

## Letter

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### Activation behaviour of $\text{ZrCrNiM}_{0.05}$ metal hydride electrodes ( $\text{M} \equiv \text{La}$ , $\text{Mm}$ (misch metal), $\text{Nd}$ )

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#### 1. Introduction

Metal hydrides are expected to act as new negative electrodes for rechargeable batteries with high electrochemical capacity. Much research has been carried out on the  $\text{La-Ni}$ ,  $\text{Ti-Ni}$  and  $\text{Zr-Ni}$  systems as potential electrodes [1–4]. Recently, among these alloys, zirconium-based metal hydrides have been studied because they retain a large hydrogen-absorbing capacity and relatively good durability for charge–discharge cycling [4, 5]. However, they have the disadvantage of requiring many charge–discharge cycles for activation. This can be overcome to some extent by an oxidation treatment in oxygen gas [5] or an anodic oxidation treatment of the particle surface [4]. Nevertheless, charge–discharge cycles for activation are still required.

In this study, in order to solve this problem by making use of the easy activation behaviour of lanthanum-based electrodes reported previously [6], light rare earth metals such as lanthanum, misch metal ( $\text{Mm}$ ) and neodymium are added in small amounts to  $\text{ZrCrNi}$  alloy and the activation behaviour of the resulting electrodes is investigated during charge–discharge cycling. In order to study the effect of an added element, the activation behaviours of  $\text{Zr}(\text{V}_{0.33}\text{Ni}_{0.67})_{2.4}$  and  $\text{Zr}(\text{V}_{0.33}\text{Ni}_{0.67})_{2.4}\text{La}_{0.05}$  are compared.

#### 2. Experimental details

$\text{ZrCrNi}$  and  $\text{ZrCrNiM}_{0.05}$  alloys were prepared by arc melting in an argon atmosphere. The alloys were crushed and ground mechanically and sieved to  $-325$  mesh. In order to identify their crystal structures, X-ray diffraction measurements were performed. The electrodes were prepared by pressing the alloy powder after mixing it with nickel and polytetrafluoroethylene powder: 0.2 g of alloy powder, 0.04 g of nickel powder and 0.04 g of polytetrafluoroethylene powder were mixed and then pressed into a pellet of 10 mm diameter and about 1 mm thickness. A half-cell was constructed using a

platinum wire as counterelectrode and a saturated calomel electrode (SCE) as reference electrode. In order to charge and discharge the half-cell and to measure the discharge potential, a d.c. power supply (5–100 mA) and a chart recorder were used respectively. The electrodes were charged with a current density of  $10 \text{ mA cm}^{-2}$  for 12 h in 30 wt.% KOH electrolyte. The discharge capacities were then measured under conditions of a constant current density of  $10 \text{ mA cm}^{-2}$  at room temperature and a discharge end potential of  $-0.75 \text{ V (SCE)}$ . Subsequently, the electrodes were charged and discharged galvanostatically. From the change in  $C/C_{\text{max}}$  ( $C$  ( $\text{mA h g}^{-1}$ ), discharge capacity;  $C_{\text{max}}$ , maximum capacity) with the number of cycles, the activation behaviour of each electrode was observed.

### 3. Results and discussion

Figure 1 shows typical X-ray diffraction patterns of the ZrCrNi and ZrCrNiLa<sub>0.05</sub> alloys. For the case of ZrCrNi all peaks represent the typical C-14 hexagonal structure without any second phases. However, in the case of ZrCrNiLa<sub>0.05</sub> two new small peaks around  $2\theta = 37.8^\circ$  and  $40.23^\circ$  along with peaks of the C-14 hexagonal structure are observed. Two small peaks are also observed in the X-ray diffraction patterns of the ZrCrNiMm<sub>0.05</sub> and ZrCrNiNd<sub>0.05</sub> alloys. The positions of the two small peaks are almost the

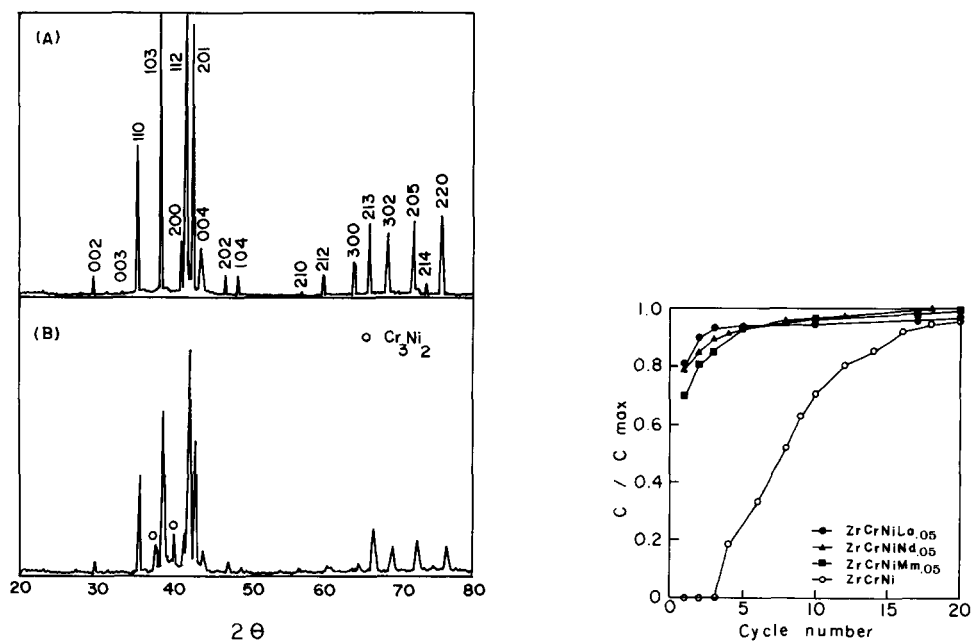


Fig. 1. X-ray diffraction patterns for (A) ZrCrNi and (B) ZrCrNiLa<sub>0.05</sub>.

Fig. 2. Variation in discharge capacity with number of charge-discharge cycles for ZrCrNi and ZrCrNiM<sub>0.05</sub> (M = La, Mm, Nd) at room temperature.

same as those of the  $\text{Cr}_3\text{Ni}_2$  phase [7]. Thus the second phase existing in the  $\text{ZrCrNiM}_{0.05}$  alloys is identified as  $\text{Cr}_3\text{Ni}_2$ .

Figure 2 shows the variations in  $C/C_{\text{max}}$  of the  $\text{ZrCrNi}$  and  $\text{ZrCrNiM}_{0.05}$  electrodes with the number of cycles. The discharge of the  $\text{ZrCrNi}$  electrode is zero up to the third cycle and then increases gradually with increasing number of cycles. This electrode is activated fully after at least 20 cycles. This result is in agreement with previous reports on the activation behaviour of zirconium-based metal hydride electrodes [4, 5]. However,  $\text{ZrCrNiM}_{0.05}$  electrodes with discharge capacities greater than  $200 \text{ mA h g}^{-1}$  in the initial cycle are mostly activated in less than 5 cycles.  $\text{ZrCrNiM}_{0.05}$  electrodes require almost no preliminary cycling or pretreatment for activation. This result indicates that the poor activation characteristics of  $\text{ZrCrNi}$  anodes can be improved by the addition of light rare earth elements.

Considering the X-ray diffraction patterns of the alloys, it is found that the second phase  $\text{Cr}_3\text{Ni}_2$  is present in the  $\text{ZrCrNiM}_{0.05}$  alloys. Therefore it is considered that the improvement in the activation characteristics of  $\text{ZrCrNi}$  by the addition of light rare earth metals may be attributed to the formation of the second phase  $\text{Cr}_3\text{Ni}_2$  and the effect of the added elements.

In order to investigate the effect of the second phase  $\text{Cr}_3\text{Ni}_2$ , a  $\text{ZrCr}_{1.1}\text{Ni}_{1.1}$  alloy of non-stoichiometric composition was prepared. The X-ray diffraction pattern of this sample shows two extra peaks at  $2\theta = 37.88^\circ$  and  $40.28^\circ$  together with peaks of the C-14 hexagonal structure. The activation behaviour of this electrode is shown in Fig. 3. The activation of this electrode is achieved after 8 charge-discharge cycles. It is found that the activation process for the  $\text{ZrCr}_{1.1}\text{Ni}_{1.1}$  anode is easier than that for  $\text{ZrCrNi}$  (Fig. 2). Therefore it is believed that second phase  $\text{Cr}_3\text{Ni}_2$  contributes to the easy activation behaviour of  $\text{ZrCrNiM}_{0.05}$  electrodes.

In order to investigate the effect of the added elements, La atoms were added in small amounts to  $\text{Zr}(\text{V}_{0.33}\text{Ni}_{0.67})_{2.4}$  as reported by Wakao *et al.* [4].

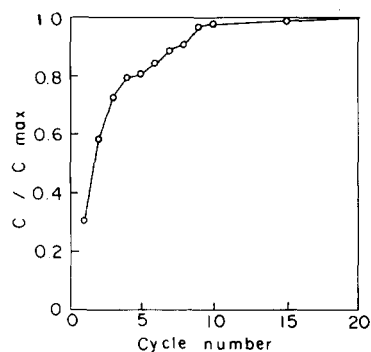


Fig. 3. Variation in discharge capacity with number of charge-discharge cycles for  $\text{ZrCr}_{1.1}\text{Ni}_{1.1}$  at room temperature.

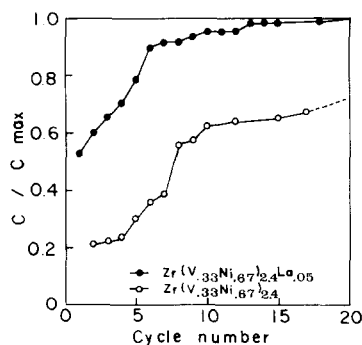


Fig. 4. Variation in discharge capacity with number of charge-discharge cycles for  $\text{Zr}(\text{V}_{0.33}\text{Ni}_{0.67})_{2.4}$  and  $\text{Zr}(\text{V}_{0.33}\text{Ni}_{0.67})_{2.4}\text{La}_{0.05}$  at room temperature.

The activation behaviour of the  $\text{Zr}(\text{V}_{0.33}\text{Ni}_{0.67})_{2.4}\text{La}_{0.05}$  electrode is examined under the same cyclic conditions for activation. In Fig. 4 this result is represented together with the activation behaviour of the  $\text{Zr}(\text{V}_{0.33}\text{Ni}_{0.67})_{2.4}$  electrode. It is observed that  $C/C_{\text{max}}$  of  $\text{Zr}(\text{V}_{0.33}\text{Ni}_{0.67})_{2.4}\text{La}_{0.05}$  at each cycle is larger than that of  $\text{Zr}(\text{V}_{0.33}\text{Ni}_{0.67})_{2.4}$ . This means that the activation of  $\text{Zr}(\text{V}_{0.33}\text{Ni}_{0.67})_{2.4}\text{La}_{0.05}$  is easier than that of  $\text{Zr}(\text{V}_{0.33}\text{Ni}_{0.67})_{2.4}$ . In this case, from the X-ray diffraction pattern, the second phase  $\text{Cr}_3\text{Ni}_2$  cannot be observed. Therefore the improved activation behaviour of  $\text{Zr}(\text{V}_{0.33}\text{Ni}_{0.67})_{2.4}\text{La}_{0.05}$  seems to originate from the added La atoms.

From the above results it is obvious that the activation characteristics of zirconium-based alloys can be improved by the addition of light rare earth elements and this improvement in activation behaviour is probably due to the formation of a second phase and/or a change in the surface layer caused by the added elements. However, the details of the effect of the formation of the second phase and the effect of the added elements on the improvement in activation are not yet completely understood. In order to clarify the mechanism, further studies, *e.g.* surface analysis, will be done.

#### 4. Summary

In order to improve the activation characteristics of ZrCrNi electrodes, small amounts of elements (lanthanum, misch metal, neodymium) were added to stoichiometric ZrCrNi. These  $\text{ZrCrNiM}_{0.05}$  ( $\text{M} \equiv \text{La, Mm, Nd}$ ) electrodes do not require many charge-discharge cycles nor any pretreatment for activation. The improvement in the activation of  $\text{ZrCrNiM}_{0.05}$  might be due to the formation of  $\text{Cr}_3\text{Ni}_2$  and/or a change in the surface layer caused by the added elements.

#### References

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