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# New activation process for Zr-Ti-Cr-Mn-V-Ni alloy electrodes: The hot-charging treatment

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## Abstract

To improve the activation behavior of $AB_2$ type Zr-Ti-Cr-Mn-V-Ni multi-component alloys, a new activation process called the hot-charging treatment has been developed. Alloy electrodes were immersed in KOH solution and charged simultaneously at various electrolyte temperatures and charge current densities. It was found that the activation behavior and the rate capability of this alloy electrode were greatly improved after the hot-charging treatment, and furthermore the treated electrode was fully activated after the first cycle. The effects of this treatment have been discussed on the basis of the results of scanning electron microscopy and auger electron spectroscopy.

*Keywords:* Hot-charging; Activation; Crack; Rate capability

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## 1. Introduction

Zr-based Laves phase electrode material, which has a large discharge capacity and relatively good cyclic durability, has the disadvantage of poor activation in KOH solution [1–4]. This is usually associated with the dense Zr oxide film through which hydrogen cannot easily penetrate [5].

In order to improve the activation behavior of these alloy systems, several activation processes have been proposed [6–11]. Yan et al. [6] used a hot alkaline treatment, immersing electrodes in hot KOH solution to modify the natural oxide layer. This process resulted in the corrosion-induced charging of the alloy with atomic hydrogen generated during the surface corrosion reaction, leading to particle cracking and improved activation behavior. Iwakura et al. [7] improved the activation properties of $ZrV_{0.5}Mn_{0.5}Ni$ alloy electrodes by immersing the electrode in an alkaline solution containing $KBH_4$ as a reducing agent. During this treatment, absorption of hydrogen atoms released from $BH_4^-$ was observed, which induced a new surface on the alloy by volume expansion. Since the activation process is accompanied by cracks on the electrode surface as reported by the aforementioned researchers, it is reasonable to further investigate the activation method in view of facilitating the crack formation during the pretreatment.

In this study, to improve the activation behavior of the $AB_2$ type Zr-Ti-Cr-Mn-V-Ni multi-component alloys studied earlier [3], the hot-charging treatment with simultaneous immersing and charging in hot KOH solution is performed. The effects of the solution temperature and the charging current density during the hot-charging treatment on the activation behavior are discussed with the experimental results of scanning electron microscopy (SEM), inductively coupled plasma spectroscopy (ICPS) and auger electron spectroscopy (AES).

## 2. Experimental details

Zr-Ti-Cr-Mn-V-Ni multi-component alloy samples were prepared by arc melting in an argon atmosphere. To ensure homogeneity, they were remelted several times and mechanically pulverized in air and sieved to -325 mesh. The alloy powder (0.2 g) was mixed with 50 wt.% copper powder and pressed at 5 ton $cm^{-2}$ to form a pellet of 10 mm in diameter.

During the hot-charging treatment, electrodes were immersed in 6 *M* KOH solution at controlled temperatures in the range of 50–80°C and charged simultaneously at a

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charging current density in the range of 50–300 mA $g^{-1}$ for 8 h. The treated electrodes were then cooled and discharged at 25 mA $g^{-1}$ to determine a quantity ($C_o$) charged during the hot-charging treatment. Since $C_o$ is associated with the crack formation on the electrode surface by volume expansion, surface analyses of electrodes after hot-charging treatment were performed by SEM and AES.

The charge–discharge cycle test was carried out in a half cell experiment using a cycle tester. The electrode was charged for 10 h at 50 mA $g^{-1}$ and discharged at 50 mA $g^{-1}$ to a cut-off voltage of −0.7 V vs. Hg/HgO at 30°C.

KOH solutions after the hot-charging treatment were analyzed for soluble species by ICPS.

## 3. Results and discussion

Fig. 1 shows the discharge capacities of the alloy electrodes treated by the hot-charging process at various temperatures and charging current densities as a function of the cycle number. The initial discharge capacities, indicating a direct measure of electrochemical activation, increased as the temperature and/or charging current density during the hot-charging treatment increased. Particularly at 80°C and even low charging current densities, the activation was completed after the first cycle.

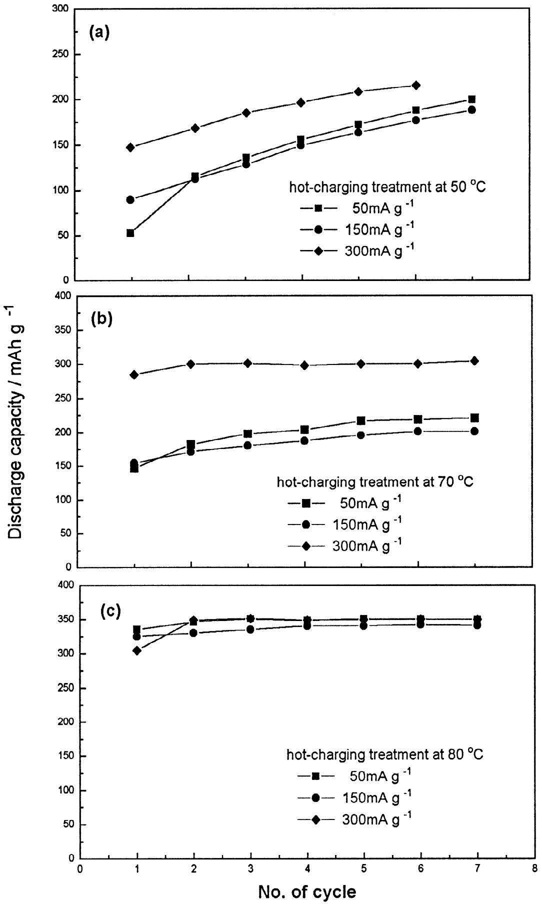

Fig. 1. Discharge capacities of alloy electrodes treated by the hot-charging process at (a) 50°C, (b) 70°C and (c) 80°C with various charging current densities as a function of the cycle number. Symbols: ■ 50 mA $g^{-1}$; · 150 mA $g^{-1}$; ♦ 300 mA $g^{-1}$. Charge–discharge cycle test was performed at 50 mA $g^{-1}$, respectively.

Fig. 2 shows the variation in discharge capacity with cycle number for electrodes untreated and treated in hot alkaline solution at 80°C for 8 h and by the hot-charging process at 80°C and 50 mA $g^{-1}$ for 8 h. It was found that the untreated electrode and the electrode treated in hot alkaline solution were fully activated at 30 cycles and 20 cycles, respectively. However, the hot-charging treated electrode shows a maximum capacity of approximately 350 mAh $g^{-1}$ at the first cycle. From the above results we found that a charging during the pretreatment as well as a solution temperature plays a key role on the easy activation.

First, in order to explain the effects of the charging current density, the quantity ($C_o$) charged during the hot-charging process was measured. $C_o$ increased with following sequence of 10.4 mAh $g^{-1}$ at 50 mA $g^{-1}$, 55.5 mAh $g^{-1}$ at 150 mA $g^{-1}$ and 108 mAh $g^{-1}$ at 300 mA $g^{-1}$ at a controlled temperature of 50°C. At other temperatures the same trend was observed and $C_o$ was significantly greater at higher temperatures. From the X-ray analysis we also observed that the unit cell volume for the hot-charging treated electrode expanded up to 22%. Therefore it is suggested that volume expansion by a large $C_o$ during the hot-charging process results in the pulverization of the alloy particles and the formation of a new clean surface having a high catalytic activity, which improves the activation behavior of treated electrodes.

Second, in order to explain the effects of temperature during the pretreatment, ICPS analysis of the solution after the hot-charging treatment was performed. The ionic concentrations of Zr and Mn in the electrolyte solution

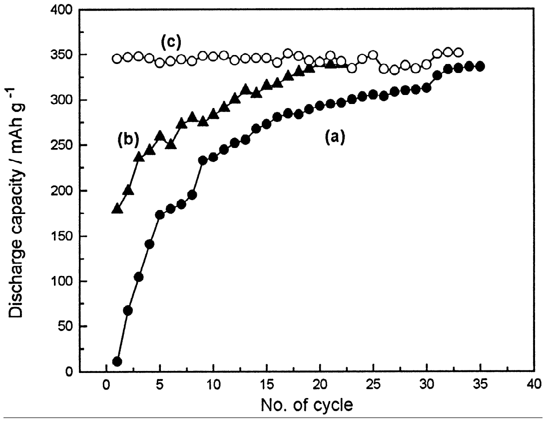

Fig. 2. Discharge capacities of the alloy electrodes untreated (a) and treated in KOH solution at 80°C for 8 h (b) and by the hot-charging process at 80°C and 50 mA $g^{-1}$ for 8 h (c). Charge current: 50 mA $g^{-1}$. Discharge current: 50 mA $g^{-1}$.

were 1.39, 0.52 ppm at 50°C; 2.88, 0.88 ppm at 70°C; and 5.82, 1.76 ppm at 80°C respectively. Also, a partial dissolution of V at 80°C was observed. These results show that the partial dissolution of alloy components occurs during the hot-charging treatment and increases at high temperature.

The ratio of the discharge capacity at a high discharge current to the discharge capacity at a low discharge current (50 mA $g^{-1}$) is a measure of the rate capability of an electrode. Fig. 3 shows the rate capabilities for the untreated and the hot-charging treated electrodes after full activation. The hot-charging treated electrode had a rate capability of 85% at 500 mA $g^{-1}$ after the first cycle. The rate capability of the untreated electrode was 42% at a same discharging current, even after 35 cycles. It is found that the hot-charging process has a favorable effect on the rate capability of this alloy electrode, in addition to improving activation property as shown in Fig. 2.

In order to investigate the effects of the hot-charging treatment on the surface of the alloy electrode, SEM and AES analysis was performed. Fig. 4 shows SEM photographs of untreated and treated electrodes after activation. There are many cracks on the surfaces of both electrodes and the surface morphology of the treated electrode after 1 cycle is similar to that of the untreated electrode after 35 cycles. These results conform that a large quantity ($C_o$) charged during the hot-charging treatment induce the pulverization of the alloy particles and the formation of a new clean surface by volume expansion.

The AES depth profiles for the constituent elements of the untreated and the hot-charging treated electrodes after activation are shown in Fig. 5. The contents of Zr and V on the surface of both electrodes were significantly decreased. It is well known that these results are ascribed to the easy dissolution of their oxides [9,13]. We also confirmed by means of X-ray photoelectron spectroscopy (XPS), that Zr and V on the alloy surface were fully oxidized to $ZrO_2$ and $V_2O_5$ and Ni existed as the metallic state, as reported by Gao et al. [12]. However, the content of metallic Ni was enriched on the surface in the case of the treated electrode, which could allow a strong hydrogen adsorption ability and the excellent electrocatalytic activity, as found in the work of Züttel et al. [9]. Conclusively, it is suggested that because the hot-charging treatment of the electrode resulted not only in the formation of a new surface by volume expansion but also in the formation of a Ni enriched region on the surface by partial dissolution of the constituent elements, activation property and rate capability of the Zr-Ti-Cr-Mn-V-Ni electrode were greatly improved.

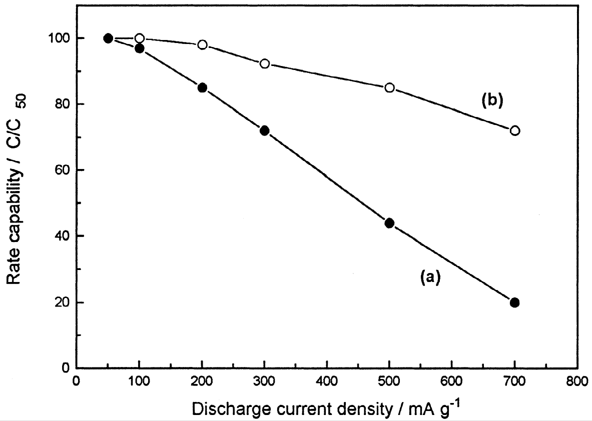

Fig. 3. The rate capabilities for the untreated (a) and the hot-charging treated (b) electrodes after full activation.

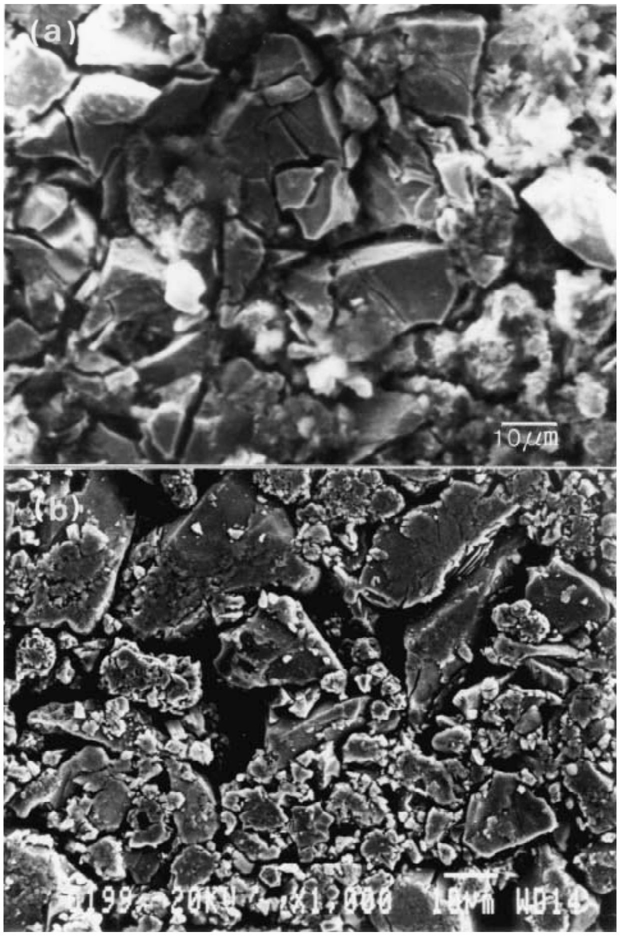

Fig. 4. SEM photographs of the surface of electrodes untreated (a) and treated (b) by the hot-charging process (a) after 35 cycles and (b) after 1 cycle.

## 4. Conclusions

We have proposed that the activation behavior and the rate capability of the $AB_2$ type alloy electrodes can be improved by immersing the electrode in hot alkaline solution and charging simultaneously. During this treatment the charging of the alloy with atomic hydrogen occurred rapidly, resulting in the formation of cracks and a new clean surface. Furthermore, Ni with high catalytic

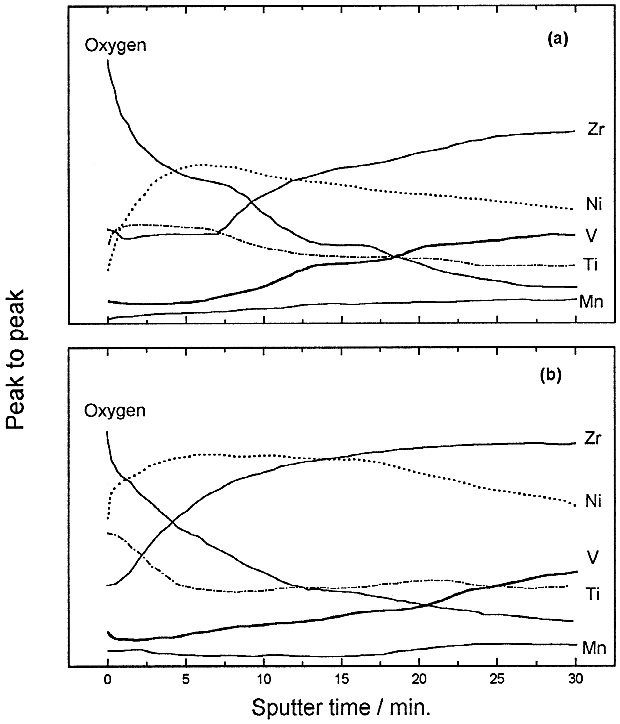

Fig. 5. AES depth profiles for the constituent elements of the untreated (a) and the hot-charging treated (b) electrodes after 35 cycles and 1 cycle, respectively.

activity was enriched near the surface by dissolving the surface oxide layer. Owing to the aforementioned effects Zr-Ti-Cr-Mn-V-Ni alloy electrodes treated with this process at 80°C and more than 50 mA $g^{-1}$ were fully activated after the first cycle and had a high rate capability of 85% at 500 mA $g^{-1}$.

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