sample on the diffraction peaks. However, there is no other obvious phenomena, which can illustrate that it is just a simple physical mixture during ball milling under argon

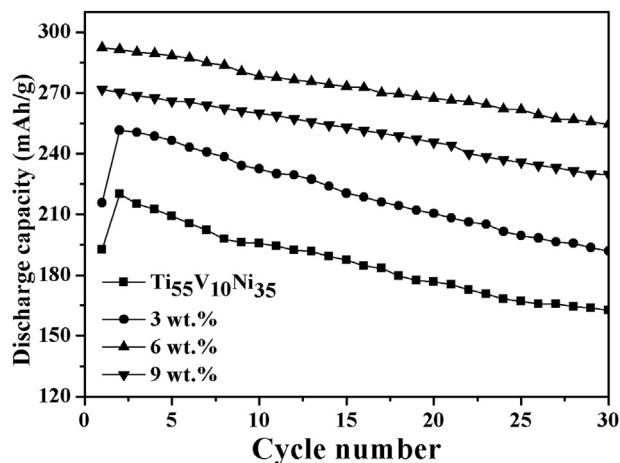


Fig. 2. Discharge capacities as a function cycle number for  $Ti_{55}V_{10}Ni_{35}$  and composite material electrodes.

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