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Various ways including substitution and protection used to improve the cyclability of 'MgNi' electrodes

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Abstract

Three different treatments have been investigated to improve the cyclability in KOH electrolyte of 'MgNi' used as hydrogen storage electrode material for Ni–MH batteries. Whereas hydrophobic molecule grafting does not give significant improvement, replacement of Mg by Ti or coating the 'MgNi' powder with copper in a supercritical CO_2–EtOH mixture increase strongly the resistance of the electrode against hydroxylation: the capacity after 12 cycles is 98% higher for '$Mg_{0.5}Ti_{0.5}Ni$' and 45% higher after coating by a thin copper film in comparison with the raw 'MgNi' material.

Keywords: Mechanical grinding; Electrochemistry; 'MgNi' electrodes; Coating; Supercritical fluid

1. Introduction

The 'MgNi' mixture prepared by mechanical grinding is one of the most promising materials for the negative electrode of Ni–MH batteries, because it can absorb and desorb high quantities of hydrogen at room temperature and normal pressure (i.e. previous studies found 1.8 H per formula unit equivalent to 580 mAh/g) [1–6]. Even if this theoretical capacity is higher than that of $LaNi_5$-based alloys [7], 'MgNi' presents a poor cyclability in KOH electrolyte. The hydroxylation of Mg into $Mg(OH)_2$ during cycling explains this behaviour. In this paper, three ways to protect 'MgNi' are investigated and discussed: (i) replacement of Mg by Ti [8,9], (ii) organic molecule grafting at the particles surface and (iii) coating with copper in supercritical fluid [10].

2. Experimental details

Pure elemental powders (purity$>$99.5%) of Mg, Ni, Ti were introduced with stainless steel balls (ball-to-powder weight ratio=13:1) in vials under an argon atmosphere. They were ground in a Fritsch P5 planetary ball mill at 200 rpm, in a discontinuous mode (12 h milling followed by 12 h rest) [11].

The milled samples were checked by X-ray diffraction (XRD; Philips PW1820 diffractometer using Cu Kα radiation) to obtain information about the phase composition and the crystallinity.

Electrodes were made by mixing the active powder of '$Mg_{1-x}Ti_xNi$' ($0\leq x\leq 0.5$) and graphite (mass ratio=1:1) with 1 wt.% Teflon and by cold pressing this mixture at 100 MPa on a nickel foam. KOH (8.7 M) was used as electrolyte and a $Ni(OH)_2/NiOOH$ electrode as positive one. In order to avoid limitation from this electrode, its capacity was five times larger than that of the negative electrode. A high current density (130 mAh/g corresponding to one fifth of the theoretical capacity) was found during cycling to be close to the application conditions. Charging and discharging were limited, respectively, in time (6 h) and in potential (0.9 V). All measurements were reproduced twice and when the difference exceeded 5%, they were reproduced twice again.

3. Results and discussion

3.1. Replacement of Mg by Ti

A previous work [12] showed that reactive mechanical

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grinding of a (Ti+Ni) mixture gives an amorphous compound that has a relatively low intrinsic capacity (i.e. lower than 150 mAh/g) but a good cycling life (i.e. less than 10% decrease after 80 cycles). Then, replacement of Mg by Ti in 'MgNi' is supposed to improve the cyclability of this mixture.

Preliminary studies on (Mg+Ni) and (Mg_2Ni+Ni) materials showed that under our milling conditions a 72 h discontinuous grinding gives high capacities. This milling duration has then been retained for the experiments on the substitution of Ti for Mg. Four different compositions, '$Mg_{1-x}Ti_xNi$' ($x=0$, 0.1, 0.3 and 0.5) have been investigated.

Fig. 1 shows the X-ray powder patterns of those samples. In each case, the X-ray diffraction patterns show a diffuse peak, characteristic of an amorphous phase, centred around 42°, whose intensity decreases with the magnesium content. A residual peak characteristic of Ni (i.e. 51.8°) could be seen in all the samples but is more evidenced for the non- and the less-substituted ones. The mechanical properties (high ductility) of titanium may be responsible for the increase of amorphisation with this metal content.

Fig. 2 shows the capacity of these materials as a function of cycle number. The high current density used allows to reach a capacity of only 220 mAh/g for 'MgNi'. Replacing Mg by Ti increases strongly the initial capacity of the material. This could be correlated with the former result: if the crystallite size decreases (i.e. the Ti content increases), the number of grain boundaries increases leading to an easier hydriding. The initial capacity of '$Mg_{0.5}Ti_{0.5}Ni$' is slightly lower than those of '$Mg_{0.7}Ti_{0.3}Ni$' presumably due to the lower Mg content (main absorbing element).

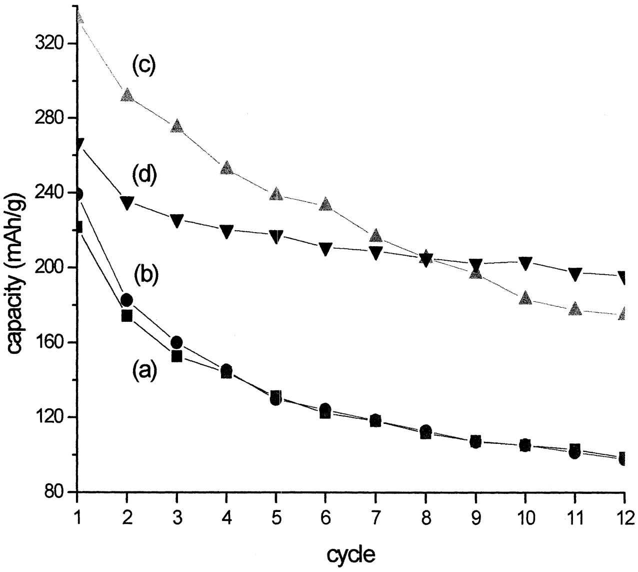

Fig. 2. Electrochemical behaviour of (a) 'MgNi', (b) '$Mg_{0.9}Ti_{0.1}Ni$', (c) '$Mg_{0.7}Ti_{0.3}Ni$' and (d) '$Mg_{0.5}Ti_{0.5}Ni$' after 72 h milling.

The most interesting result concerns the cycling behaviour of the substituted samples. After 12 cycles, the capacities of $Mg_{0.7}Ti_{0.3}Ni$ and $Mg_{0.5}Ti_{0.5}Ni$ are, respectively, 77% and 98% higher than that of non- or less-substituted materials. The most substituted material loses only 26% of its initial capacity while 'MgNi' loses 55%.

The XRD patterns of the electrodes after cycling (recovered in the dehydrided state) are shown in Fig. 3. They have been zoomed to see the peaks ascribed to active material (greater peaks are attributed to graphite and nickel foam). The diffuse peak remains while the peaks ascribed to $Mg(OH)_2$ appear, in contrast to Lei et al. who reported the presence of peaks characteristic of MgO [2]. The intensity of those peaks is rather high for the unsubstituted alloy but decreases with increasing Ti content. As this result cannot be only correlated to the less important

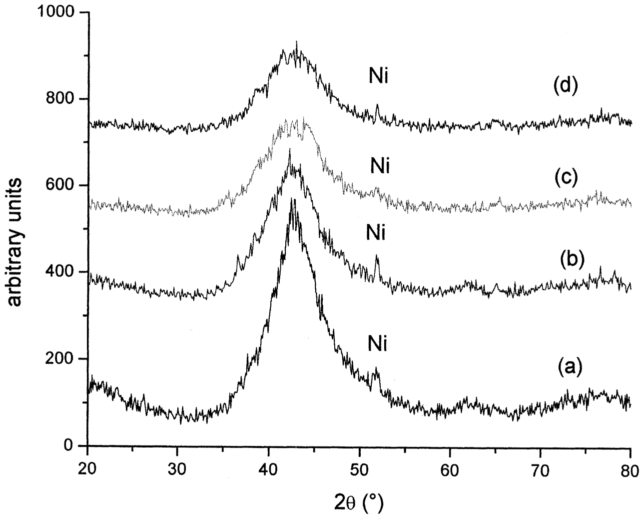

Fig. 1. XRD patterns of (a) 'MgNi', (b) '$Mg_{0.9}Ti_{0.1}Ni$', (c) '$Mg_{0.7}Ti_{0.3}Ni$' and (d) '$Mg_{0.5}Ti_{0.5}Ni$' after 72 h milling.

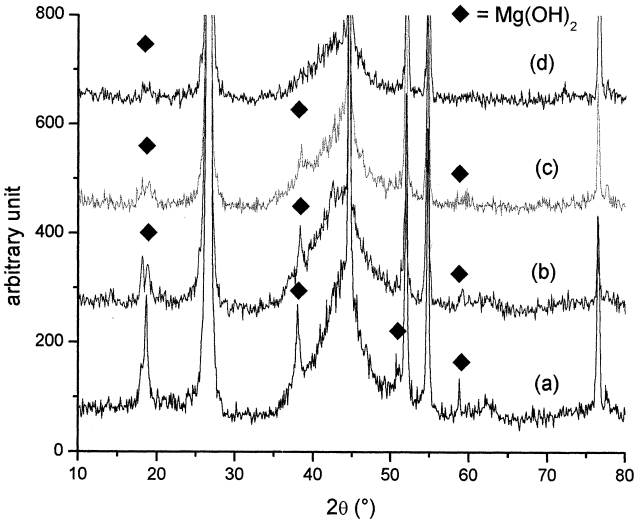

Fig. 3. XRD patterns of (a) 'MgNi', (b) '$Mg_{0.9}Ti_{0.1}Ni$', (c) '$Mg_{0.7}Ti_{0.3}Ni$' and (d) '$Mg_{0.5}Ti_{0.5}Ni$' electrodes after 12 cycles.

percentage of Mg, microprobe and transmission electron microscopy (TEM) analysis are in progress to explain this phenomenon. However, it is clear that titanium protects magnesium against hydroxylation and so improves the cyclability of the electrodes.

3.2. Hydrophobic silane grafting

The grafting of organometallic molecules such as organosilanes is widely used for improving chemical bonding with polymer matrix or for hydrophobizing mineral fillers, for example [13].

The silane group can link with metal oxides at the surface of the particles. If this silane group is linked to a hydrophobic chain, the compounds were expected to repel OH^- anions. Two treatments have been performed onto 'MgNi' using 1H,1H,2H,2H-perfluorooctyltriethoxysilane ($C_{14}H_{19}F_{13}O_3Si$) without and with a preliminary treatment with tetraethoxysilane $[(C_2H_5O)_4Si]$.

XRD patterns do not show any difference between the grafted and the ungrafted samples, as expected if the molecule layer is thin. The wettability tests prove that the grafting has been realised (i.e. raw 'MgNi' sinks in water while it floats after treatment). Electrochemical cycling shows no improvement of the behaviour, both treatments giving the same curves as the unprotected sample (e.g. approximately 240 mAh/g as initial capacity and 70 mAh/g after 12 cycles at C/5 for the first treatment compared with 260 mAh/g and 70 mAh/g, respectively for the raw material).

Two explanations could be suggested: (i) an insufficient coverage of the initial powder surfaces by the silane molecules, and/or (ii) a decrepitation phenomenon during cycling that creates new unprotected surfaces.

Experiments are in progress to try (i) to optimise the covering process and (ii) to protect the materials by a polymerisation all around the particles that could give a more dense film and limit the decrepitation effects.

3.3. Copper deposition in supercritical CO_2

This method has been successfully applied to individualise $SmCo_5$ particles [10]. Copper is a first choice metal because of its high electric conductivity. Moreover, a coating of copper could give a uniform film, dense enough to avoid the attack of OH^- without limiting the hydrogen diffusion.

Operating in supercritical fluid enables to control precisely the distribution and the thickness of the covering. The operating conditions are 200 °C and 200 bar to be over both the supercritical point of the CO_2–EtOH (80:20) solvent and the decomposition temperature of the precursor [copper(II) hexafluoroacetylacetonate hydrate]. Preliminary experiments have been conducted using 'MgNi' milled discontinuously for 96 h, with a weight ratio 'MgNi'/precursor=1/1 (i.e. 'MgNi'/Cu=5/1).

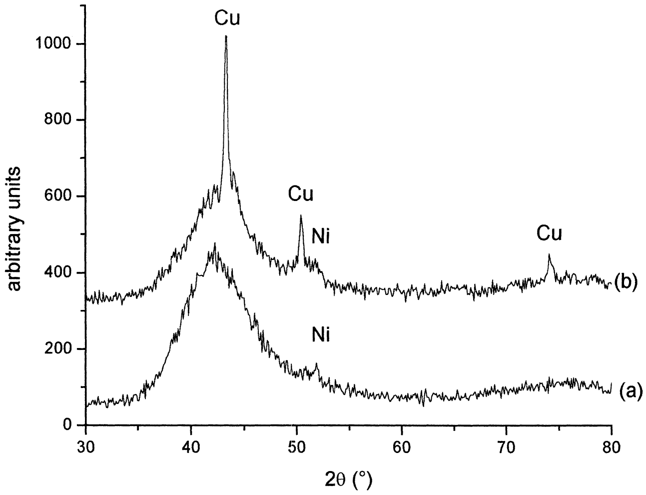

Fig. 4. XRD patterns of (a) raw and (b) copper coated 'MgNi' milled for 96 h discontinuously.

As expected, the peaks characteristic of Cu appear on the XRD patterns of the treated material (Fig. 4), highlighting the decomposition of the precursor in metallic copper.

The electrochemical behaviour is shown in Fig. 5. The lower (240 mAh/g instead of 260 mAh/g) initial capacity obtained after treatment could be explained by the presence of the copper layer that does not absorb hydrogen but increases slightly the mass of the sample. After three cycles, the capacity of the coated powder is 30 mAh/g higher than that of the raw material and this value is kept constant until the twelfth cycle, highlighting a partial protection of the material. This result cannot be satisfying

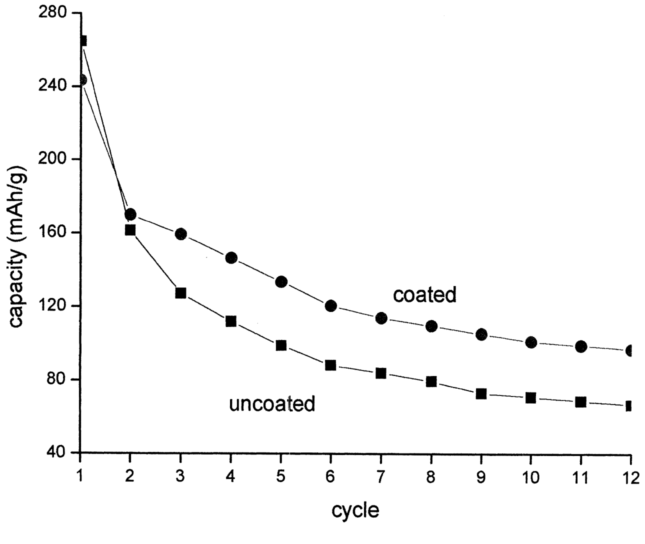

Fig. 5. Electrochemical behaviour of raw and copper coated 'MgNi' milled for 96 h discontinuously.

but suggests that a best protection could be obtained by increasing the relative quantity of precursor.

4. Conclusion

Through the three ways envisaged to protect ‘MgNi’ against hydroxylation, replacing Mg by Ti (which also ameliorates the milling efficiency) and coating the particles with copper in supercritical fluid show a significant improvement in the cycling behaviour (leading, respectively, to 98 and 45% higher capacities than ‘MgNi’ after 12 cycles). Nevertheless, this last treatment has to be optimised by changing the weight ratio ‘MgNi’/precursor. A better cycling life is expected by combining those two protections, i.e. coating with copper the titanium substituted mixtures.

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