Characterization of $Mg_{0.9}Ti_{0.06}V_{0.04}Ni_x$ (x=1.0-1.3) Negative Electrodes for Use in Nickel-Metal Hydride Batteries

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We have already reported that an amorphous MgNi alloy prepared by mechanical alloying (MA) was able to charge and discharge even at room temperature and a composite prepared by ball-milling with graphite showed discharge capacity over 500 mAh g^{-1} [1]. In addition, charge-discharge cycle performance was improved by simultaneous substitution of a part of Mg with Ti and V, and a $Mg_{0.9}Ti_{0.06}V_{0.04}Ni$ alloy exhibited the best cycle performance [2]. In the present study, the content of Ni in the $Mg_{0.9}Ti_{0.06}V_{0.04}Ni$ alloy was varied in anticipation of the improvement of the kinetics in the discharge process. For this purpose, $Mg_{0.9}Ti_{0.06}V_{0.04}Ni_x$ (x=1.0-1.3) were prepared by MA and characterized electrochemically and physicochemically.

The $Mg_{0.9}Ti_{0.06}V_{0.04}Ni_x$ (x=1.0-1.3) alloy powders were prepared from a mixture of Mg, Ni, Ti and V powders (total mass of 1 g) by MA under Ar atmosphere using a planetary mill with an acceleration of ca. 30 m s^{-2} for 36 h. The $Mg_{0.9}Ti_{0.06}V_{0.04}Ni_x$ negative electrodes were prepared based on ref. [2]. Charge-discharge tests of the electrodes were carried out in (6 M KOH + 1 M LiOH) solution at 30 ^oC. Each electrode was charged at 100 mA g^{-1} for 6 h, and discharge to –0.6 V vs. Hg/HgO at 50 mA g^{-1} after resting for 10 min. In the measurement of high-rate dischargeability (HRD), each electrode was discharged at various current density after charging at 100 mA g^{-1} for 6 h and resting for 10 min. The HRD value at the discharge current density of 50 mA g^{-1} was taken as 100.

In X-ray diffraction patterns for the $Mg_{0.9}Ti_{0.06}V_{0.04}Ni_x$ (x=1.0-1.3) powders prepared by MA, only one broad diffraction peak was observed, which was similar to that of the MgNi alloy. Since it has been found by TEM and electron diffractometry that the MgNi had an amorphous structure [3], the $Mg_{0.9}Ti_{0.06}V_{0.04}Ni_x$ is also likely to have the same structure.

Figure 1 shows discharge capacities of the $Mg_{0.9}Ti_{0.06}V_{0.04}Ni_x$ (x=1.0-1.3) negative electrodes as a function of cycle number. The maximum discharge capacity was obtained at 1st cycle irrespective of the Ni content and was decreased with an increase of the Ni content. Charge-discharge cycle performance was a little improved.

Figure 2 shows HRD values of the $Mg_{0.9}Ti_{0.06}V_{0.04}Ni_x$ (x=1.0-1.3) negative electrodes as a function of discharge current density. The HRD value increased with the Ni content. In the case of the $Mg_{0.9}Ti_{0.06}V_{0.04}Ni_{1.3}$ negative electrode, the HRD value was ca. 70 % even at 1 A g^{-1}. Such high value seems to originate from the improvement of the kinetics in the discharge process with the increased Ni content.

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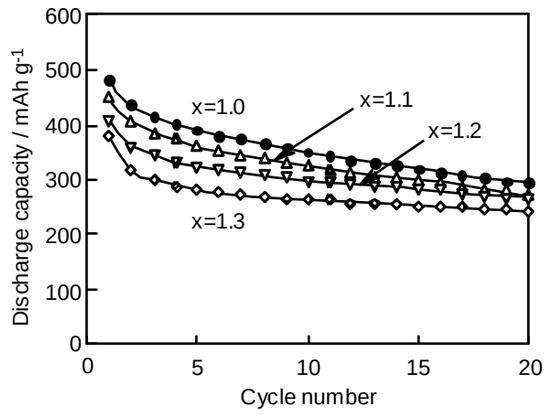

Fig.1 Discharge capacities of the $Mg_{0.9}Ti_{0.06}V_{0.04}Ni_x$ (x=1.0-1.3) negative electrodes as a function of cycle number.

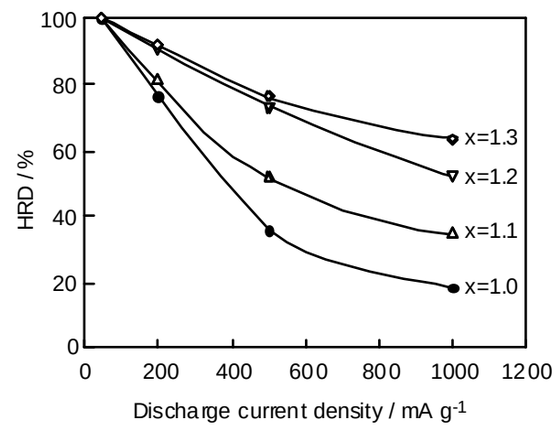

Fig. 2 HRD values of the $Mg_{0.9}Ti_{0.06}V_{0.04}Ni_x$ (x=1.0-1.3) negative electrodes as a function of discharge current density.