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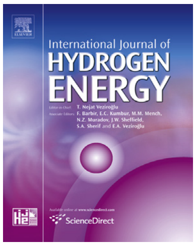

Electrochemical properties of Ti_2Ni hydrogen storage alloy

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ABSTRACT

In this paper, the long cycling behavior, the kinetic and thermodynamic properties of Ti_2Ni alloy used as negative electrode in nickel-metal hydride batteries have been studied by different electrochemical techniques. Several methods, such as, galvanostatic charge and discharge, the constant potential discharge and the potentiodynamic polarization are applied to characterize electrochemically the studied alloy. The studied electrodes are observed before and after electrochemical tests at different temperatures by scanning electron microscopy.

The amorphous Ti_2Ni is activated after five cycles and the achieved maximum discharge capacity is about 67 mAh g^{-1} at ambient temperature. Despite the low values of the maximum discharge capacity and the cycling stability (17%) and the steep decrease of the discharge capacity after activation, this alloy conserves a good stability lifetime during a long cycling. A good correlation is observed between the evolution of the discharge capacity and those of the redox parameters during a long cycling.

The enthalpy change, the entropy change and the activation energy of the formation reaction of the Ti_2Ni metal hydride are evaluated electrochemically. The found values of the enthalpy change, the entropy change and the activation energy are about −43.3 kJ mol^{-1}, 51.7 J K^{-1} mol^{-1} and 34.9 kJ mol^{-1}, respectively.

Introduction

Hydrogen may constitute the main energy vector in the future [1]. The key to using it effectively and safely is the research and development of novel storage systems. One of the best solutions is to store it at the solid state in the form of metal hydride, it is the main materials in the negative electrodes of nickel-metal hydride (Ni-MH) secondary batteries [2]. Additionally, the Ni-MH batteries have attracted much attention due to their high energy density, good discharge ability at low temperature, long cycle life, no memory effect and environment cleanness [3–8].

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A large number of hydrogen storage alloys have been developed [9]. Ti_2Ni alloy is one of promising material for hydrogen storage [10,11] by considering their structural characteristics and magnetic properties [12–22]. This material absorbs hydrogen even at ambient temperature [23–25]. Its structure is characterized by $Fd\bar{3}m$ space group symmetry, Atoms Ti_1, Ti_2 and Ni occupy 48f, 32e and 16c sites, respectively [26] and theoretical electrochemical capacity equals 500 mAh g^{-1}. This high capacity thanks to high number of interstitial sites for hydrogen storage [15] and high affinity of Ti for hydrogen and accelerated hydrogen absorption kinetics by Ni addition. The group of Luan et al. prepared Ti_2Ni alloy by arc melting. Maximum experimental discharge capacity measured by the group equaled 160 mAh g^{-1}. The difference between the theoretical and the experimental value capacity was according to the formation and accumulation of irreversible $Ti_2NiH_{0.5}$ [16]. Zhao et al. prepared Ti_2Ni alloy also by an induction melting method, the apparent activation energy for hydrogen diffusion within the bulk alloy was 10,7 KJ mol^{-1}, the alloy had a maximum discharge capacity of 235.5 mAh g^{-1} at a current density of 60 mA g^{-1} and a high rate discharge ability of 73.3% at 300 mA g^{-1} [18]. Hu et al. have investigated the electrochemical characteristics of Ti–V–Ni quasicristals and revealed that the maximum discharge capacity could reach 271.3 mAh g^{-1} for $Ti_{1.4}V_{0.6}Ni$ [27]. Moreover M. Balcerzak studied the electrochemical properties of the nanocrystalline Ti_2Ni alloy, prepared by mechanical alloying and annealing at 750 °C for 0.5 h under an argon atmosphere, the Ti_2Ni alloy had a maximum discharge capacity of 256 mAh g^{-1} and corrosion current density $5.96.10^{-2}$ A cm^{-2}, the maximum discharge capacity obtained for Ti_2Ni mixed with Pd is 274 mAh g^{-1} [28]. Substitution of Pd for Ni in Ti_2Ni-type alloy could also affect improvement of charge–transfer reaction, due to a better electrochemical catalytic activity for charge transfer reaction of Pd than Ni [29,30]. The maximum discharge capacity achieved at the first discharge process was about 220 mAh g^{-1} for the $Ti_{49}Zr_{26}Ni_{22}Pd_3$ electrode [31]. Besides, Xiangyu Zhao et al. [32] prepared $Ti_{2-x}Zr_xNi$ ($x = 0$, 0.2, 0.4) alloys by mechanical milling fallowed by a heat treatment. The obtained non–equilibrium $Ti_{1.6}Zr_{0.4}Ni$ and $Ti_{1.8}Zr_{0.2}Ni$ alloys had a maximum discharge capacities of about 214.5 mAh g^{-1} and 251.6 mAh g^{-1}, respectively, at 313 K. It must be noted that the non-equilibrium $Ti_{1.6}Zr_{0.4}Ni$ alloy presents the best cycling stability, attributed to the non-equilibrium phase structure and a protective surface layer, showed a stable discharge capacity of about 210 mAh g^{-1} at 313 K, which was evidently higher than that of the non-equilibrium Ti_2Ni alloy. X. Li et al. elaborated Ti_2Ni by a planetary high energy ball mill during 60 h. Amorphous Ti_2Ni had the discharge capacity at 102 mAh g^{-1} at a current density of 40 mA g^{-1} [33]. Highest capacity reached for Ti_2Ni was 280 mAh g^{-1} at the first cycle and dropped to less than 100 mAh g^{-1} after 50 cycles [34].

The studied Ti_2Ni alloy was prepared by mechanical alloying for elemental powders in a previous work [35]. In this paper, we present a detailed description of the behavior during a long cycling, the thermodynamic and kinetic properties of Ti_2Ni alloy, in order to achieve a better understanding of the mechanism of its electrochemical hydrogen absorption.

Experimental

Commercial elemental powders of Ti (99.9% purity, particle size <150,GoodFellow), Ni (99.5% purity, particle size<250, GoodFellow) were stoichiometrically loaded into stainless steel vials (volume 50 ml) with two stainless steel balls (diameter 20 mm) in a glove box filled with argon. 2 wt% alcohol was added as a process control agent. The ball to powder weight ratio is 3.3. The milling was carried out in a planetary high-energy ball mill (Retsch PM 400) at speed of 400 rpm under argon atmosphere at room temperature. For the purpose of dissipating heat that would otherwise give rise to high temperature, the milling was interrupted every 30 min.

The "latex" technology has been used for the electrode preparation Ninety percent of the alloy powder was mixed with 5% of a black carbon to obtain a good conductivity and 5% of polytetrafluoroethylene (PTFE) to give elasticity to the electrode. Two pieces of 0.5 cm^2 of this latex have been pressed on each side of a nickel grid, playing the role of a current collector [36]. This assembly forms the negative electrode of Ni-MH battery. All the electrochemical measurements were performed at different temperatures, in a conventional three electrodes open-air cell coupled directly with an EC-Lab V10.12 system constituted by a potentiostat/Galvanostat/EIS. A nickel mesh and on Hg/HgO electrode have been used as a counter electrode and a reference electrode, respectively. The electrolyte consisted of a KOH (1 M) solution, which was stirred by a continuous flow of argon through the cell.

The electrochemical isotherms were conducted in a galvanostatic mode after activation, the electrodes are fully charged at C/30 regime for 45 h (50% over charge). We realize several successive discharges of 5% of state of discharge at D/30 rate during 1.5 h until the complete discharge electrodes. After every discharge, we open the circuit until the stabilization of the potential (OCV) [37].

The constant discharge potential (CPD) was applied after activation and at different temperatures using a chronoamperometry method.

The activation and cycling at ambient temperature, on the electrodes were realized by galvanostatically charging and discharging at a C/10 rate.

The potentiodynamic polarization tests were carried out, during a long cycling at ambiant temperature at a scan rate of 1 mV s^{-1}, the potential scan direction, is performed from (−1200) to (−600 mV) versus Hg/HgO, to estimate the exchange current density and the corrosion potential of the electrodes in KOH solution.

The samples were observed before and after electrochemical tests at different temperatures by Scanning Electron Microscopy to determine the alloy particle size (SEM JEOL JSM-5800 LV).

Results and discussion

Activation and long cycling of the Ti_2Ni electrode at ambient temperature

The intermetallic alloy is said activated, by electrochemical cycling, when its electrochemical capacity has reached a

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