

Effects of Nb and Pd on the electrochemical properties of a Ti–Ni hydrogen-storage electrode

C.S. Wang^{*}, Y.Q. Lei, Q.D. Wang

Department of Materials Science and Engineering, Zhejiang University, Hangzhou, 310027, China

Received 5 May 1997; accepted 6 June 1997

Abstract

The effects of Nb and Pd on the electrochemical properties of a Ti–Ni hydrogen-storage electrode are studied. The results show that adding Pd or Nd to the alloy can slow down the rate of decay of the exchange current during charge-discharge cycling and is also useful in increasing the discharge capacity and cycle life of Ti–Ni electrodes. © 1998 Elsevier Science S.A.

Keywords: Alloy; Hydrogen storage; Titanium-nickel electrode; Discharge capacity; Cycle life

1. Introduction

The Ti–Ni system has been investigated by several workers [1–5] as a hydrogen-storage material for negative electrodes of alkaline storage batteries. It is known that both Ti_2Ni and TiNi in the Ti–Ni system absorb hydrogen at ambient temperature. Ti_2Ni electrochemically absorbs a large amount of hydrogen but desorbs irreversibly. TiNi absorbs/desorbs about one H-atom, reversibly during low-rate discharge [1]. In a sintered $Ti_2Ni/TiNi$ mixed-phase electrode, hydrogen transfers from Ti_2NiH_x to the TiNi phase through its phase boundary into the electrolyte [2]. This means that the irreversibility of Ti_2NiH_x is caused by its poor discharge kinetics and not by its high stability. It is generally accepted that oxidation and segregation of titanium are prominent factors associated with the capacity loss during charge–discharge cycling. Increasing the Ni content [6,7], substituting Zr [8] and B [9] for Ni, and Ni or Cu micro-encapsulation all enhance markedly the cycle life of Ti–Ni electrodes.

It is also possible that the oxide film on the Ti–Ni electrode surface is an important determinant of cycle life, especially when the film is thick. Many researchers [10–12] reported that doping the passive TiO_2 film with small amount of Pt or Pd can drastically increase the catalytic properties of the film, due to the formation of impurity

band conduction in the TiO_2 . In previous work [5], we have proposed a mathematical model for the cycle life of Ti–Ni hydride electrodes based upon electron-transfer reaction theory on oxide-covered metal electrodes. The experimental data on Ti–Ni hydride electrodes fit the model well. The study reported here examines the effects of adding Pd, Pt and Nb to Ti–Ni alloy on the hydrogen evolution reaction (HER). Because of the high cost of Pd and the similar electrochemical catalytic properties of $MoCo_3$ [13], the effects of adding $MoCo_3$ to Ti–Ni alloy are also evaluated.

2. Experimental

Alloys were prepared by melting Ti (99%), Ni (99.9%), Pd (99.1%), Nb (99.9%), Co (99.9%) and Mo (99.9%) pellets in arc furnace. Ingots were pulverized into fine powder by hydrogen decrepitation, through electrochemical charging and discharging cycling. Hydride electrodes were made by mixing the alloy powder with finely powdered electrolytic copper (300 mesh) at a weight ratio of 1:2. The mixture was cold-pressed into small (10-mm inside diameter) copper caps to form test electrodes. Electrochemical charge–discharge tests were carried out in an open, standard three-electrode cell, in which the counter electrode was nickel oxyhydroxide, the reference electrode was Hg/HgO/6 M KOH, and the electrolyte used in all experiments was 6 M KOH solution. The discharge capaci-

^{*} Corresponding author.

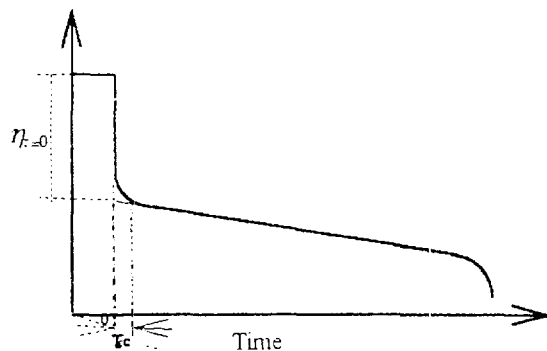


Fig. 1. Galvanostatic overvoltage transient at negative electrode.

ties of hydride electrodes were determined by the galvanostatic charge–discharge method. To reduce the ohmic drop between the working electrode and the reference electrode, a Lugging capillary was placed close to the hydride electrode. Powder X-ray diffraction (XRD) data were obtained from 360 mesh inactivated alloy powders using a Rigaku C-max-III B diffractometer with $\text{CuK}\alpha$ radiation. The alloy electrode samples were analysed by XPS (VG Escalab MKII) both before and after electrochemical charge–discharge cycling. After the electrodes had undergone 30 cycles, the KOH solution was rinsed off the electrodes with distilled water. The electrodes were dried in argon and then placed in an ultrahigh vacuum chamber at about 10^{-9} Torr. Al $\text{K}\alpha$ radiation was used for XPS. The spectra were recorded with a constant pass energy of 50 eV which corresponds to an energy resolution of about 2 eV. The sputter depths (Ar^+ , 4 keV) were estimated by using a standard rate of 8 nm min^{-1} .

The electrochemical polarization curves were plotted by the transient technique. At 0.85 V (vs. Hg/HgO) potential, a charge current pulse ($-I_1$) was applied to the hydride electrode, and the potential decay was recorded immediately on a X - Y recorder (YEW, IM3035c), from which the parameter $\eta_{t=0, -I_1}$ was obtained. The electrode was then discharged at 5 mA g^{-1} to the original potential.

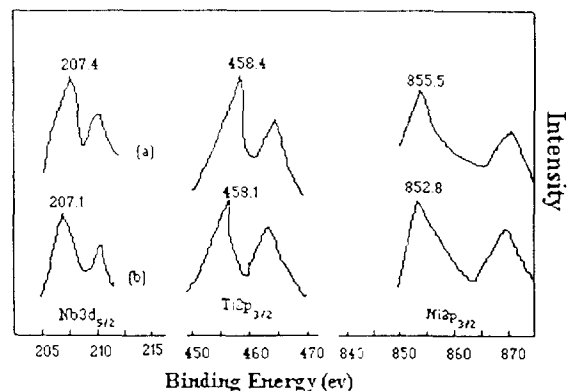


Fig. 3. $\text{Ti}_{2p_{3/2}}$, $\text{Ni}_{2p_{3/2}}$ and $\text{Nb}_{3d_{5/2}}$ XPS spectra of a $\text{Ti}_{50}\text{Ni}_{41}\text{Nb}_9$ powder electrode after 30 cycles: (a) before sputtering, (b) after sputtering off 600 Å.

After a rest for 15 min, a discharge current pulse (I_1) was applied and the potential change was recorded. By charging at 5 mA g^{-1} to the original potential and changing the current, a series of ($\eta_{t=0, \mp I_1} \mp I_1$) data were obtained. Typical potential decay curves at the negative electrode are shown in Fig. 1.

3. Results and discussion

3.1. Surface state of Ti–Ni hydride electrode

It is generally believed [9] that part of the titanium in the Ti–Ni alloy is segregated to the surface and exists in the form of an oxide in 6 M KOH electrolyte after electrochemical cycling. The arrows in Fig. 2 mark the oxide film formed on a plate $\text{Ti}_{50}\text{Ni}_{41}\text{Nb}_9$ electrode (size $10 \times 10 \times 0.5 \text{ mm}$) which had been immersed in 6 M KOH for 10 days after 30 cycles.

Both titanium and niobium segregate to the surface on cycling. Fig. 3 shows the Ti_{2p} , Nb_{3d} , Ni_{2p} core level spectra of a $\text{Ti}_{50}\text{Ni}_{41}\text{Nb}_9$ powder electrode after 30

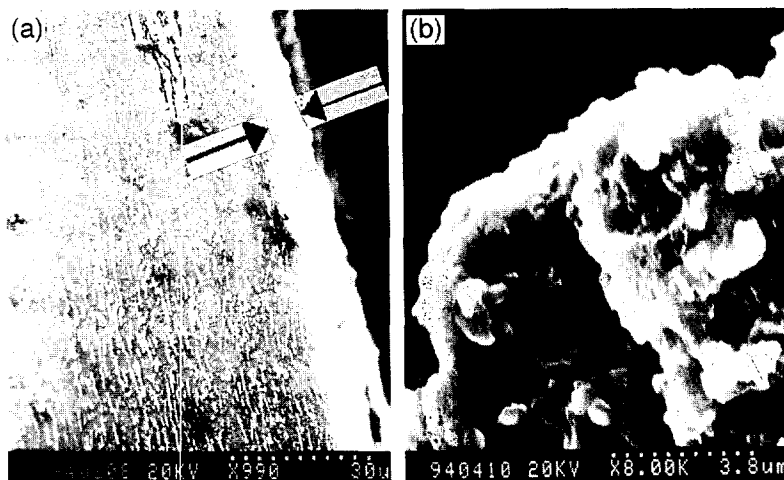


Fig. 2. Electron micrograph of a plate $\text{Ti}_{50}\text{Ni}_{41}\text{Nb}_9$ electrode that has been kept in 6 M KOH for 10 days after 30 charge–discharge cycles. Magnification: (a) $\times 990$; (b) $\times 8000$.

charge–discharge cycles, both before and after sputtering. The $Ti_{2p3/2}$, $Ni_{2p3/2}$ and $Nb_{3d5/2}$ spectra of the original surface consisted of peaks at 458.404, 355.5 and 207.4 eV, respectively. The peak positions shifted to 458.1, 852.8 and 207.1 eV after sputtering off about 600 Å by Ar^+ bombardment. This shows that titanium, nickel and niobium on the original surface exist as TiO_2 , $Ni(OH)_2$ and Nb_2O_5 , respectively, and titanium and nickel exist in the metallic state in the bulk. The atomic concentration ratio of these elements (i.e., nickel, titanium and niobium) on the original surface was 1:1.28:0.43, but changed to 1:1.22:0.28 at a depth of about 600 Å. The difference between the compositions before and after sputtering shows that there is strong segregation of titanium and niobium on the alloy surface. The segregation of niobium may inhibit segregation of titanium.

From the above analysis, it can be concluded that the oxide film on a $Ti_{50}Ni_{41}Nb_9$ electrode consists of TiO_2 , Nb_2O_5 and $Ni(OH)_2$. Thus, the electron-transfer reaction of the hydride electrode is on oxide-covered hydride electrodes, not on the hydride electrode itself. The oxidation of the hydride electrode decreases both the discharge capacity and the cycle life. This is because the oxidation decreases the amount of hydrogen-storage elements, behaviour which is called thermodynamic degradation [5]. At the same time, oxidation also decreases the exchange-current density I_0 [5] and the hydrogen diffusion coefficient D [14]. This is called kinetic degradation. The effects of the oxide film on the electrochemical properties are discussed in Section 3.2.

3.2. Electrochemical characteristics of hydride electrodes with modified intermetallics

The cycle life and discharge-rate capabilities for different alloy electrodes are plotted in Figs. 4 and 5, respectively. The $Ti_2Ni_{0.8}Pd_{0.3}$ alloy electrode shows high dis-

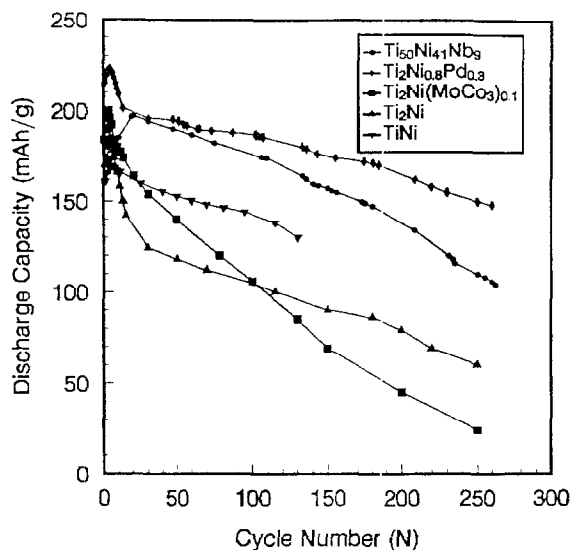


Fig. 4. Plots of cycle-life behaviour for the different alloy electrodes.

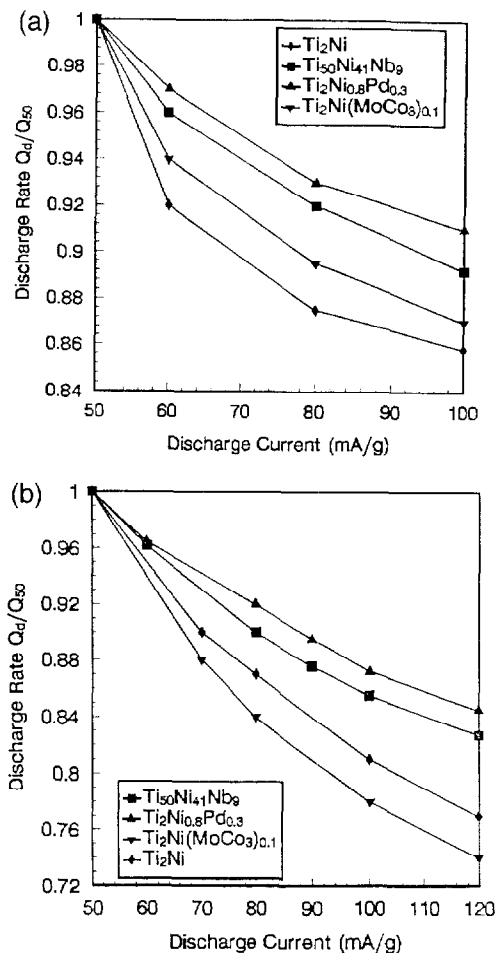


Fig. 5. Effects of Pd, $MoCo_3$ or Nb addition or substitution in a Ti-Ni electrode on discharge rate capabilities: (a) at 100 charge–discharge cycles, (b) at 200 charge–discharge cycles.

charge capacity on cycling and high-rate dischargeability after 100 cycles. A similar trend is also evident for the Nb substituted $TiNi$ alloy electrode. Adding $MoCo_3$ to a Ti_2Ni alloy electrode increases the initial performance, but the capacity decreases quickly on cycling. The high-rate dischargeability of this electrode after 200 cycles also decreases sharply, although the value before 100 cycles is higher compared with that for an untreated Ti_2Ni electrode (see Fig. 5).

3.3. Effects of Pd and $MoCo_3$ addition on electrochemical catalysis properties of Ti_2Ni

The reason for Pd increasing the cycle life of Ti_2Ni electrodes can be explained by its anti-corrosion ability [15] and by its high electrochemical catalytic activity for the $Ti_2NiPd_{0.3}$ electrode in charge–discharge cycling. The variation of electrochemical polarization with charge–discharge cycles is shown in Fig. 6. The electrochemical polarization of both $Ti_2Ni_{0.8}Pd_{0.3}$ and Ti_2Ni increases with cycling, but the increment of electrochemical polarization for the $Ti_2Ni_{0.8}Pd_{0.3}$ electrode is lower than that

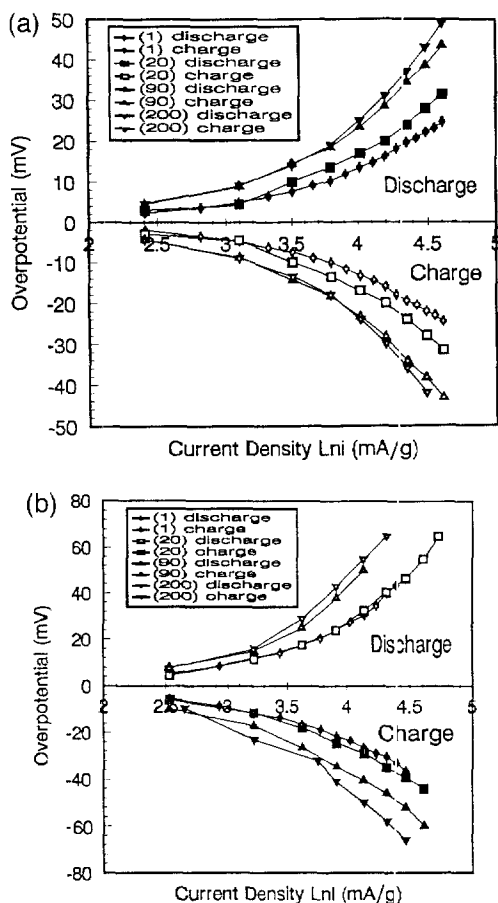


Fig. 6. Relationship of electrochemical polarization curve with cycle number for: (a) $Ti_2Ni_{0.8}Pd_{0.3}$ and (b) Ti_2Ni electrodes. The data in parentheses indicate the cycle number.

for the Ti_2Ni electrode. The higher high-rate discharge-ability of $Ti_2Ni_{0.8}Pd_{0.3}$ is believed to be associated with its smaller electrochemical polarization. $Ti_2Ni_{0.8}Pd_{0.3}$ alloy is composed of $Ti(NiPd)$ and $Ti_2(NiPd)$ phases, as shown in Fig. 7.

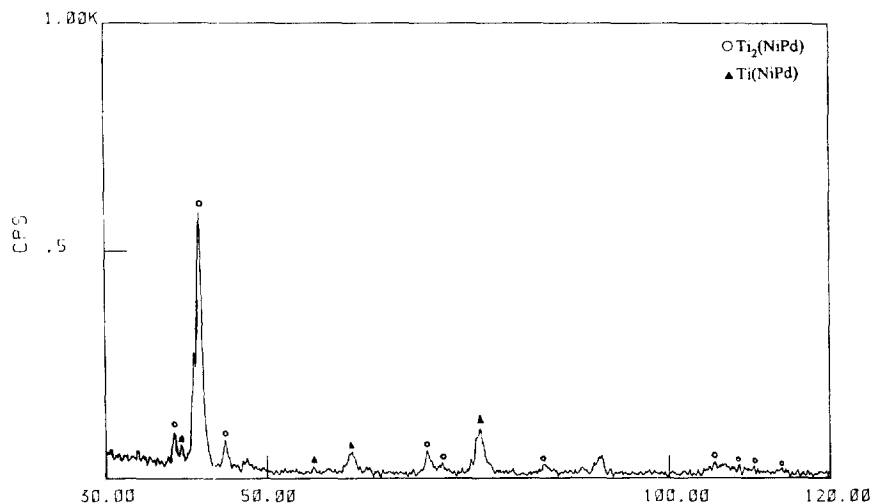


Fig. 7. XRD pattern of a $Ti_2Ni_{0.8}Pd_{0.3}$ electrode.

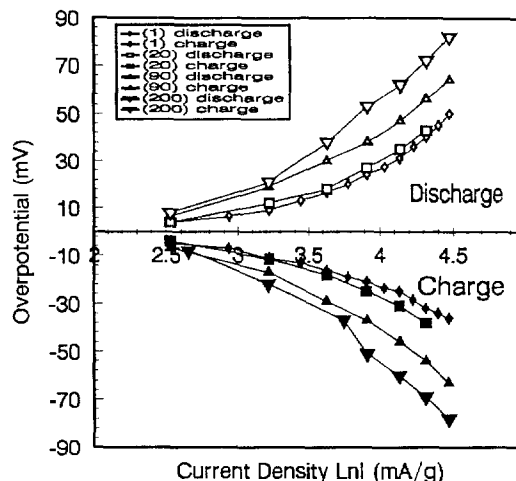


Fig. 8. Relationship of electrochemical polarization curve with charge-discharge cycle number for a $Ti_2Ni(MoCo_3)_{0.13}$ electrode. Data in parentheses indicate the cycle number.

As mentioned above, TiO_2 is formed on the $Ti_{50}Ni_{41}Nb_9$ electrode surface and is heavily doped with Nb and Ni. The way of electron transfer at film-covered electrodes depend on the thickness of the oxide film [15]. When the film is sufficiently thin, electrons exchange with the underlying metal itself. The film acts as a barrier for electron transfer and the current decreases strongly with the film thickness [15]. For the $Ti_2Ni_{0.8}Pd_{0.3}$ alloy electrode, Pd atoms decrease the TiO_2 film thickness [12], and thus, decrease the barrier for electron transfer. The Pd atoms and defects may also produce localized states the band gap of the Ti_2O film. These states may serve as intermediates for resonance tunnelling or even form impurity band conduction in Ti_2O when the electrode is heavily doped with Pd and Ni [15]. The electron-transfer process may, therefore, occur predominantly via a tunnelling mechanism with the underlying metal or even via resonance tunnelling though intermediate states that could lead

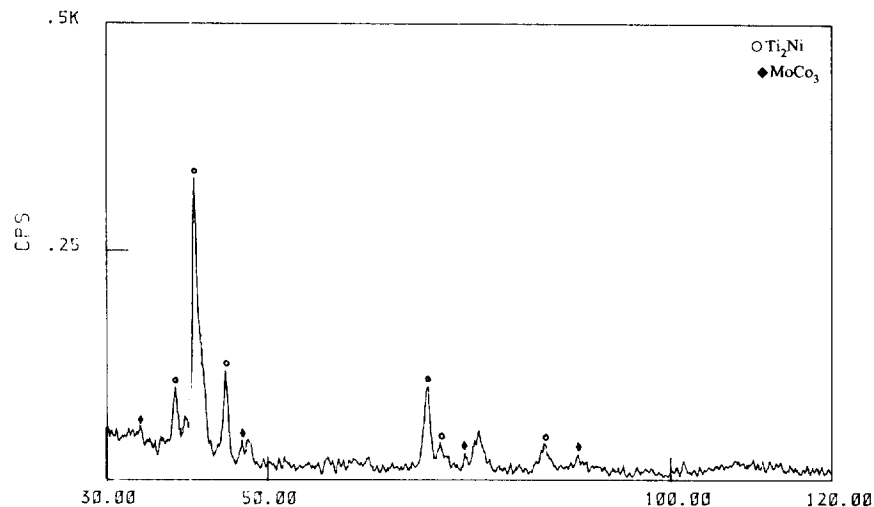


Fig. 9. X-ray diffraction pattern for $\text{Ti}_2\text{Ni}_1(\text{MoCo}_3)_{0.13}$.

to the formation of a band situated close to the Fermi level [10]. Both effects of Pd on Ti_2O film increase the catalytic properties of the Ti–Ni electrode, as shown in Fig. 6. Also, the enhancement of the cycle life by increasing the concentration of Ni in Ti_xNi alloy [6,7] or Zr in Ti–Ni–Zr alloy [8] can be explained by the formation of impurity band conduction in TiO_2 .

The MoCo_3 compound has been shown to be highly electrocatalytic for the HER, but Co is not stable in 6 M KOH, and forms $\text{Co}(\text{OH})_2$ during the charge–discharge processes [16]. The formation of $\text{Co}(\text{OH})_2$ leads to high electrochemical polarization (Figs. 8 and 9) and high concentration polarization. The discharge capacity decreases rapidly with cycle number (Fig. 4) for the same reason. The rapid decay of electrocatalytic activity causes the

electrochemical polarization to increase markedly compared with that of Ti_2Ni (Figs. 6(b) and 8).

3.4. Effects of Nb substitution for Ni in a Ti–Ni electrode

The $\text{Ti}_{50}\text{Ni}_{41}\text{Nb}_9$ is composed of three phases, namely, Ti_2Ni , TiNi and pure Nb. Part of the Nb is dissolved in TiNi and Ti_2Ni , as shown in Fig. 10.

It has been shown that Nb reacts with hydrogen and forms two types of hydrides, viz., NbH , NbH_2 . The pressure plateau for NbH_2 is between 0.1 and ~ 1 atm. [17]. NbH_2 can absorb/desorb hydrogen reversibly. Also, Nb_2O_5 is the same type of semiconductor as TiO_2 [15]. An oxide which contains a very high concentration of same type of localized states, with orbital overlapping and forms an impurity band [15], may participate in the conduction

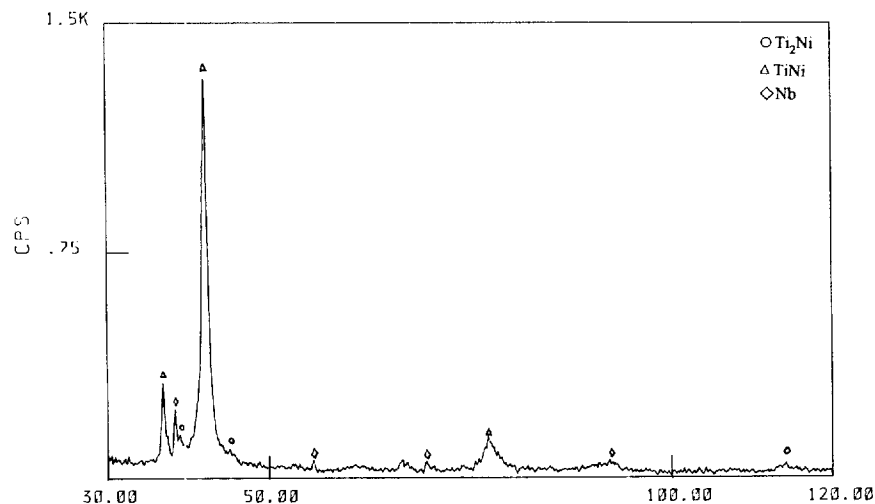


Fig. 10. X-ray diffraction pattern for $\text{Ti}_{50}\text{Ni}_{41}\text{Nb}_9$.

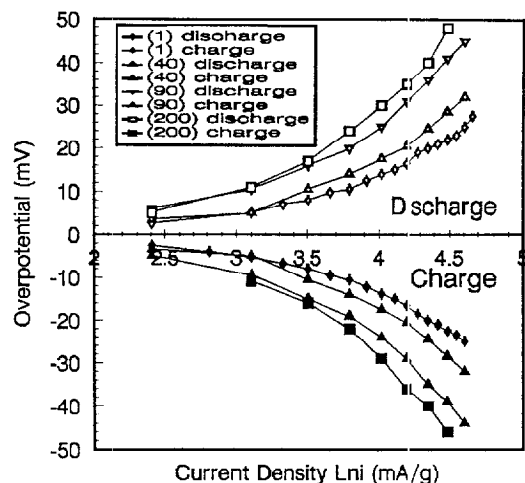


Fig. 11. Relationship of electrochemical polarization curve with charge-discharge cycle number for $\text{Ti}_{50}\text{Ni}_{41}\text{Nb}_9$ electrode. The data in parentheses indicate the cycle number.

process and in the electron-transfer reaction. Further, Nb decreases the corrosion rate of Ti. All of these factors may contribute to the lowering of the charge-discharge overpotentials, as shown in Fig. 11. Therefore, Nb substitution for Ni in a Ti-Ni electrode increases the discharge capacity (Fig. 4).

4. Conclusions

Oxide films are generally formed on the $\text{Ti}_{50}\text{Ni}_{41}\text{Nb}_9$ electrode surface in 6 M KOH electrolyte. The titanium, nickel, niobium are present in the form of oxides or hydroxides on the original surface of the electrode both before and after charge-discharge cycling. The segregation of titanium and niobium is strong on the surface of the electrode. The oxides increase the electrochemical polarization of hydride electrode, and decrease the discharge capacity. The addition of Pd into the Ti_2Ni electrode enhances the cycle behaviour due to its higher electrocat-

alytic activity for the HER in the electrochemical cycle. Nb substitution for Ni in TiNi electrodes increases the discharge capacity and cycle life due to its enhancement of the electron-transfer ability. Formation of $\text{Co}(\text{OH})_2$ on the surface of a $\text{Ti}_2\text{Ni}(\text{MoCo}_3)_{0.13}$ electrode decreases the cycle life, although it increases the discharge capacity in initial stages of charge-discharge cycling.

Acknowledgements

This project is supported by the National Nature Science Foundation of China.

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