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A surface modification for hydrogen storage intermetallic particles by sol-gel method

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Abstract: *A new process for the surface modification of hydrogen storage intermetallic particles used as anode material in secondary batteries is proposed in this article. The copper oxide particles coverage obtained by the sol-gel method is proposed to produce, under operational conditions of a Ni-MH battery, a metallic framework that tolerates the volume changes in charge/discharge cycles and does not inhibit the hydrogen absorption. Furthermore it was noticed an enhancement on the discharge capacity of the electrode material that can be related to a new hydrogen storage phase or to an inhibition of the surface oxidation promoted by the film coverage.*

Key words: hydryde, Ni-MH, sol-gel, surface modification, copper oxide.

1. INTRODUCTION

Nickel-metal hydride batteries (Ni-MH) are becoming a very interesting system to replace the nickel-cadmium (Ni-Cd) ones used in portable electronic devices or even in electrical vehicles. The advantages of the Ni-MH over the Ni-Cd system are: higher energy capacity, faster rate of charging, longer life span and, most importantly, lower toxicity compared to the Ni-Cd battery. Despite the advantages of using the Ni-MH system, its wide application of that system is limited by the phenomenon of deterioration of the MH anode. This deterioration takes place as a consequence of the charge/discharge cycles. The charging process is directly related to hydrogen absorption, which causes a volume increase of the unit cell in the hydrogen storage material. The hydrogen absorbed is subsequently oxidized in the discharging step that, in its turn, causes a decrease of the unit cell volume. The sequence of charge/discharge cycles results in the pulverization of the hydrogen storage particles and the consequent anode deterioration.

The above-explained deterioration process in the Ni-MH battery anode can be remarkably minimized by surface modification of the hydrogen storage intermetallic particles. As a general goal, these treatments aim to provide a suitable mechanical support that inhibits the pulverization of the particle due to the volume changes. On that account, one of the most frequently investigated surface modification process is the microencapsulation of the particles with a copper layer produced by a chemical plating method [1-6]. The microencapsulation provides a thin and porous metallic copper layer on the particle that is able to withstand the volume changes while permitting the hydrogen absorption [1, 2]. As a consequence one can achieve a longer life span for the anode, without a decline in the charging capacity. However, the microencapsulation is still an expensive process that limits its wide in practice. Other surface modification processes to minimize the anode deterioration have been evaluated. Iwakura *et al.* [7] have obtained encouraging results by mixing electrically conducting metal oxides with

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the hydrogen storage alloy particles. The authors are not aware of any other report published on that subject. Matsuoka et al. [8] have modified hydrogen storage alloy particles by immersing them in an alkaline potassium borohydride solution. The authors attributed the improvement in the charging characteristics to the effect of the reducing agent as an electron source for minimizing the barrier surface oxide films. Naito et al. [9] have studied the influence of surface modification by electroless coatings. Despite the fact that the authors reported an actual improvement in the dischargeability of the modified surface material, it is generally accepted that the low expansion coefficient of the plated material can limit the charging step by limiting the volume increase. From the studies reported above, one can conclude that improvements of the existing surface modification methods, and/or the development of alternative ones to minimize the anode deterioration, are still required for the Ni-MH batteries to become widely used.

This paper presents an alternative surface modification for hydrogen storage alloys particles based on the sol-gel surface deposition of copper oxides. Under cathodic polarization (charging step), a porous copper framework it produced, which mechanically supports the volume changes and also permits the hydrogen absorption by the intermetallic particles.

2. EXPERIMENTAL

$MmNi_{3.4}Co_{0.8}Al_{0.8}$ (Hydrogen Laboratory, UNICAMP, Campinas, Brazil), named Mm, or $LaNi_5$ (Johnson Matthey, 99.9%), alloy particles (ϕ < 38 μm) were added to an ethylene glycol (Synth) containing copper sulfate hexahydrate (Merck) solution at 90ºC, for 12 hours, under vigorous mechanical stirring [10]. The viscous product was heated at a rate of 2º/ min. for 24 hours at 200ºC, in air, in order to achieve the oxide coverage. The material was investigated by Scanning Electron Microscopy (SEM – Jeol JSM-T330A), X-ray diffraction (XRD - Rigaku RINT Ultima+ X-Ray Diffractometer) and Temperature Programmed Reaction (TPR – Micromeritics, Pulse Chemisorb 2705) and Surface Area Determination (BET – Micromeritics) techniques.

The particles were mechanically mixed with Cu powder (Synth 99%) in a 1:3 ratio and cold-pressed at 5 tf cm^{-2} for 15 minutes to form pellets that were used as electrode in the electrochemical experiments. For non-modified and modified electrode material it was used 0.025g of the hydrogen storage alloy dispersed in 0.075g of Cu powder. A current collector obtained from cold pressing 0.9g of Cu powder was employed for all electrodes. The pellets produced presented an average thickness of 3 mm and a geometric surface area of 0.52 cm^2. The electrode materials were charged for 1.5h at 200 mA g^{-1} and discharged at the same current density to -0.5V *vs*. Hg/ HgO reference system. All electrochemical experiments were performed in 6.3 mol dm^{-3} KOH (Merck) solutions at 70ºC in a cell open to the air. The BET surface area for Mm particles was 0.1222 ± 0.0276 m^2 g^{-1} and for Mm surface modified particles was 1.3813 ± 0.0114 m^2 g^{-1}.

3. RESULTS AND DISCUSSION

Fig. 1 presents SEM micrographs of the electrode materials

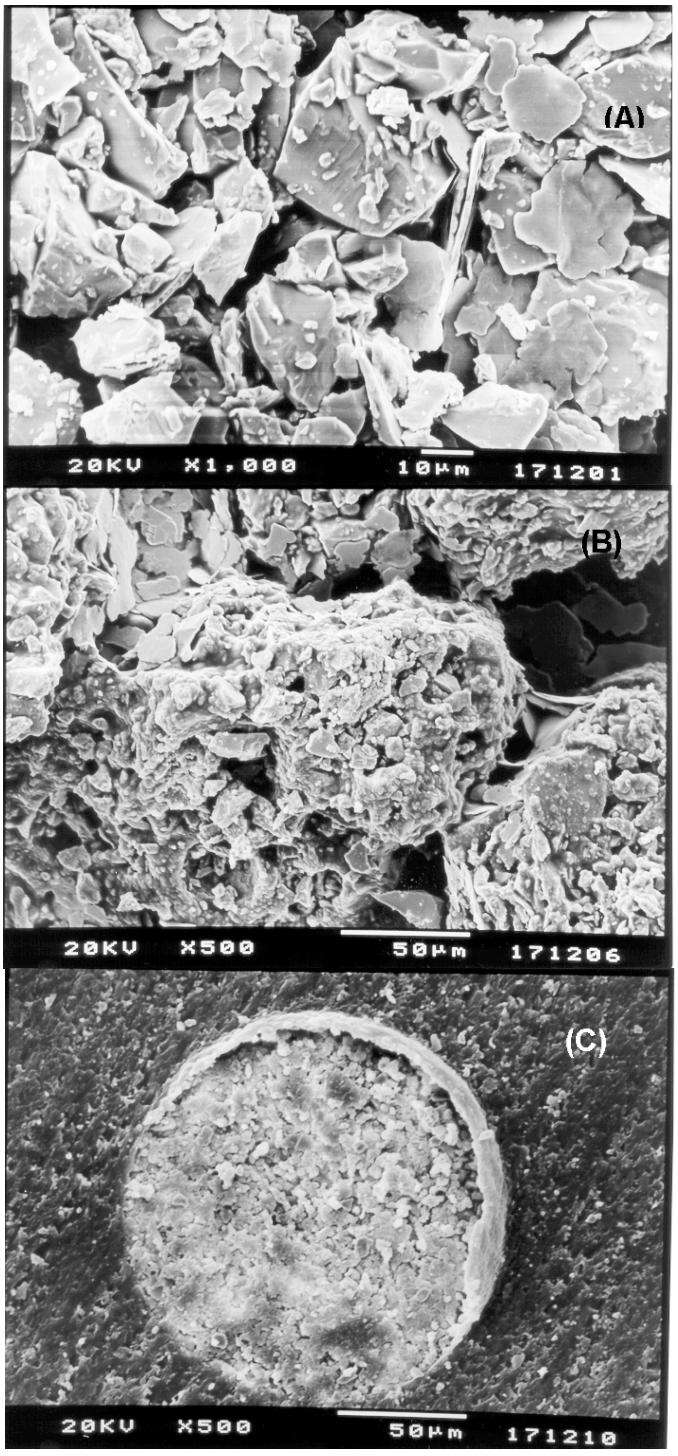

Fig. 1. Scanning electron micrographs of the (A) Mm+Cu powder pellet; (B) Mm surface-modified +Cu powder pellet and (C) Mm particles coated with copper oxides by sol-gel method.

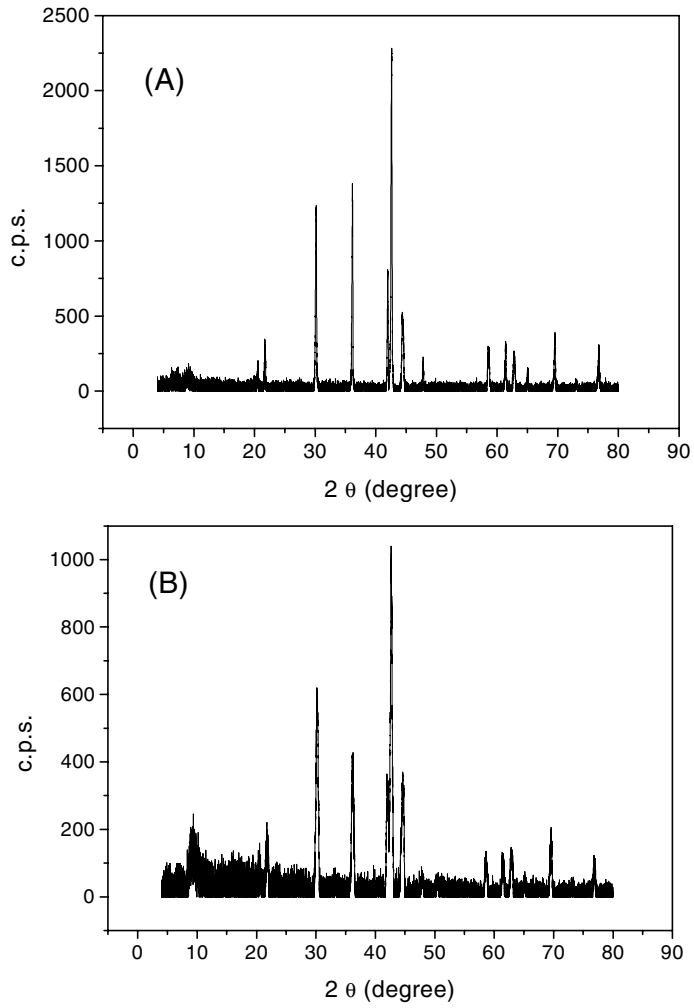

Fig. 2. XRD patterns of Mm particles before (A, powder diffraction setup) and after (B, thin-film setup) the surface modification by sol-gel method. (Cu Kα, 20 KV, 2 mA, 0.200 deg./min, sampling width 0.002deg.)

under investigation. Photographs (A) and (B) were taken from the electrode surface (pellets), respectively for the non-modified and modified particles and (C) is micrograph of the material produced after the surface modification, dispersed in an epoxy resin matrix. In the absence of the surface modification (Fig. 1A), the hydrogen storage particles, identified as the smaller particles, are almost individually distributed over the surface of the metallic copper particles. On the one hand, such a distribution may provide a better current distribution for the intermetallic particles but, on the other, it may enhance the anode deterioration during cycling due to the particle pulverization. Conversely, the surface film application (Fig. 1B) has produced agglomeration of the intermetallic particles where the particles are bound by the copper oxide film. This feature is supposed to minimize the anode deterioration by providing a mechanical support for the volume changes in the particle. In Fig. (C) there is a better view of the hydrogen storage intermetallic particles agglomerate.

Fig. 2 shows the X-Ray Diffraction profiles obtained for the non-modified and modified particles. For non-modified particles it was used an experimental setup for Powder Diffraction while for the modified particles it was used a thin-film setup as an attempt to better characterize the surface film on the particles. Despite all attempts it was not possible to characterize the coating material and only the Mm particle alloy was detected by the X-Ray Diffraction. The data suggest the coating consists on a thin film of amorphous or nanoparticle material that can not be characterized by such technique. It should be pointed out that the sol-gel or polymeric method employed to coat the particles, usually produces small particles, well distributed and improves the homogeneity of the coating film [11]. This feature of the method should assist in the production of a mechanically resistant, expansible and porous support for the hydrogen storage alloy particles.

For a better understanding and characterization of the coating material under reducing conditions (cathodic polarization and hydrogen gas evolution) the temperature programmed reaction experiment was carried out. Fig. 3 displays the corresponding TPR curves. The curve for the surface modified material exhibits two merged reaction peaks in the region of 420ºC, which are related to the copper oxides reaction, and two more peaks (inset), at 150 and 300ºC, related to the hydrogen interaction (absorption) with the Mm alloy, also observed with the unmodified particles. The copper oxides merged peaks should be indicative of a multiphase material that is produced by the sol-gel method. Moreover, by inspection of the expanded region related to the particle interaction with hydrogen, it can be seen that: a) a brand new phase, characterized by the shifting of the lower temperature peak from 220 to 150 ºC, has been produced and b) the total amount of hydrogen interacting with the sample has increased by 49% (compared with the equivalent amount of unmodified sample), which can be associated either with an inhibition of the particle surface oxidation (introduced by the sol-gel method used) or with an enhancement of the hydrogen sorption on the sample due to the new phase formation. Furthermore, the data indicate that the copper oxides on the surface are reduced to metallic copper and, additionally, that this coating does not obstruct the hydrogen from interacting with the Mm particle. From the results presented, it seems that the reduction of the oxides in the coating produces a metallic copper framework that provides the indispensable permeability to hydrogen. However, the conclusive effect of this framework on the Mm particle charging capacity has to be elucidated from the electrochemical evaluation.

A remarkable property of the modified material was the increase in the number of charge/discharge cycles achieved by the electrode material before any surface deterioration was detected. Usually the deterioration process for hydrogen

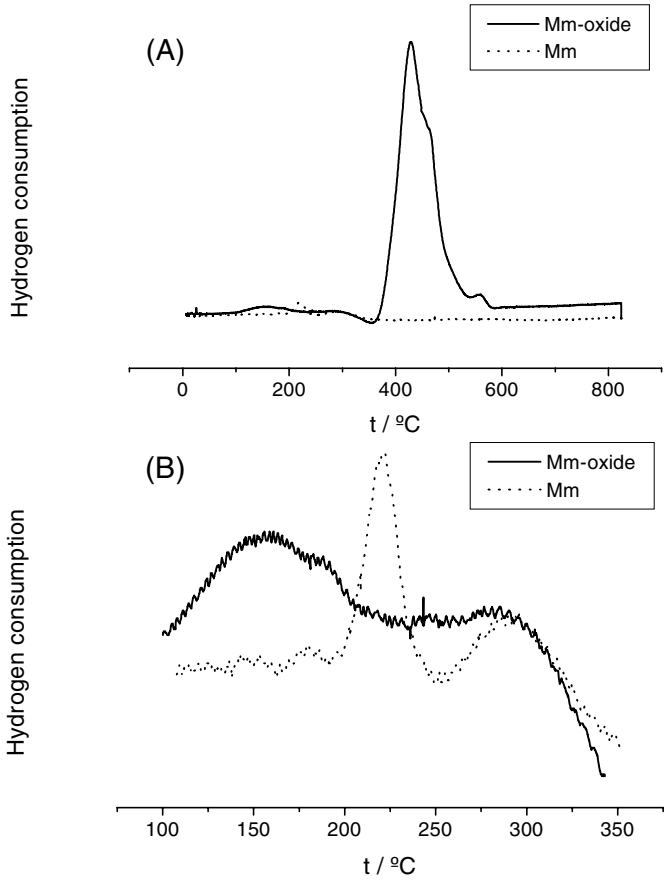

Fig. 3. Temperature programmed reaction spectrum obtained for the Mm and Mm surface modified materials. (A) whole temperature range and (B) expanded low temperature range. (700mmHg, H_2/5% N_2 24 mL min^{-1}, heating rate 5ºC/min., 1.95 mg Mm and 2.25 mg Mm-oxide).

storage materials is due to the particle volume changing in the charge-discharge processes. Such volume changing causes a pulverization of the hydrogen storage alloy particle and, consequently, the electrode deterioration. In order to better evaluate and to accelerate the deterioration of the electrode, it was produced electrode pellets by using pure commercially available $LaNi_5$. Fig. 4 shows the discharge capacity curves obtained for the electrode produced with pure $LaNi_5$ and with $LaNi_5/Cu_xO_y$. One observes that the surface modified electrode reached 100 cycles while the other electrode presented a significant deterioration and a consequent decrease in the electrode performance about the 40th cycle. It must be pointed out that the experimental conditions applied were not worthwhile for obtaining useful discharge capacities, however, those conditions could promote and accelerate the electrode deterioration as earlier mentioned. From the obtained results one can suggest that the surface modification has provided the electrode surface with an additional mechanical support that inhibited the particle deterioration resulted from the volume changing in the charge-discharge cycles.

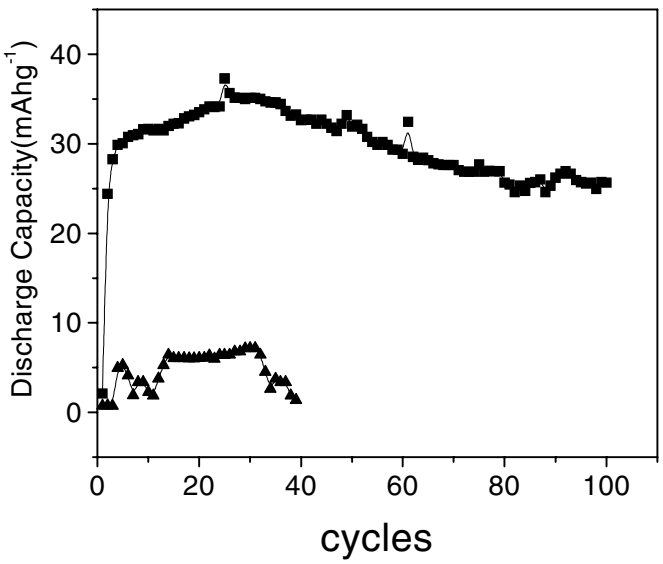

Fig. 4. Discharge capacity curves for pure $LaNi_5$ (▲) and $LaNi_5/Cu_xO_y$ (■) pellets in 6.3 mol dm^{-3} KOH solutions at 70ºC.

Fig. 5 presents the discharge capacity curves for the Mm and surface modified electrodes. It can be observed that the activation process should be the same for the non-modified and modified materials, which is suggested by the profiles of the discharge capacity curves for lower number of cycles [12]. In the experimental conditions used, the electrode Mm/Cu_xO_y reached more than 200 charge/discharge cycles (c.a. 800 h under the cycling process) with no visually detectable surface deterioration. A significant improvement in the charge capacity was observed for the surface modified electrode material. As suggested earlier from the TPR experiment, the

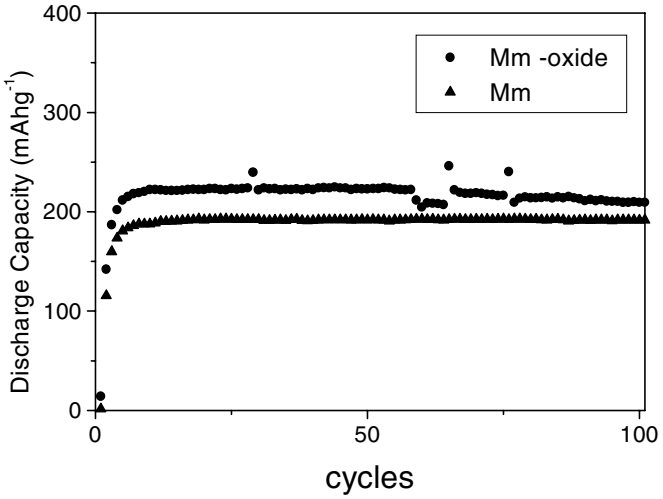

Fig. 5. Discharge capacity curves obtained for the studied materials in 6.3 mol dm^{-3} KOH solutions at 70ºC.

applied surface modification did not inhibit the interaction of hydrogen with the intermetallic particle. The obtained improvement of the electrode discharge capacity can be resulted from: a) the development of a new hydrogen storage phase on the particle surface; b) the inhibition of the surface alloy oxidation due to the presence of the oxide film; c) the improvement of the electrical conductivity among the alloy particles or d) a combination of the mentioned effects. However, more detailed studies must be done to get a deeper understanding of this phenomenon. The promising results obtained from the surface modification applied to hydrogen storage alloys indicate that it should be considered for practical purposes and, therefore, further studies are being performed to obtain a better understanding of the effect of the surface modification effect on the charge capacity and long time operation of the hydrogen storage alloy electrodes.

4. CONCLUSION

The experimental results obtained point to an important role for the copper oxide coating in the charge/discharge process. The sol-gel or polymeric method enabled a homogeneous copper oxide surface coating to be formed. Furthermore, the data obtained suggested that this material consists of nanoparticles. Under reducing conditions (for instance, cathodic polarization and presence of hydrogen gas) it was suggested that the surface oxides are electrochemically/ chemically reduced to produce a metallic framework wrapping the hydrogen storage intermetallic particles. This framework was conveniently permeable to the hydrogen and provided a mechanical support that minimized the electrode deterioration. An appreciable enhancement of the charge capacity could be due to the development of a new hydrogen storage phase or to the inhibition of the surface oxidation introduced by the surface modification methodology.

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