

Short Communication

# Low-temperature surface micro-encapsulation of $Ti_2Ni$ hydrogen-storage alloy powders

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## Abstract

$Ti_2Ni$  hydrogen-storage alloy powder has been micro-encapsulated with a Ni–P coating in an electroless plating solution both at a conventional high temperature of 80 °C and at room temperature (25 °C). The performance of electrodes fabricated from  $Ti_2Ni$  powder that has been micro-encapsulated at room temperature is compared with that of electrodes fabricated from both uncoated  $Ti_2Ni$  alloy powder and powder micro-encapsulated at high temperature. The low-temperature surface modification proves to be an effective means of improving the performance characteristics of negative electrodes and, concurrently, is found to simplify greatly the powder surface modification process.

*Keywords:* Hydrogen-storage alloy powders; Titanium; Nickel; Micro-encapsulation

## 1. Introduction

The surface micro-encapsulation of hydrogen-storage alloys has already proved effective as a means of improving the following performance characteristics of nickel/metal-hydride batteries [1–4]: cycle life; high-rate charge/discharge capability; capacity; and low-temperature discharge capability. The electroless plating process is, however, usually carried out at temperatures in the general range of 60 to 90 °C. This manifests several inherent disadvantages when compared with electroless plating at room temperature, namely:

(i) consumption of more energy for heating of the bath solution;

(ii) waste of chemicals due to evaporation at higher temperatures which, in turn, increases the cost of the surface-modification process;

(iii) easy decomposition of electroless plating solution, especially for the plating of powders: one of the most serious problems of the electroless plating technique, and

(iv) chemicals, some of them toxic, on evaporation at the higher temperatures create a possible environmental hazard and, thereby, increase the safety precautions that must necessarily be undertaken by the manufacturers.

These problems are effectively eliminated in low-temperature plating, especially for the surface micro-encapsulation of hydrogen-storage alloy powders since they are highly electrocatalytic.

To the knowledge of the authors, there have been no low-temperature micro-encapsulation studies of titanium-based hydrogen-storage alloys. Room-temperature micro-encapsulation of  $Ti_2Ni$  hydrogen-storage alloys was therefore investigated via the performance of electrodes fabricated from surface-modified alloy powder. The results are compared with the performance of both electrodes fabricated from  $Ti_2Ni$  powders micro-encapsulated at high temperature and bare (non-micro-encapsulated) alloy electrodes.

## 2. Experimental

$Ti_2Ni$  alloy was made by using a vacuum arc furnace under argon protection. The alloy was then crushed to powder (less than 100 mesh), which was then micro-encapsulated at room temperature in solution. The composition and conditions of the solution are given in Table 1.

The  $Ti_2Ni$  hydrogen-storage electrodes were prepared by casting the micro-encapsulated powder (1 g) with

Table 1  
Composition of solution to micro-encapsulate Ti<sub>2</sub>Ni alloy at room temperature<sup>a</sup>

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Nickel sulphate hexahydrate (99%) (Ni <sub>2</sub> SO <sub>4</sub> ·6H <sub>2</sub> O): 100 to 120 g l <sup>-1</sup>
Sodium hypophosphite hydrate (99%) (NaH <sub>2</sub> PO <sub>2</sub> ·H <sub>2</sub> O): 50 g l <sup>-1</sup>
Propionic acid (99%) (C <sub>2</sub> H <sub>5</sub> CO <sub>2</sub> H): 10 cm <sup>3</sup> l <sup>-1</sup>
Citric acid, trisodium salt (99%) (NaO <sub>2</sub> CCH <sub>2</sub> C(OH)(CO <sub>2</sub> Na)CH <sub>2</sub> CO <sub>2</sub> Na·2H <sub>2</sub> O): 75 g l <sup>-1</sup>
Acetic acid, sodium salt (99%) (CH <sub>3</sub> CO <sub>2</sub> Na): 80 g l <sup>-1</sup>
Thiourea (99%) (H <sub>2</sub> NCSNH <sub>2</sub> ): 10 mg l <sup>-1</sup>
pH: 7.50 to 9.00
Temperature: 25 °C

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<sup>a</sup> All chemicals were supplied by Aldrich Chemical Company, Inc.

PVA (polyvinyl alcohol, 2 wt.% aqueous solution) in a ratio of 10:1 on to foam nickel. The resulting material (1 cm × 1 cm) was then dried and pressed.

The electrodes were charged to the gassing voltage, followed by a rest period of 30 min. They were then discharged galvanostatically at a current density of 20 mA g<sup>-1</sup> (the final voltage was -0.20 V versus Hg/HgO reference electrode).

### 3. Results and discussion

X-ray diffraction (XRD) results confirmed that the alloy was pure Ti<sub>2</sub>Ni (Fig. 1(a)). In addition, experimental results revealed that the cycle life of Ti<sub>2</sub>Ni electrodes, both uncoated and coated, is short. In order to increase the cycle life, small amounts of substituent elements must be added to the Ti<sub>2</sub>Ni alloy. Nevertheless, since this study is concerned with the possibility of a room-temperature micro-encapsulation technique for hydrogen-storage alloys, undoped Ti<sub>2</sub>Ni alloys were used in order to simplify the examination of room-temperature micro-encapsulation effects.

#### 3.1. Discharge capability

It can be seen from the data presented in Fig. 2 that electrodes fabricated from bare Ti<sub>2</sub>Ni powder are incapable of being further discharged after 3 cycles. By contrast, electrodes fabricated from Ti<sub>2</sub>Ni powder micro-encapsulated with Ni-P coating at 80 °C can be discharged for up to 6 cycles (Fig. 3). This demonstrates a significant beneficial effect of the alloy surface modification technique on electrode performance.

As is well known, there are two reasons for the failure of hydrogen-storage electrodes, namely, oxidation and disintegration. The results show the mitigating effect of Ni-P micro-encapsulation of Ti<sub>2</sub>Ni powders at high temperature on these processes. The discharge curves of the electrodes fabricated from powder micro-encapsulated at room temperature are shown in Fig. 4. It is readily apparent that the discharge

performance of the alloy is greatly improved over that for an alloy prepared at high temperature (cf., Fig. 4 with Fig. 3). This indicates an even further elimination of the oxidation and the disintegration processes.

#### 3.2. Capacity decay

The results given in Figs. 3 and 4 show clearly that the capacity of electrodes fabricated from micro-encapsulated powder is greater than the capacity of electrodes made from uncoated powders. In a study of the surface modification of misch-metal based alloys, Iwakura et al. [5] indicated that electroless Ni-P deposits on the surface of hydrogen-storage alloys probably serve as a micro-current collector and, thus improve the utilization efficiency of the active material. That is, the capacity of the electrode is increased. The capacity of titanium-based alloys might be increased in the same way.

The capacity-decay curves are shown in Fig. 5. As mentioned above, the cycle life of titanium-based hydrogen-storage alloy electrodes is short. This is a direct indication of the rapid decay of electrode capacity. The graph shows that capacity decay of electrodes fabricated from coated powder proceeds more slowly than that of electrodes produced from uncoated powders. The room-temperature coated electrodes exhibit by far the least decay in capacity.

It is interesting to note that the three capacity-decay curves overlap each other during the first two discharge cycles (Fig. 5). Two factors may explain the capacity decay of Ti<sub>2</sub>Ni electrodes. The XRD curve (Fig. 1(b)) reveals the formation of two new phases after the charge/discharge cycles, namely, (Ti<sub>2</sub>Ni)H<sub>0.5</sub> and (Ti<sub>2</sub>Ni)<sub>2</sub>O. In the early cycles, the formation of the low-capacity hydride phase, (Ti<sub>2</sub>Ni)H<sub>0.5</sub> dominates the decay in capacity. As the formation of (Ti<sub>2</sub>Ni)H<sub>0.5</sub> is internal and independent of surface micro-encapsulation, the three curves overlap each other. After this period, oxidation of the Ti<sub>2</sub>Ni phase dominates the capacity decay process, and (Ti<sub>2</sub>Ni)<sub>2</sub>O is formed on the powder surface. This possibly explains the subsequent sharp drop in the uncoated alloy capacity in

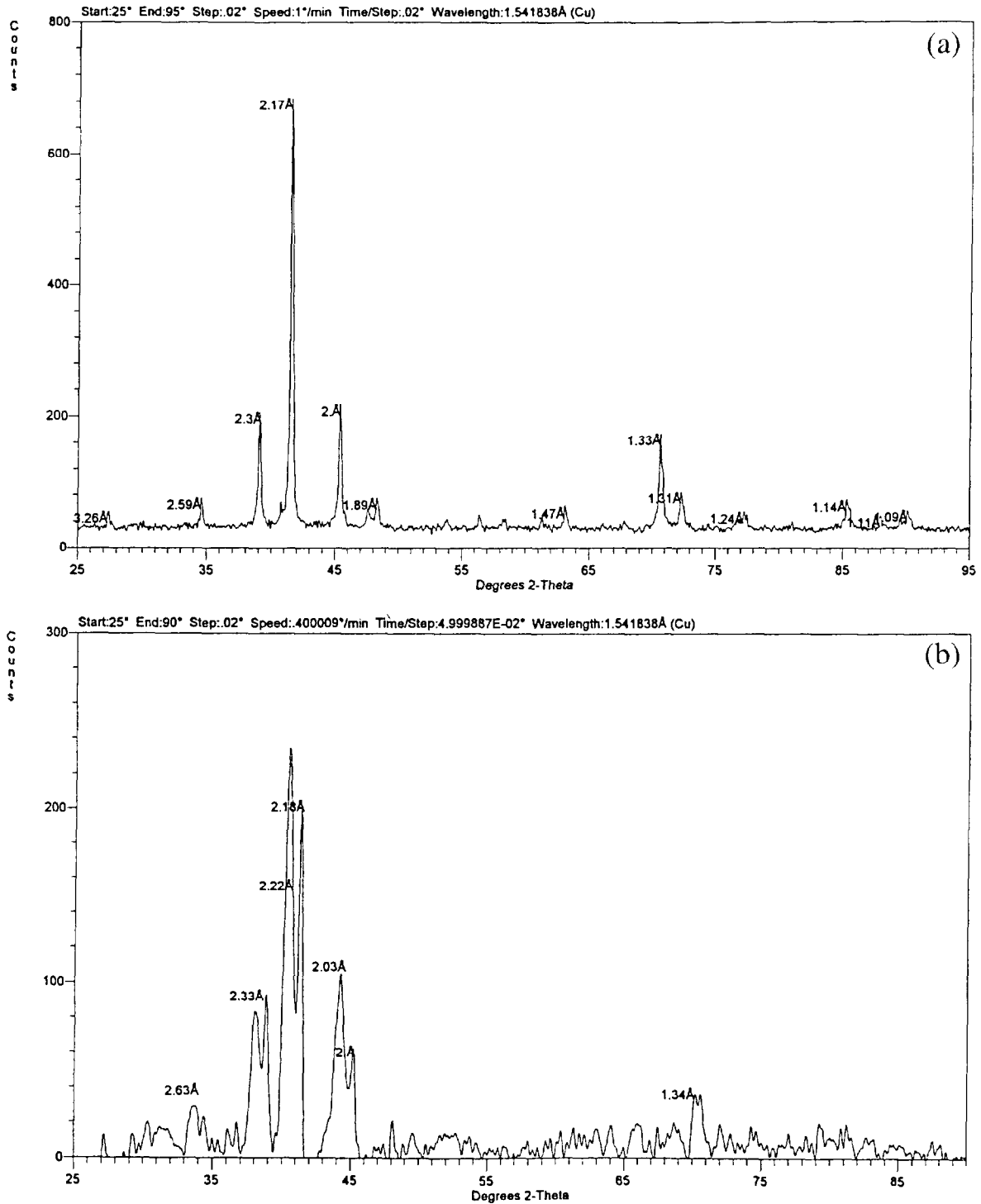


Fig. 1. X-ray diffraction of the alloys: (a) before, and (b) after charge/discharge cycles.

comparison with the much slower capacity reduction displayed by the coated alloys. The fact that the capacity decay of the low-temperature micro-encapsulated alloy is much slower than that of its high-temperature counterpart might be attributed to the fact that low-temperature micro-encapsulation creates a more condensed coating with lower porosity and, thereby, provides the alloy with better protection from oxidation.

### 3.3. Surface morphology

As reported by many authors, the cycle life of negative electrodes is critically dependent on surface morphology [6,7]. In order to clarify the effects of surface micro-encapsulation, surface morphology was examined by scanning electron microscopy (SEM), as shown in Fig. 6. It can be seen that the  $Ti_2Ni$  powders are covered

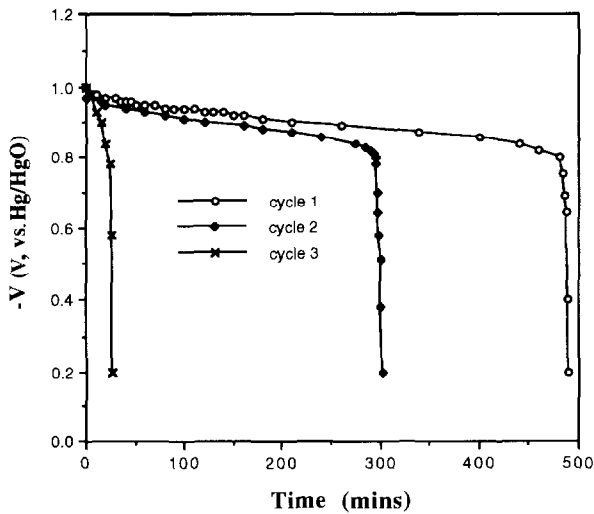


Fig. 2. Discharge cycling of an uncoated  $Ti_2Ni$  alloy electrode at a current density of  $20\text{ mA g}^{-1}$  in  $6\text{ M KOH}$ .

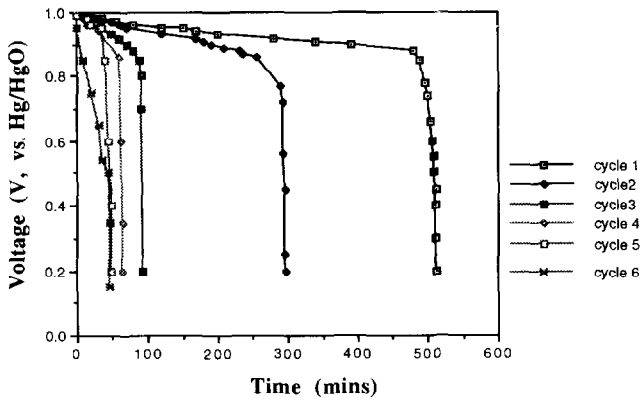


Fig. 3. Discharge cycling of an electrode fabricated with  $Ti_2Ni$  alloy powder micro-encapsulated at  $80\text{ }^\circ\text{C}$ . Discharges performed at a current density of  $20\text{ mA g}^{-1}$  in  $6\text{ M KOH}$ .

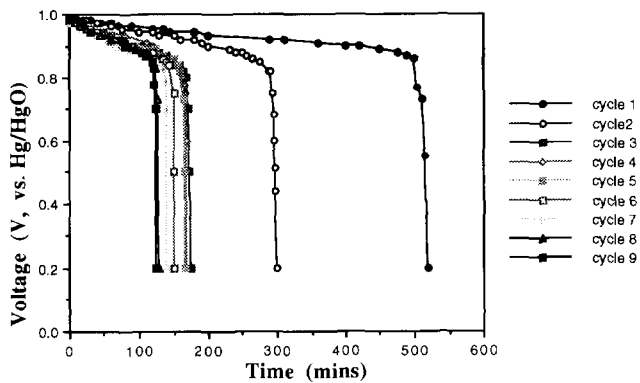


Fig. 4. Discharge cycling of a low-temperature, micro-encapsulated,  $Ti_2Ni$  alloy electrode. Discharges performed at a current density of  $20\text{ mA g}^{-1}$  in  $6\text{ M KOH}$ .

with electroless Ni-P deposits that have a spherical shape (cf., (c), (e) with (a) in Fig. 6).

The uncoated powder suffers serious disintegration after 3 cycles (cf., (a) with (b), Fig. 6). This indicates

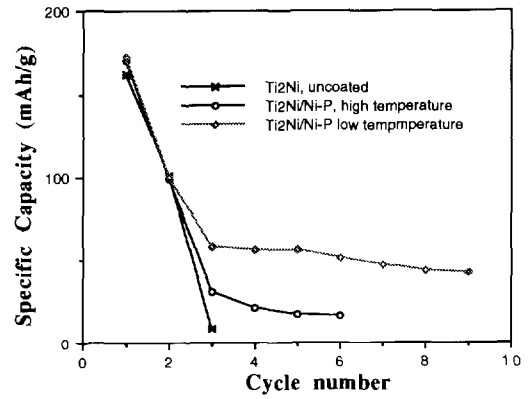


Fig. 5. Capacity decay of  $Ti_2Ni$  alloys prepared with different treatments.

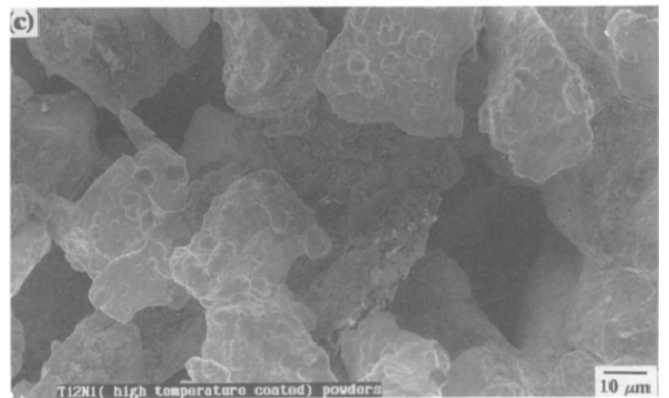
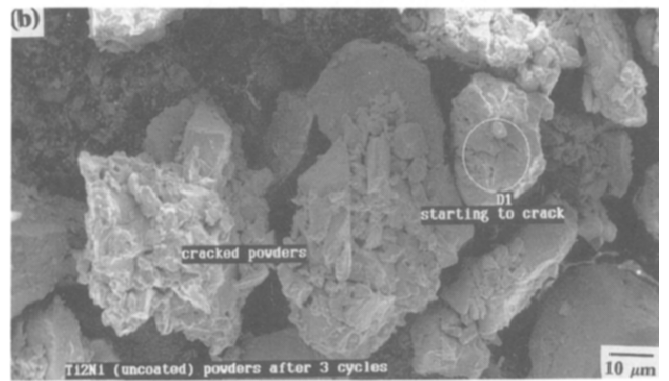
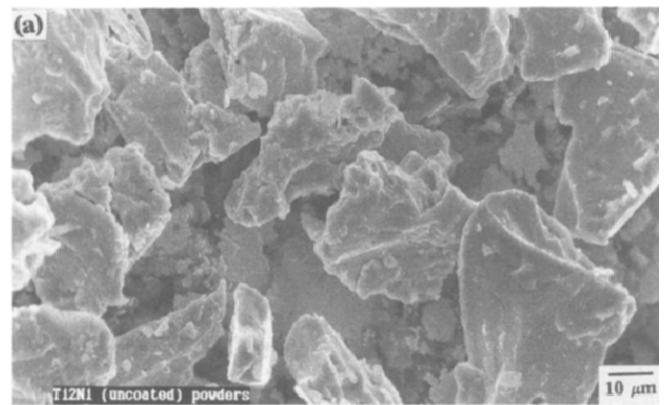


Fig. 6.

(continued)

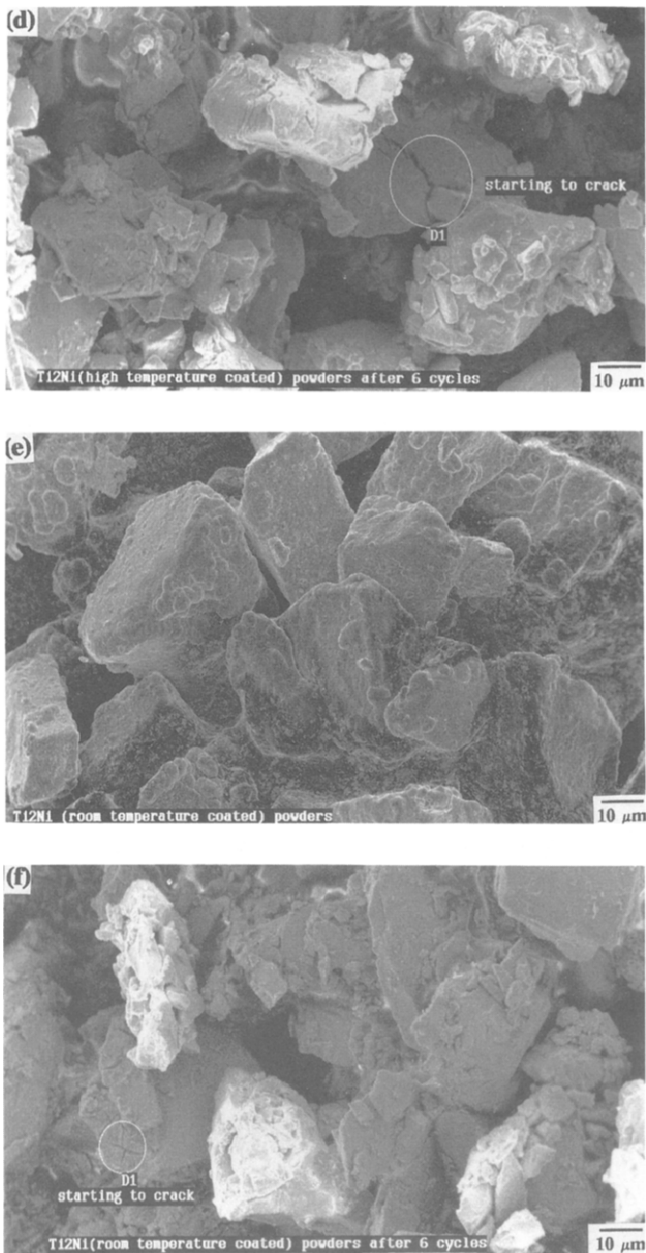


Fig. 6. Electron micrographs of  $\text{Ti}_2\text{Ni}$  alloy powders: (a) without coating before charge/discharge cycling; (b) without coating after 3 cycles; (c) coated at  $80^\circ\text{C}$  before charge/discharge cycling; (d) coated at  $80^\circ\text{C}$  after 6 cycles; (e) coated at  $25^\circ\text{C}$  before charge/discharge cycling, and (f) coated at  $25^\circ\text{C}$  after 6 cycles.

a total loss of alloy hydrogen-storage capability. By contrast, after 6 cycles, the powder micro-encapsulated at  $80^\circ\text{C}$ , shows only partial disintegration (cf., (c) and (d), Fig. 6), whilst the powder coated at room temperature exhibits cracks that are indicative of the dis-

integration process only at its very initial stage (cf., (c) and (f), Fig. 6).

The SEM observations prove that disintegration of the powder is undoubtedly a major contributor to the loss of hydrogen-storage ability and, consequently, failure of the hydrogen-storage electrodes (see, Fig. 6(a)). Further indicated is the fact that a general electroless nickel plating deposit is effective for the prevention of alloy disintegration, and will thus increase alloy cycle life. As mentioned above, the powder coated at room temperature was, after 6 cycles, only at the very beginning of the disintegration process. This demonstrates that the low-temperature micro-encapsulation technique, as presented here, is more effective than existing high-temperature processes.

#### 4. Conclusions

From the results and discussions given above, it can be concluded that:

1. The performance (i.e., cycle life, specific capacity, capacity decay) of  $\text{Ti}_2\text{Ni}$  hydrogen-storage alloy powder micro-encapsulated at room temperature is far superior to that of  $\text{Ti}_2\text{Ni}$  alloy powders that are either uncoated or coated at higher temperatures.
2. There are three possible causes of capacity decay of  $\text{Ti}_2\text{Ni}$  hydrogen-storage electrodes, namely: formation of irreversible  $(\text{Ti}_2\text{Ni})\text{H}_{0.5}$ ; oxidation of alloy material, and disintegration of alloy structure.

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