

## Electrochemical Characterization of Rare Earth-Free Negative Electrodes for Nickel-Metal Hydride Battery Applications

Hiroshi Inoue, Norihiro Kotani, Masanobu Chiku and Eiji Higuchi

Department of Applied Chemistry  
Graduate School of Engineering  
Osaka Prefecture University  
Sakai, Osaka 599-8531, Japan

### Introduction

Rare Earth-based AB<sub>5</sub>-type hydrogen storage alloys and superlattice alloys have been used as negative electrodes for commercial nickel-metalhydride (Ni-MH) batteries. For improving energy density of Ni-MH batteries, the development of hydrogen storage alloy negative electrodes with high hydrogen storage capacity is significant. Rare earth elements are useful for not only hydrogen storage alloys but also magnetic and luminescent materials. The rare earth elements, however, are found in limited countries and not easily isolated, so that they are sometimes expensive like noble metals. Therefore, we currently take interest in the development of rare earth-free hydrogen storage alloys with high hydrogen capacity.

V-based hydrogen storage alloys with a body-centered cubic structure as a primary phase have a high volumetric hydrogen storage capacity, and therefore are potential candidates as negative electrode active materials for Ni-MH batteries. In our previous study, we found that the TiV<sub>0.9</sub>Ni<sub>0.5</sub> electrode showed the highest discharge capacity (390 mAh g<sup>-1</sup>) among the TiV<sub>1.4-x</sub>Ni<sub>x</sub> (0 ≤ x ≤ 1) electrodes<sup>1</sup> and the TiV<sub>2.1</sub>Ni<sub>0.3</sub> alloy, which was the primary phase of TiV<sub>0.9</sub>Ni<sub>0.5</sub>, had a much higher discharge capacity (470 mAh g<sup>-1</sup>) than the original TiV<sub>0.9</sub>Ni<sub>0.5</sub> alloy.<sup>2</sup> However, the TiV<sub>2.1</sub>Ni<sub>0.3</sub> alloy exhibited poor charge-discharge cycle durability because of the dissolution of the V constituent in the 6 M KOH electrolyte solution. In order to suppress the deterioration of the TiV<sub>2.1</sub>Ni<sub>0.3</sub> alloy, we examined various surface modification techniques, and found their usefulness.<sup>3</sup> Recently, we found that bulk modification, such as partial substitution of V with Cr, was also useful for improving cycle durability.<sup>4</sup> In this study we examined electrochemical properties of TiV<sub>2.1-x</sub>Cr<sub>x</sub>Ni<sub>0.3</sub> (x = 0.4-1.0) alloys.

### Experimental

The TiV<sub>2.1-x</sub>Cr<sub>x</sub>Ni<sub>0.3</sub> (x = 0.4-1.0) alloy ingots were prepared by arc-melting a mixture of Ti, V, Cr and Ni powders under an argon atmosphere.<sup>4</sup> The alloy ingot was then put in a stainless steel reactor tube and broken with high pressure hydrogen. The coarsely broken alloys were further pulverized with an agate mortar and pestle and sieved to particle sizes of 25-106 μm.

The negative electrodes used in this work were prepared by using our previously published procedure.<sup>4</sup> The electrolyte solution was 6 M KOH, and the positive and reference electrodes were a NiOOH/Ni(OH)<sub>2</sub> and Hg/HgO electrodes, respectively. In charge-discharge cycle tests, the negative electrodes were charged at 100 mA g<sup>-1</sup> for 8 h and discharged at 50 mA g<sup>-1</sup> to the cut-off potential of -0.75 V versus Hg/HgO. After each charging, the circuit was kept open for 10 min. High-rate dischargeability (HRD) was defined as the ratio of discharge capacity at various specific currents to that at 25 mA g<sup>-1</sup>. All electrochemical measurements were carried out at 303 K.

### Results and Discussion

The TiV<sub>2.1-x</sub>Cr<sub>x</sub>Ni<sub>0.3</sub> (x=0.4-1.0) alloys were composed of a primary phase and a secondary phase similar to the previously reported TiV<sub>2.1</sub>Ni<sub>0.3</sub> alloy. The V and Cr content in the primary phase was higher than that in the secondary phase, whereas the Ti and Ni content were lower in the primary phase.

Figure 1 shows charge-discharge cycle performance of the TiV<sub>2.1-x</sub>Cr<sub>x</sub>Ni<sub>0.3</sub> (x=0.4-1.0) alloy electrodes. For the alloy electrodes with x=0.4 and 0.5, the maximum discharge capacity was obtained at 2nd cycle. For the decay of discharge capacity for initial 15 cycles, the alloy electrode with x=0.4 was smaller than that with x=0.5, but over 15 cycles the capacity decay for the latter was smaller than that for the former. In contrast, for the alloy electrode with x=1.0, discharge capacity was steadily increased for initial 20 cycles. However, the maximum discharge capacity was less than half of that of the alloy electrodes with x=0.4 and x=0.5.

Figure 2 shows high-rate dischargeability of the TiV<sub>2.1-x</sub>Cr<sub>x</sub>Ni<sub>0.3</sub> (x=0.4-1.0) alloy electrodes. The HRD of the alloy electrode with x=0.5 was similar to that with x=0.4, and much better than that with x=1.0.

### Acknowledgement

This work was partly supported by Kawasaki Heavy Industries (KHI) Ltd. in the New Energy and Industrial Technology Organization (NEDO) "Development of Technology for Safe, Low-cost, Large-size Battery Systems" project.

### References

1. H. Inoue, S. Arai, C. Iwakura, *Electrochim. Acta*, **41**, 937 (1996).
2. C. Iwakura, W. -K. Choi, R. Miyauchi, H. Inoue, J. *Electrochem. Soc.*, **147**, 2503 (2000).
3. For example, H. Inoue, R. Miyauchi, R. Shin-ya, W. -K. Choi, C. Iwakura, J. *Alloys Comp.*, **330-332**, 597 (2002).
4. H. Inoue, S. Koyama, E. Higuchi, *Electrochim. Acta*, **59**, 23 (2012).

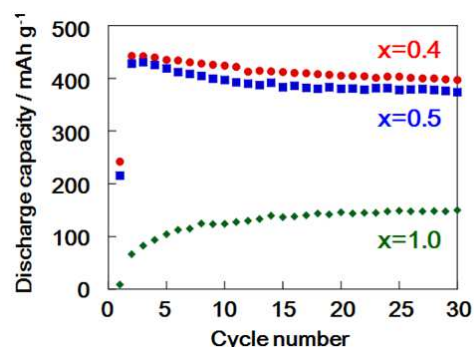


Fig. 1 Charge-discharge cycle

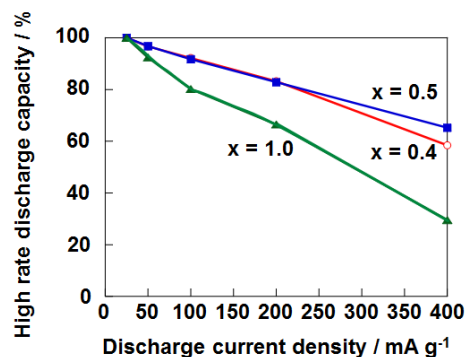


Fig. 2 High-rate dischargeability.