

## Electrochemical properties of $\text{Ti}_{0.17}\text{Zr}_{0.08}\text{V}_{0.35}\text{Cr}_{0.10}\text{Ni}_{0.30}$ alloy electrode

YUJUN CHAI<sup>1</sup>, ZHIYING LI<sup>2</sup>, WENYA YIN<sup>1</sup>, XINBO ZHANG<sup>1</sup> and MINSHOU ZHAO<sup>1,\*</sup>

<sup>1</sup>Key Laboratory of Rare Earth Chemistry and Physics, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun, 130022, China

<sup>2</sup>State Key Laboratory of Electroanalytical Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun, 130022, China

(\*author for correspondence fax: +86-431-5698041, E-mail: zhaoms@ciac.jl.cn)

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### Abstract

The electrochemical properties of the  $\text{Ti}_{0.17}\text{Zr}_{0.08}\text{V}_{0.35}\text{Cr}_{0.10}\text{Ni}_{0.30}$  alloy electrode were investigated. This alloy has good cycle life at 303 K, 313 K, and even at 323 K, but the discharge capacity decreases gradually at 333 K with increasing cycle number. Both the charge–discharge efficiency and the charge–discharge voltage reduce. The electrochemical impedance spectra indicate that the charge–transfer resistance decreases while the exchange current density increases as temperature increases. The apparent activation energy of the charge–transfer reaction is about  $50 \text{ kJ mol}^{-1}$ , which is higher than that on the  $\text{AB}_5$  type alloy electrode.

### 1. Introduction

Recently vanadium and vanadium-based solid solution alloys have attracted considerable interest because of their high theoretical discharge capacity. Takahashi [1, 2] reported that hydrogen storage alloys,  $\text{V}_3\text{TiNi}_{0.56}$  and  $\text{V}_3\text{TiNi}_{0.56}\text{Hf}_{0.24}$  had higher discharge capacity than  $\text{AB}_5$  type alloy and  $\text{Ti}_{22}\text{V}_{66}\text{Ni}_{12}$  had discharge capacity up to  $800 \text{ mAh g}^{-1}$  at 293 K. Thereafter, the properties of  $\text{TiV}_{2.1}\text{Ni}_x$  alloy electrodes were studied and it was shown that this negative electrode had higher discharge capacity than the above-mentioned alloy [3, 4]. Pan et al. [5, 6] studied  $(\text{Ti}_{0.8}\text{Zr}_{0.2})(\text{V}_{0.533}\text{Mn}_{0.107}\text{Cr}_{0.16}\text{Ni}_{0.2})$  ( $x=2, 3, 4, 5, 6, 7$ ) multiphase hydrogen storage electrode alloys and pointed out that the alloys had good cycling stability and high rate dischargeability at 303 K. Up to now, the influence of temperature on the discharge capacity of the multiphase alloy has received little attention.

Our results indicated that Ti–Cr–V solid solution alloy itself has no electrochemical activity in KOH solution, and the addition of Ni is essential if the alloy is used as metal hydride electrode. Therefore we have designed Ti–Zr–V–Cr–Ni alloys and found that they have good electrochemical properties as potential negative electrode materials for Ni–MH batteries. In the present work, the electrochemical properties of  $\text{Ti}_{0.17}\text{Zr}_{0.08}\text{V}_{0.35}\text{Cr}_{0.10}\text{Ni}_{0.30}$  alloy were investigated.

### 2. Experimental

The sample of  $\text{Ti}_{0.17}\text{Zr}_{0.08}\text{V}_{0.35}\text{Cr}_{0.1}\text{Ni}_{0.3}$  alloy was melted by arc melting under argon. In order to produce homogeneous alloy, the ingot was turned over and remelted at least four times. Thereafter, the as-cast alloy was crushed mechanically in air and further pulverized with a mortar to a powder of 300 mesh. The electrode was prepared by mixing the alloy powder with porous nickel powder in a weight ratio of 1:5 and cold-pressing the mixture to form pellets. Prior to electrochemical testing, the alloy electrode was activated by immersion in 6 M KOH aqueous solution for two days. The positive electrode was a sintered  $\text{Ni}(\text{OH})_2/\text{NiOOH}$  plate. The charge and discharge test was carried out using a DC-5 battery testing instrument under computer control. The alloy electrode was charged at a current density of  $120 \text{ mA g}^{-1}$  for 4 h and discharged at a current density of  $60 \text{ mA g}^{-1}$  to a cut-off voltage of 0.8 V in a water bath.

The concentration of alloy elements in the KOH solution after 15 charge–discharge cycles was examined by emission spectrochemical analysis with radio frequency inductively coupled plasma (ICP). Electrochemical impedance spectroscopy (EIS) measurements were conducted at 50% depth of discharge using a Solartron 1470 Battery Test Unit and a 1255B Frequency Response Analyzer. The EIS spectra were obtained in the frequency range  $10^5$ – $10^{-2}$  Hz with AC amplitude of 5 mV under open circuit conditions.

3. Results and discussion

Figure 1 gives the relation between the discharge capacity of  $\text{Ti}_{0.17}\text{Zr}_{0.08}\text{V}_{0.35}\text{Cr}_{0.10}\text{Ni}_{0.30}$  alloy electrode and the cycle number at different temperatures. It can be seen that the electrode has good cyclic stability both at 303 and 313 K. The capacity retention after 50th cycles is about 97 and 95%, respectively. When the temperature rises to 323 K the discharge capacity of the electrode remains stable after some cycles. It reaches a maximum at the first cycle at 333 K and then decreases slightly, as shown in Figure 1 b. It can be concluded that this material has potential at medium and high temperatures as the negative electrode material in Ni/MH batteries. The concentration of alloy elements in KOH solution

after 15 charging-discharging cycles at various temperatures was examined and the results are shown in Table 1. Vanadium and zirconium were dissolved in the KOH solution. The concentration of vanadium clearly increases with increasing temperature. The dissolution

Table 1. Concentration of element dissolved in the KOH electrolyte after 15 charging-discharging cycle

Temperature/K	Concentration/mg/L				
	Ti	Zr	V	Cr	Ni
303	–	13.5	22.3	–	–
313	–	14.5	29.0	–	–
323	–	19.7	68.9	–	–
333	–	12.0	94.1	–	–

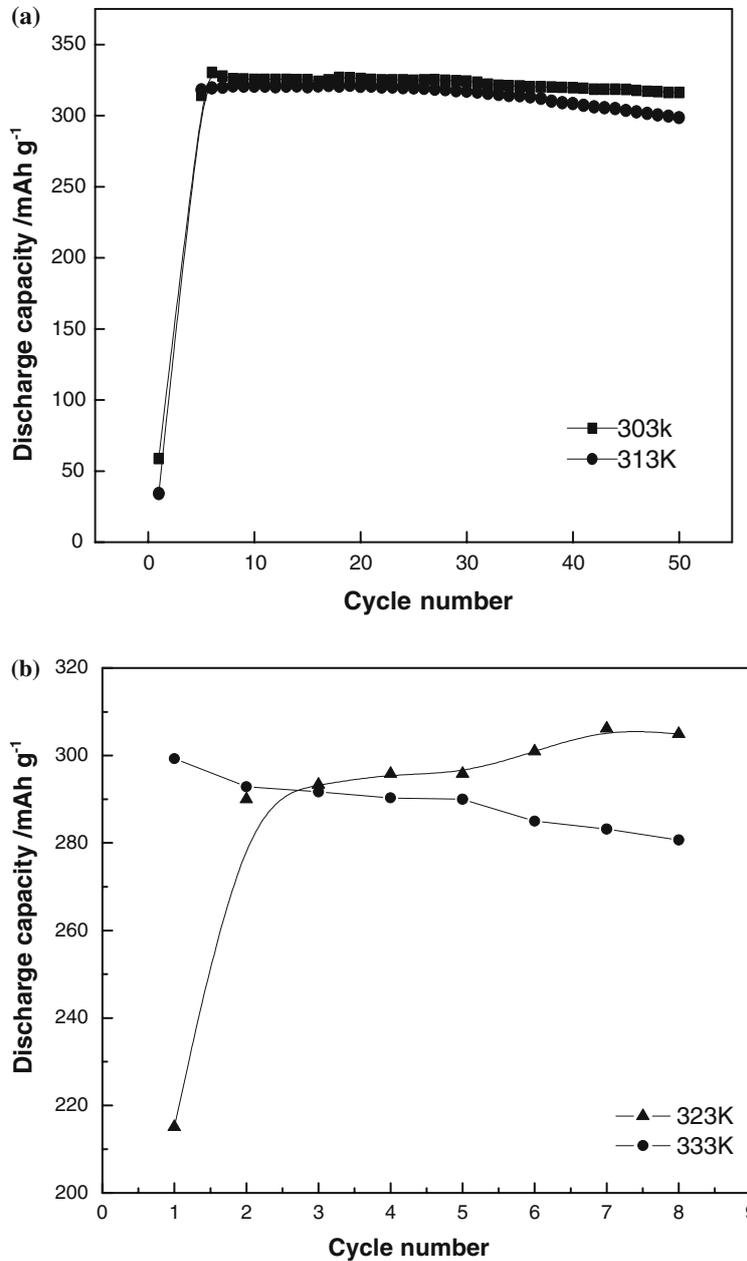


Fig. 1. Relation between discharge capacity and cycle number for  $\text{Ti}_{0.17}\text{Zr}_{0.08}\text{V}_{0.35}\text{Cr}_{0.10}\text{Ni}_{0.30}$  alloy at different temperatures (a: 303 K, 313 K; b: 323 K, 333 K).

of vanadium mainly existing in solid solution alloy leads to a decrease in the hydrogen storage capacity, and then reduces the discharge capacity of the alloy. But the concentration of zirconium in the electrolyte changes only slightly with increasing temperature, which indicates that the dissolution of this element is not sensitive to temperature. During the charge–discharge cycles, zirconium, chromium and titanium form a dense oxide film on the electrode surface, which reduces the dissolution of vanadium further [7].

The charge–discharge curve at the 8th cycle at various temperatures is shown in Figure 2. The charge voltage and discharge voltage decrease gradually with increasing temperature. The charge–discharge efficiency at the 8th cycle at different temperatures is 83.7, 81, 78.6 and 74.7%, respectively. There are two discharge voltage plateaus in the discharge curve. The first is related to the electrochemical reaction of  $(V,M)H_2$  to  $(V,M)H$ , and another small plateau appears between A and B. The discharge curve of this alloy electrode is similar to that of

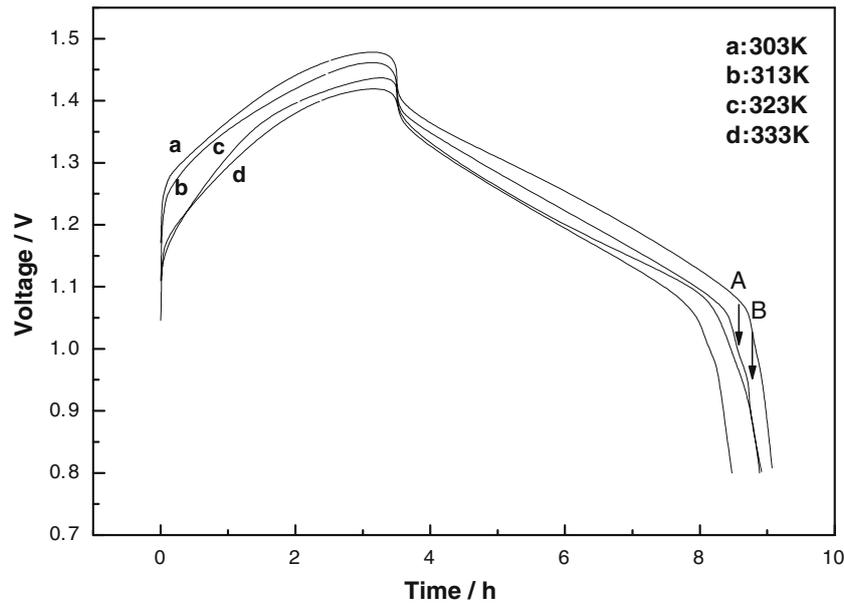


Fig. 2. Charge–discharge curves of  $Ti_{0.17}Zr_{0.08}V_{0.35}Cr_{0.10}Ni_{0.30}$  with current density of  $60\text{ mAhg}^{-1}$  alloy at various temperatures at 8th cycle number.

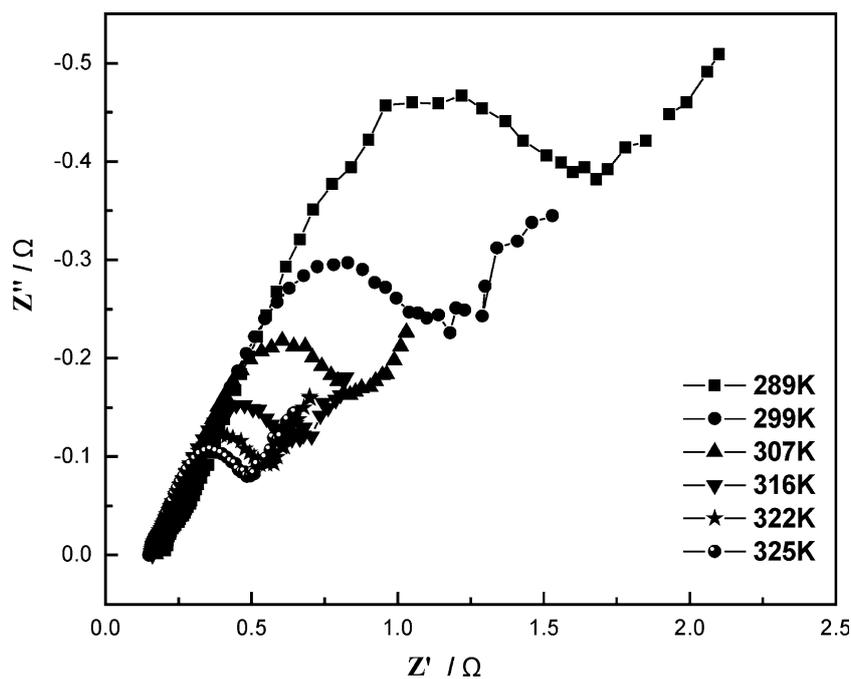


Fig. 3. EIS of  $Ti_{0.17}Zr_{0.08}V_{0.35}Cr_{0.10}Ni_{0.30}$  alloy at various temperatures.

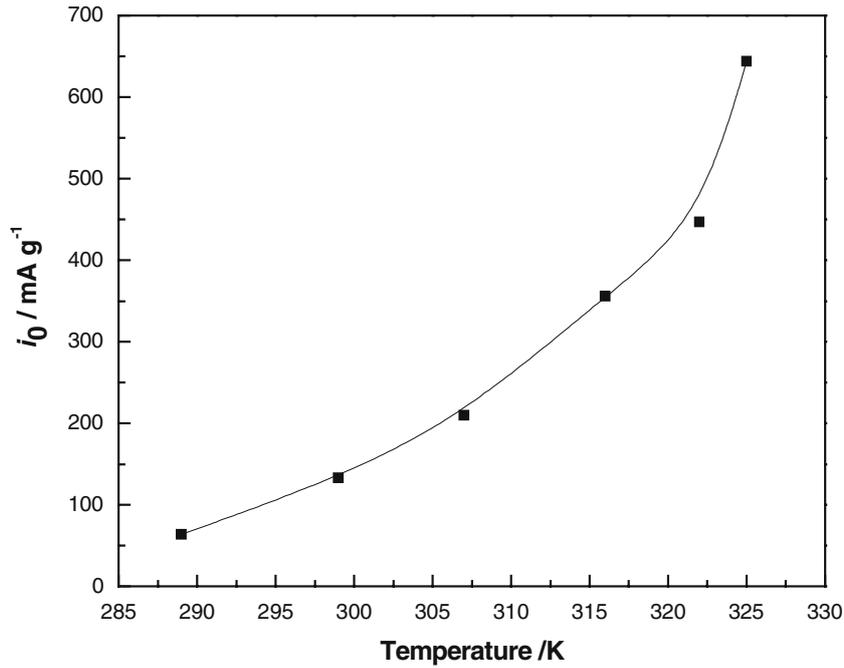


Fig. 4. Exchange current density of  $\text{Ti}_{0.17}\text{Zr}_{0.08}\text{V}_{0.35}\text{Cr}_{0.10}\text{Ni}_{0.30}$  alloy at various temperatures.

$\text{V}_3\text{TiNi}_{0.56}\text{Hf}_{0.24}$ . All have two discharge plateaus. Lei et al. [8] believed that the secondary plateau is attributable to the reaction of  $(\text{Ti,Hf})(\text{V,Ni})_2\text{H}_x$  to  $(\text{Ti,Hf})(\text{V,Ni})_2$ . We consider the secondary discharge plateau may relate to the discharge process of the secondary phases in the alloy. The hydrogen in the solid solution alloy is released and initially oxidized during the discharge process; then with increasing depth of discharge the concentration of hydrogen in solid solution is

continually reduced and thereafter the hydrogen in the secondary phases is released and oxidized, forming the second discharge plateau as described by Xu [9].

The EISs of  $\text{Ti}_{0.17}\text{Zr}_{0.08}\text{V}_{0.35}\text{Cr}_{0.10}\text{Ni}_{0.30}$  alloy at different temperatures are shown in Figure 3. The two semicircles and the straight line are related to the contact resistance between the current collector and the alloy pellet, the charge-transfer resistance on the alloy surface and hydrogen diffusion in the alloy electrode, respec-

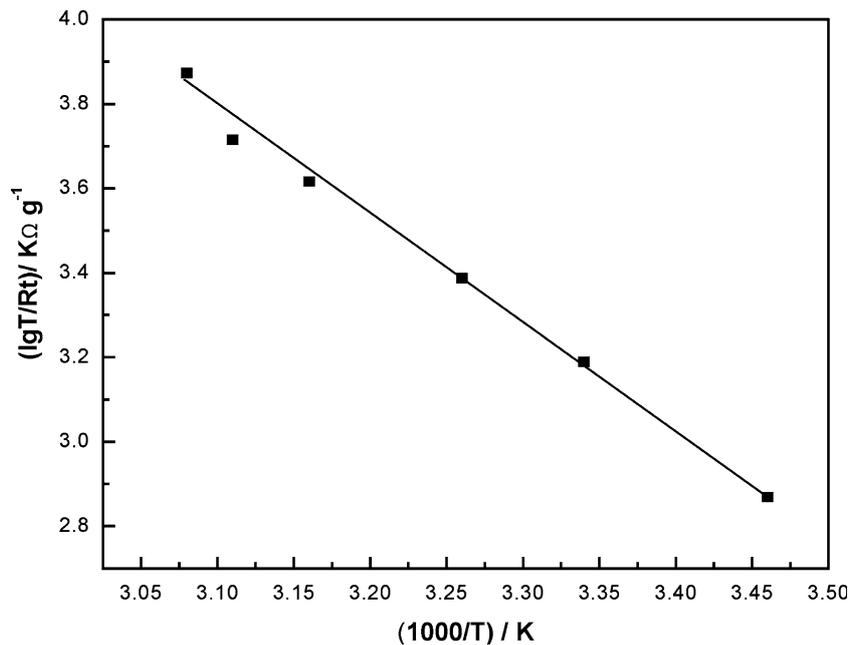


Fig. 5. Relation between  $\lg(T/Rt)$  and  $1/T$  at 50% DOD of  $\text{Ti}_{0.17}\text{Zr}_{0.08}\text{V}_{0.35}\text{Cr}_{0.10}\text{Ni}_{0.30}$  alloy.

tively. It can be seen that the charge-transfer resistance falls with increasing temperature. The exchange current density was calculated using the following equation:

$$I = \frac{RT}{FRt}$$

where  $R$ ,  $T$  and  $F$  represent gas constant, absolute temperature and Faraday constant, respectively. The charge-transfer resistance  $Rt$  was calculated according to the model proposed by Kuriyama [10]. The exchange current density increases from 64 mA g<sup>-1</sup> at 289 K to 644 mA g<sup>-1</sup> at 325 K, as shown in Figure 4, which indicates that the exchange current density is strongly dependent on temperature.

The apparent activation energy,  $\Delta H$ , of the charge-transfer reaction occurring on the electrode surface is determined by the equation [10]:

$$\lg\left(\frac{T}{Rt}\right) = \frac{\Delta H}{2.3TR} + A$$

where  $A$  is a constant and  $Rt$  is the charge-transfer resistance. The dependence  $\lg(T/Rt)$  on  $1/T$  is shown in Figure 5. From the slope of the straight line the apparent activation energy  $\Delta H$  can be calculated to be about 50 kJ mol<sup>-1</sup>, which is higher than the activation energy for the AB<sub>5</sub> alloy electrode, about 40 kJ mol<sup>-1</sup> [11].

#### 4. Conclusion

Ti<sub>0.17</sub>Zr<sub>0.08</sub>V<sub>0.35</sub>Cr<sub>0.10</sub>Ni<sub>0.30</sub> alloy electrode has good cyclic stability both at 303 K and 313 K and the discharge capacity remains stable even at 323 K, but decreases slightly at 333 K. With increasing temperature, the charge voltage, the charge-discharge efficiency and

the discharge voltage decrease while the exchange current density increases. The apparent activation energy of the charge-transfer reaction is about 50 kJ mol<sup>-1</sup>, which is higher than that of the AB<sub>5</sub> alloy electrode.

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