ELSEVIER
Journal of Alloys and Compounds 330–332 (2002) 771–775
Journal of ALLOYS AND COMPOUNDS
www.elsevier.com/locate/jallcom

Evaluation of methods to improve reproducibility in charge/discharge measurements of metal hydride battery electrodes

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Abstract

We studied reproducibility of discharge capacity, dischargeability, activation behavior, activity and porosity for charge–discharge reaction of a pellet-type electrode consisting of one part by weight of $Ti_{0.5}Zr_{0.5}Ni_{1.3}V_{0.7}Mn_{0.1}Cr_{0.1}$ and three parts of the copper powder. We examined electrodes immediately after preparation and electrodes stored for 1 month under the following conditions: vacuum, dry air and humid air. Electrolyte impregnation in vacuo was found to be very effective in improving the reproducibility of electrochemical measurements, reducing measuring effects due to the storage conditions of the electrodes.

Keywords: Metal hydride electrode; Cycle life; Discharge capacity; Laves phase; Performance standardization

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1. Introduction

Nickel–metal hydride (Ni–MH) batteries with high energy density and dischargeability have been widely used in portable appliances, electric vehicles and hybrid vehicles [1]. Hydrogen storage alloys for the negative electrode of a Ni–MH battery have been developed based on electrochemical charge–discharge cycling tests in KOH aqueous solution. A pellet-type metal hydride electrode prepared by cold-pressing a mixture of hydrogen storage alloy powder and metal powder have been widely used to evaluate electrochemical characteristics of the alloy (including: discharge capacity, dischargeability, activation behavior etc.). The technique used for the preparation of a test electrode and the electrochemical testing procedures have a great effect on the reproducibility of the measured electrochemical characteristics. It is very important for the development of Ni–MH batteries that measured results are reliable, and reproducible.

A standardization project on determination of discharge capacity of metal hydride electrodes had been organized from 1992 to 1997 in Japan [2]. In the case of mishmetal-based AB_5-type alloy, discharge capacity at 100 mA/g after 10 activation cycles was reproducible within ±5% of the average discharge capacity. However, a C14-type Laves phase alloy, $Ti_{0.5}Zr_{0.5}Ni_{1.3}V_{0.7}Mn_{0.1}Cr_{0.1}$, which is expected to be sensitive to experimental conditions, exhibited quite scattered results. Capacity measurements from 12 different research groups were different by as much as ~325 to 190 mAh/g. Here the electrodes were freshly-prepared pellet-type electrodes consisting of one part by weight of freshly ground alloy powder and three parts of copper powder. It has been reported that the scatter

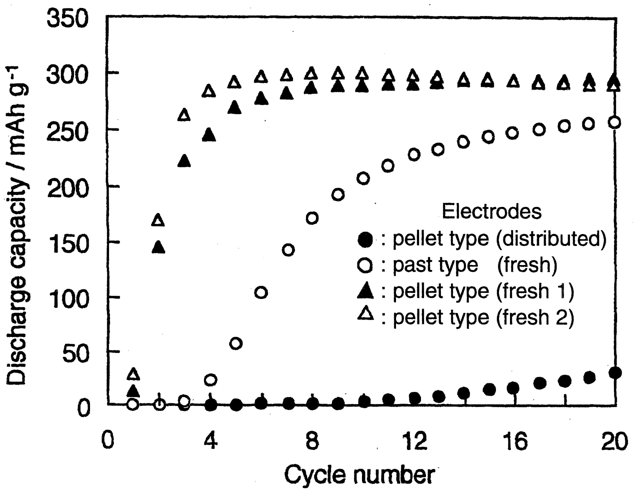

Fig. 1. Activation behavior of $Ti_{0.5}Zr_{0.5}Ni_{1.3}V_{0.7}Mn_{0.1}Cr_{0.1}$ reported in [2].

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PII: S0925-8388(01)01433-5

is caused by poor electrical contact and low porosity of the pellets due to too low and too high a pressure used in pellet preparation [2]. A pressure from 3 tons/cm^2 to 10 tons/cm^2 was suggested. Furthermore, a pellet-type electrode that has been distributed as a standard exhibited extremely poor activation characteristics as shown in Fig. 1. The discharge capacity after 20 cycles was only 30 mAh/g.

Although such results as those shown above are commonly reported, the reliability and reproducibility of the above technique have not been reported, and the possible origins of such errors were not clear. In this paper, we will report on the influence of the conditions under which the electrode have been stored and we propose the impregnation of an electrolyte into the electrode to improve the reliability and reproducibility of charge–discharge cycle testing.

2. Experimental

Electrodes were prepared based on the procedure described in [2]. The alloy, $Ti_{0.5}Zr_{0.5}Ni_{1.3}V_{0.7}Mn_{0.1}Cr_{0.1}$, was crushed to a powder of under 75 μm by hydrogenation. Fine copper powder of which average diameter is about 2.3 μm was used as a conductor and binder for all electrodes. The alloy powder was ground in a agate mortar for 5 min to obtain a fresh surface immediately before the electrode preparation. One part by weight of the alloy powder and three parts of the copper powder were mixed in an agate mortar for 5 min and pressed into an electrode pellet (about 1 g, 13 mm in diameter) using 7.5 tons/cm^2. The pellet was sandwiched between a Ni mesh (100 mesh) with a Ni wire for electrical contact. All processes of the electrode preparation were carried out in air.

The influence of storage condition of the electrode on discharge capacity, dischargeability, activation behavior, activity for charge–discharge reaction and porosity was examined by measuring electrodes which were stored under different conditions. The following electrodes were tested: an electrode immediately after alloy synthesis denoted by ‘Fresh’ and electrodes stored for 1 month with desiccators under the conditions of vacuum (‘Vac1m’), dry air (‘Dry1m’) and humid air saturated with distilled water at 30°C (‘Hum1m’). In addition, electrodes impregnating with electrolyte in vacuo or held in the electrolyte for 30 min in advance of the charge–discharge cycling were also examined in order to test the influence of the electrolyte on the electrode characteristics.

A 6 mol·dm^{-3} KOH aqueous solution, a sintered $Ni(OH)_2$/NiOOH electrode with large capacity as a counter electrode, and a Hg/HgO electrode as a reference electrode were used in all experiments. Charge–discharge cycles for activation of the electrodes were performed for 10 cycles at 100 mA/g and 20°C using a charge–discharge controller (Hokuto HJ-201B). Dischargeability of the electrodes was measured at 400 mA/g after the activation cycles. The electrodes were charged at 100 mA/g for 4 h (400 mAh/g) for all cycles, where 400 mAh/g corresponds to 120% of the capacity of the electrode. Discharge measurements were begun 30 min after each charging cycle. Discharge was terminated at −0.65 V (vs. Hg/HgO). Temperature-variable impedance measurement for the electrodes were performed after the dischargeability measurement to determine the activation energy of reaction, E_a [3]. Details of such an analysis are described in [3].

Porosity of the electrodes were determined based on weight gain when water that was degassed by heating was impregnated into the pellet for the electrodes in vacuo. The pellets were saturated by holding in water in vacuo for 10 min. The excess water on the pellets was wiped away with filter paper before weighing. Pellets made of only Cu powder under the same conditions were also examined. In addition, the amount of absorbed water in the pellets was measured after impregnation under atmospheric pressure for 10, 40 and 100 min in order to estimate absorption rate of electrolyte by the electrodes. All values obtained were averages of three measurements.

3. Results and discussion

Porosity and water absorption of the examined electrodes and porosity of a Cu pellet are shown in Fig. 2. The

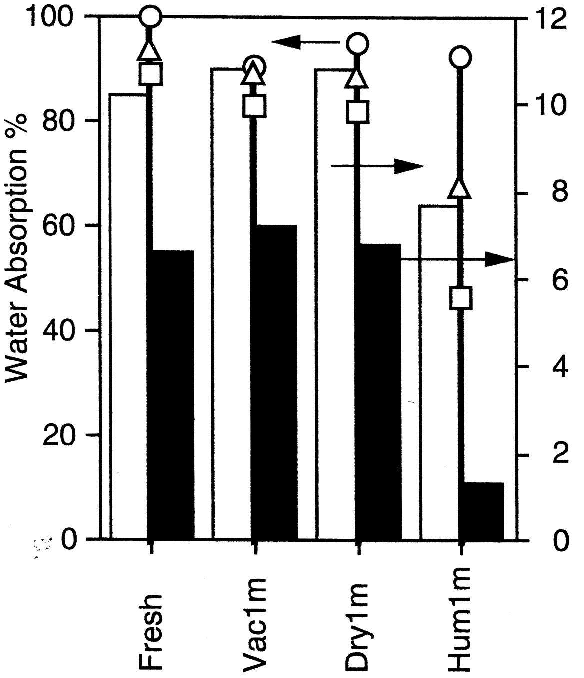

Fig. 2. Porosity of the electrodes (▭) and the copper pellets (■), and water absorption of the electrodes. The samples were examined immediately after preparation (Fresh) or after storage under various conditions (Vac1m, Dry1m and Hum1m, see text). Water absorption was measured after impregnation of water under atmospheric pressure for 10 (□), 40 (△) and 100 min (○) and in vacuo for 10 min, and is represented as a ratio to the water absorption in vacuo.

water absorption measured under atmospheric pressure have been normalized to that impregnated in vacuo. Water absorption of the Hum1m electrodes stored in humid air for 1 month was appreciably slower than that of the Fresh electrodes. Vac1m and the Dry1m were slightly lower than that of the Fresh electrodes. Only the porosity of the Hum1m electrodes was appreciably lower than those of the Fresh, Vac1m and Dry1m. It is remarkable that the Hum1m Cu pellets exhibited very low porosity. The Cu pellet had a porosity of only about 20% of the Cu pellets stored under other conditions. The color of the Hum1m Cu pellet turned to dark red. Therefore, it is concluded that precipitation of Cu oxides clogged the pores in the electrode resulting in very low porosity and slow water absorption of the Hum1m electrodes.

Discharge capacity vs. charge–discharge cycle plots during activation cycles are shown in Fig. 3. The electrodes with electrolyte impregnation in vacuo or under atmospheric pressure before charge–discharge cycles exhibited reproducible activation behavior for all the examined conditions. The Fresh and Vac1m electrodes without electrolyte impregnation also showed activation behavior similar to the electrodes with electrolyte impregnation. On the other hand, discharge capacity of the Dry1m and Hum1m electrodes were almost zero until the second or third cycle. Especially, the Hum1m electrodes showed extremely scattered activation behavior. Discharge capacity at 100 mA/g and 400 mA/g after activation cycles are shown in Fig. 4, which gives us information on dischargeability of the electrodes. Scatter of discharge capacity of the electrodes with electrolyte impregnation in vacuo was much smaller than that of the electrodes without impregnation. The average capacity for the six Fresh electrodes with electrolyte impregnation in vacuo was (333.1±2.0) mAh/g at 100 mA/g at the 10th cycle. Discharge capacity of the electrodes with electrolyte impregnation under atmospheric pressure agreed with those with impregnation in vacuo. In addition, discharge capacity at 100 mA/g was approximately independent of storage condition, although the discharge capacity at 400 mA/g decreases a little in the order of Fresh, Vac1m, Dry1m and Hum1m. Since most of the electrodes exhibited activation energy of electrochemical reaction between 38 kJ/mol and 40 kJ/mol as shown in Fig. 5, differences in the discharge capacity of the electrodes stored under various conditions are not concluded to result from differences in reactivity of their alloy surface. We believe that the differences in the activation behavior, discharge capacity and dischargeability is related to differences in the active area of the electrodes. The active area is

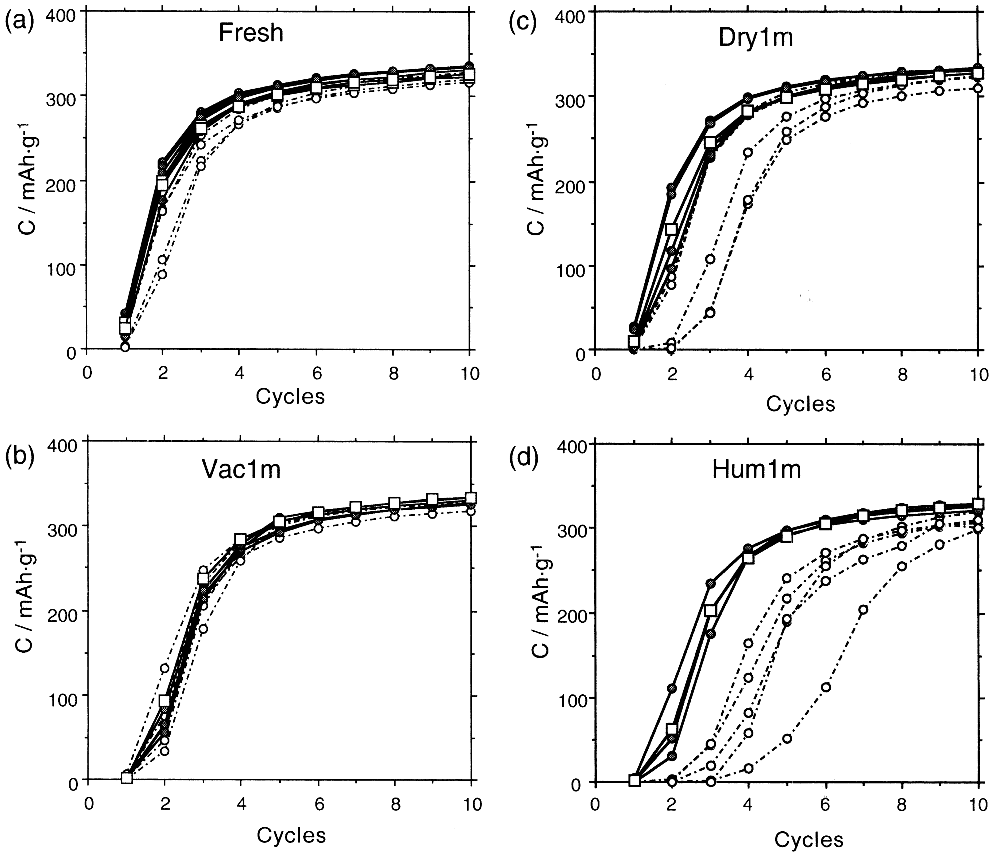

Fig. 3. Discharge capacity vs. charge–discharge cycle plots of the electrodes during activation cycles, (a) Fresh, (b) Vac1m, (c) Dry1m and (d) Hum1m. – ○ –: without impregnation of the electrolyte, – ● –: with impregnation of the electrolyte in vacuo before cycling and – □ –: with impregnation under atmospheric pressure for 30 min before cycling.

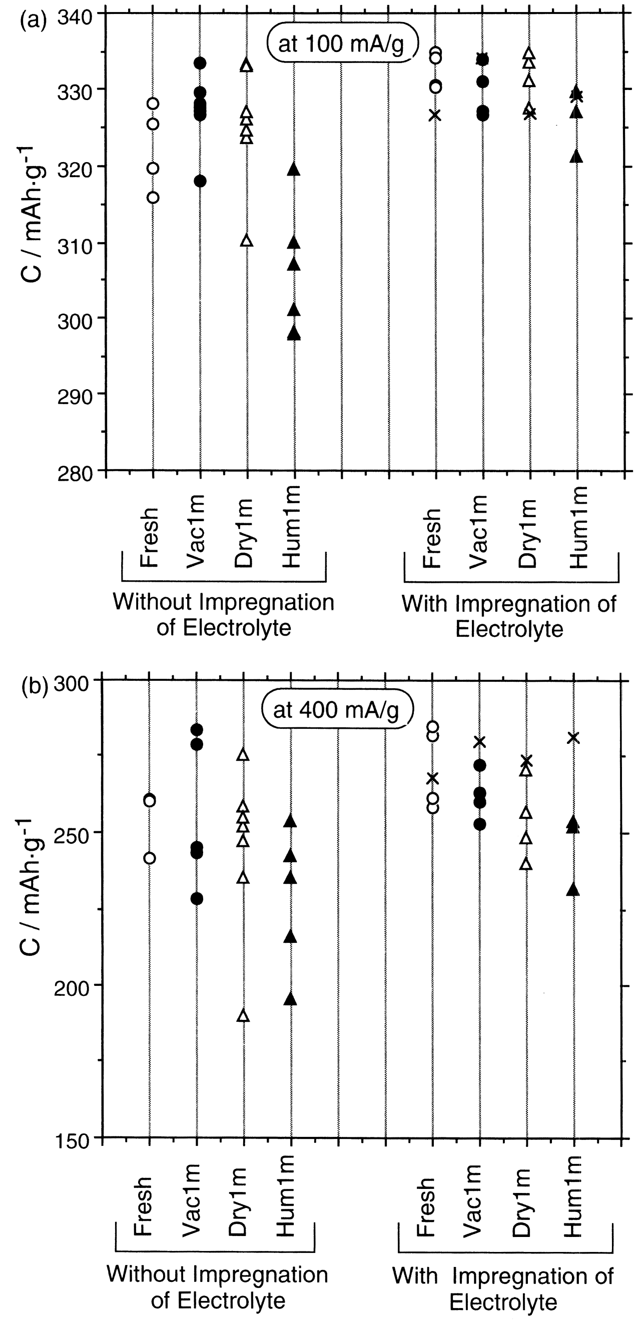

Fig. 4. Dischargeability of the electrodes, Fresh, Vac1m, Dry1m and Hum1m, after 10 activation cycles: (a) dischargeability at 100 mA/g; (b) dischargeability at 400 mA/g. ▲ indicates values of the electrodes stored under Dry1m and Hum1m conditions which indicated slow activation in the case of cycling without electrolyte impregnation in Fig. 3. × indicates values of the electrodes impregnated under atmospheric pressure for 30 min before cycling.

considered to be approximately proportional to the number of activated alloy particles, assuming that alloy particles in the electrodes have similar diameter.

A cross-sectional view of an activated electrode is shown in Fig. 6. Hydrogenation is accompanied by volume expansion which causes alloy particles to be pulverized

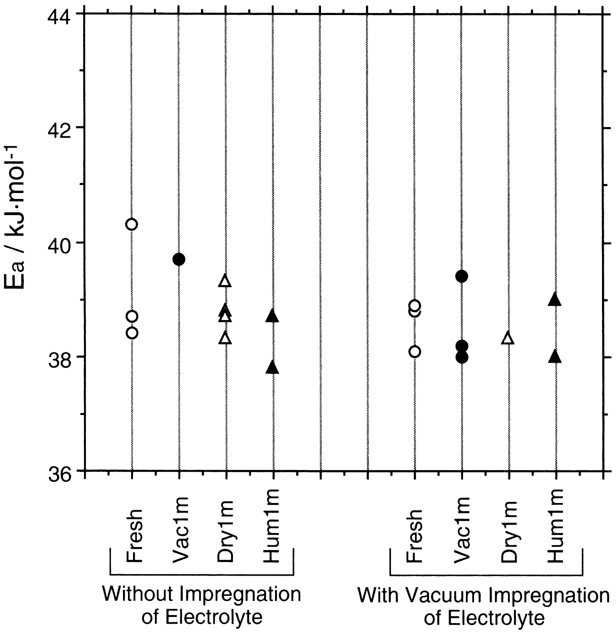

Fig. 5. Activation energy of electrochemical reaction of the electrodes, E_a, without and with electrolyte impregnation in vacuo.

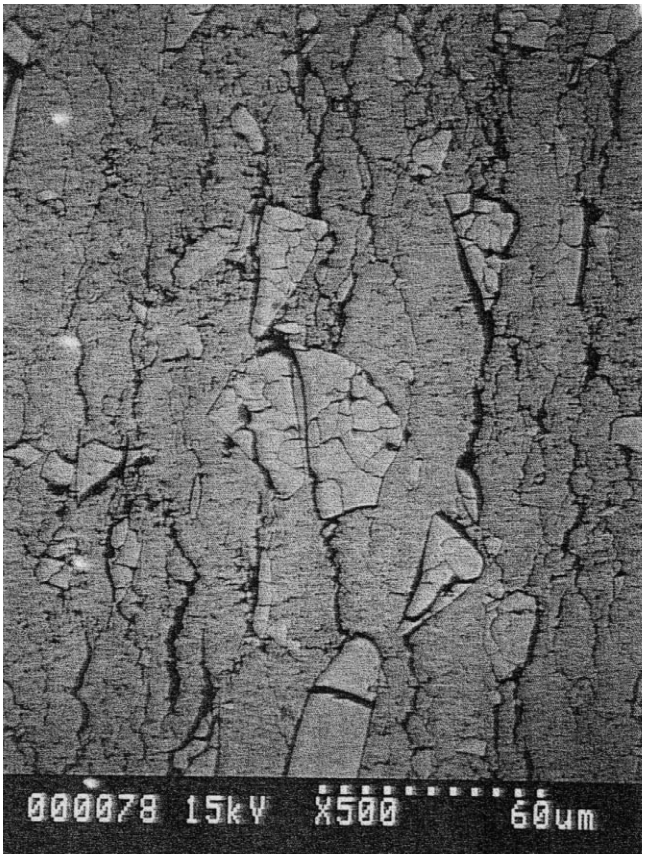

Fig. 6. A cross-sectional view of an activated electrode consisting of alloy particles (light areas) and copper powder (dark areas).

into finer particles, as well as the formation of cracks in the matrix of Cu powder. It is expected that hydrogenation of the alloy particles and formation of cracks in the Cu matrix require the penetration of the electrolyte to active particles. Therefore contact of an electrolyte with most of the alloy particles in the electrode with the first charging step is required so that most of the alloy particles can be hydrogenated and cracks can be uniformly formed in the electrode.

Based on the above discussion, the Hum1m electrode which exhibited very slow water absorption is considered to have low contact between the alloy particles and the electrolyte, when charge–discharge cycling begins without any electrolyte pretreatment. The large number of inactive alloy particles in the Hum1m electrode during initial cycles is considered to be responsible for slow activation and low dischargeability of the electrodes. Likewise in the case of the other electrodes, Fresh, Vac1m and Dry1m, differences in the depth of electrolyte impregnation is expected to cause scattered activation behavior and initial discharge capacity, if the electrodes are not sufficiently impregnated with electrolyte. Therefore, electrolyte impregnation prior to the first charging is indispensable to insure reproducible measurements of discharge capacity and dischargeability. Passivation of the alloy surface by oxidation during storage could also lead to slow activation of the electrodes due to slow hydrogenation of the alloy particles. However, this contribution is considered to be less important because of fairly good reproducibility in the activation energies independent of the storage conditions.

Very slow activations reported in [2] (Fig. 1) could be considered the result of the following: The electrode was made of alloy powder pulverized by hydrogenation. The alloy was degassed, but a small amount of hydrogen may have remained. Oxides of Cu powder may form through reaction with water produced by excess hydrogen in the alloy and oxygen impurities remaining in the electrode. These Cu oxides clog pores in the electrode inhibiting electrolyte impregnation and reducing the performance characteristics of the electrodes.

4. Conclusion

A pellet-type metal hydride electrode prepared by cold-pressing a mixture of hydrogen storage alloy powder and copper powder was examined to determine the influence of electrode storage conditions and electrolyte impregnation on the reliability and reproducibility of the electrochemical properties. Electrolyte impregnation prior to the first charging is indispensable to insure reproducible discharge capacity and dischargeability measurements. The average capacity for six Fresh electrodes with electrolyte impregnation without storage was evaluated as (333.1±2.0) mAh/g for the 10th cycle at 100 mA/g. Holding the electrodes in the electrolyte for 30 min before charge–discharge cycling also gave good reproducibility similar to in vacuo electrolyte impregnation.

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