

Performance and characterization of metal hydride electrodes in nickel/metal hydride batteries

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Abstract

In this paper, the metal hydride electrodes used in nickel/metal hydride batteries have been investigated, especially the surface properties of the electrodes, using cyclic voltammetry, electrochemical impedance spectrum, in situ laser-scanning photo-electrochemical microscopy (PEM) and ex situ scanning tunnelling microscope (STM). Our results indicate clearly that surface treatment has a great effect on the performance of the electrodes, affecting such as initial discharge capacity and capacity maintenance. Some considerations about design of the surface treatment method are described. In addition, cathodic and anodic photocurrents have been observed in the potential regions of hydride formation and hydride oxidation by using PEM techniques. Ex situ STM results showed that some Ni cluster-like compounds are formed on the electrode surface after treatment with hydrofluoric acid.

Keywords: Metal hydrides; Electrode reactions

1. Introduction

With the increasing demand for portable electronic devices and an improvement of our living environment, the development of 'green batteries' becomes more and more important in the world. The nickel/metal hydride battery is one of the 'green batteries' which give high rate capability, longer cycle life, no memory effect and no pollution. In studies of nickel/metal hydride batteries, much research has focussed on the metal hydride electrodes, especially on the preparation, performance and surface properties of the materials [1,2]. However, if the performance of the batteries needs further improvement, more fundamental studies are still needed on the electrochemical properties of the metal hydride electrodes, especially on the activation and stabilities of the materials. In this paper, we report the results of characterization of AB5-type metal hydride electrodes using different electrochemical methods and in situ or ex situ scanning probe methods. The correlation between surface properties and performance of the electrodes is stressed in this work.

2. Experimental

A solid AB5-type alloy ($AB5 = Mm(NiMnAlCo)_5$, where Mm is Mischmetal) was made into a cylindrical electrode

with a diameter of 4 mm. Then, the cylinder was pressed into a Teflon tube and used as a working electrode in cyclic voltammetric, impedance and spectroelectrochemical measurements. A slice of nickel metal and a mercury/mercuric oxide couple (Hg/HgO , 30%KOH) were used as counter and reference electrodes, respectively. The power electrodes were prepared according to the following procedure.

Approximately 0.3 g of powder was mixed with a suitable amount of binder (CMC:PTFE = 0.225:1) and cold-pressed onto nickel foam (area = 1 cm², $P = 3000$ kg mm⁻²).

Sometimes, copper or nickel powders were added to the mixture in the ratio of about 10–20%, as electrical conductors. The AB5-type alloy powder without any metal coating was provided by Tianjin Power Sources Research Institute as a gift. The electrolyte was 30% KOH + 1% LiOH.

All cyclic voltammetric and impedance experiments were performed by using an IM6 impedance analyzer (Zahner-electrik Co. Germany). The photo-electrochemical microscope (PEM) was built in the laboratory. The details of this instrument are described in a previous publication [3]. Some modifications were done in this work, i.e. a new laser system model 2017 (Spectra Physics Co. USA) was used. The power of the laser (wavelength = 514.5 nm) before focussing is 0.8 W, and the diameter of the focussed laser beam is about 100 μm. The step-length is 200 μm. The scanning tunnelling microscopy (STM) measurements were carried out using a

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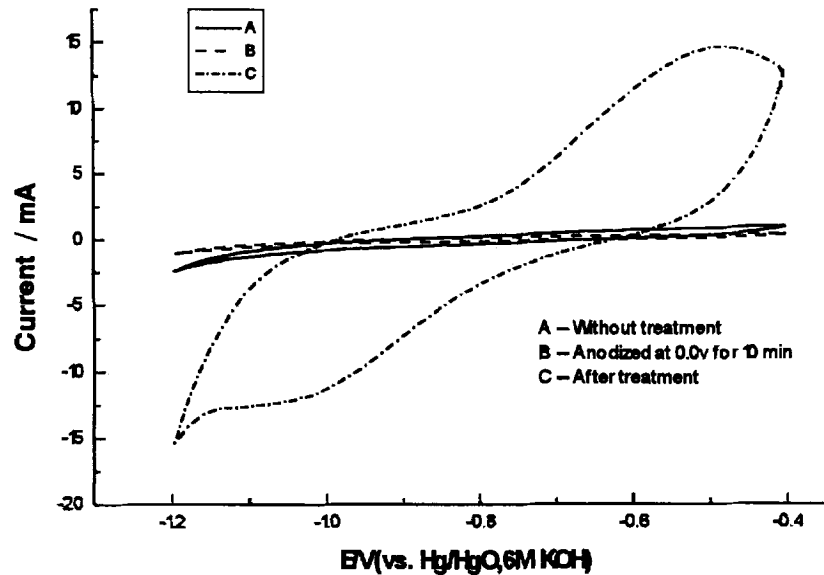


Fig. 1. Cyclic voltammograms in 6 M KOH + 1% LIOH solution of solid electrodes with and without surface treatment. A, without treatment; B, after anodizing at 0.0 V vs. Hg/HgO, 6 M KOH for 10 min; C, after surface treatment.

Nanoscope IIIa (Digital Instruments, USA). If there is no specified notation, the treatment technique described in the paper is the No. 2 method in our planned patent application [4]. It includes treatment with acidic solution containing various types of inorganic ions.

3. Results and discussion

3.1. A comparison of cyclic voltammetry and impedance spectroscopy of the electrodes, with and without surface treatment

It is well known that surface treatment plays an important role in the performance of metal hydride electrodes, such as

initial discharge capacity and cyclic stability. Most experiments have suggested that a nickel-rich surface layer is useful to get high electrochemical activity, so some 'activation' techniques have been designed for this purpose such as 'dissolution' and 'reduction'. In addition, although electroless deposition of copper and nickel on alloy powders has been used commercially, whether it is necessary and worthwhile to put a coating of metals on to the alloy can be disputed.

In our view, the 'dissolution' method, using hot KOH solution, needs several hours and the high temperature may cause the repassivation of the alloy surface. The 'reduction' method, using Na^- or KHB_4 , is not economical for industrial production. In addition, if one only wants to change the 'activation' characteristics but not the cyclic stability of the electrodes, it is not good enough for electrode performance in a

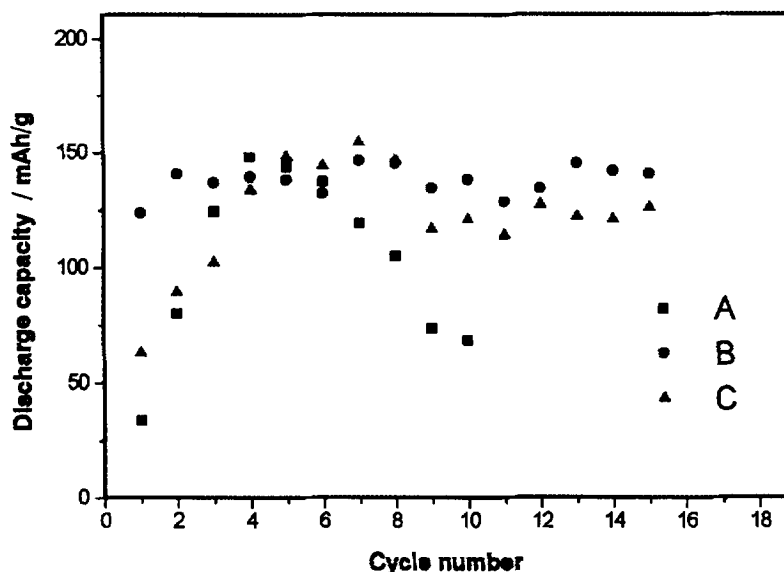


Fig. 2. Discharge capacity vs. cycle number for alloy powder electrodes in 6 M KOH + 1% LIOH solution with different surface treatments. A, without treatment; B, after treatment using method 1; C, after treatment using method 2.

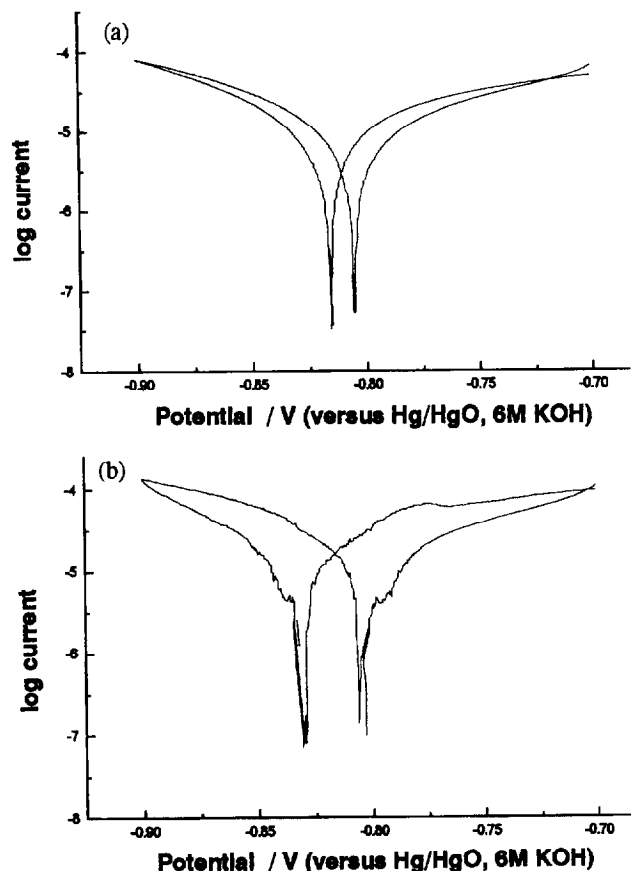


Fig. 3. Tafel curves of solid electrodes with and without surface treatment. (a) Without treatment; (b) with treatment using method 2.

practical situation. Therefore, we have devised a novel surface treatment technique [4] for AB5-type electrode materials.

The solid sample that we have used was a gift from Nankai University, China. After systematically considering possible

Table 1

A list of Tafel parameters of the electrodes with and without surface treatment. Scan rate: $V=0.25 \text{ mV s}^{-1}$

	E_a, E_c (V)	Exchange current ($\text{A cm}^{-2} \times 10^6$)	Symmetry factor α
Electrode 1 (without surface treatment)	-0.802 -0.817	2.247 4.348	0.31 0.776
Electrode 2 (with surface treatment)	-0.794 -0.830	4.084 7.081	0.233 0.653

factors that would affect the electrode performance, we originated the following idea.

The performance of metal hydride electrodes depends greatly on their surface properties, so a functional layer should be formed on the electrode surface in order to get satisfactory performance out of the electrodes. Ideally, functional layers should consist of two components: one, an active electrocatalyst (to promote the formation of metal hydride and prevent fast evolution of hydrogen gas by the Tafel reaction); the other, a protection layer which can decrease the corrosion rate of the active material and electrode substrate.

The experimental results have proved that this strategy is correct. Fig. 1 shows a set of cyclic voltammograms of AB5-type solid electrodes with and without surface treatment. It is shown that the peak current of oxidation of metal hydride on treated electrodes, using our method, is about fifteen times larger than that of an untreated electrode. However, if the electrodes had been anodized at 0.0 V for 10 min, the rate of hydrogen formation and the oxidation processes is even lower than that of untreated electrodes, due to a thicker passive film being formed on the electrode surface.

In order to check the practical significance of the effects of these pre-treatments, some hydrogen-storage powders

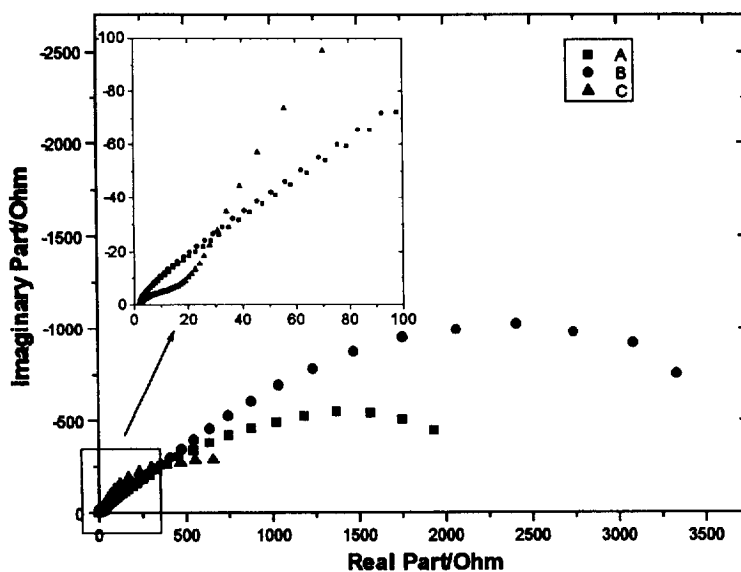


Fig. 4. Comparison of electrochemical impedance spectra (EIS, Nyquist plot measured at -0.8 V) of electrodes with different surface treatments. A, without treatment; B, the electrode was anodized at 0.0 V for 10 min; C, after treatment.

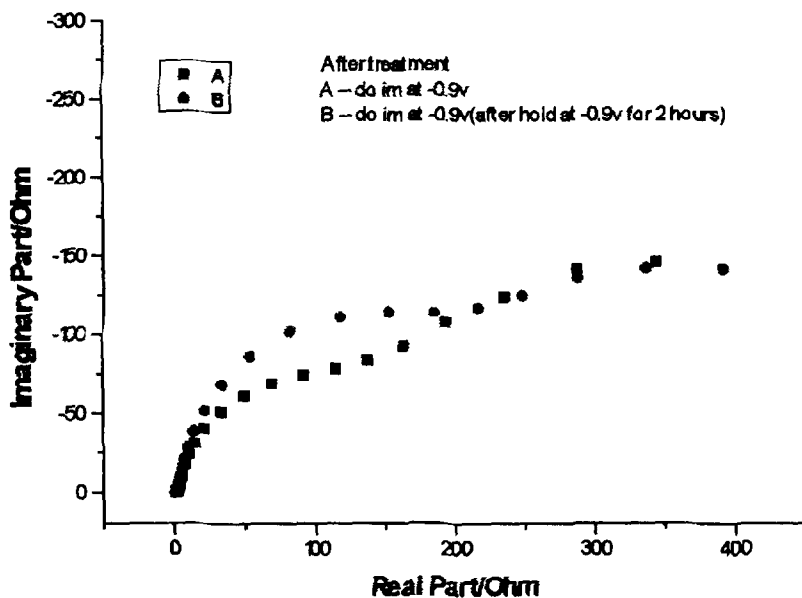


Fig. 5. Time-dependent electrochemical impedance spectra of treated electrodes. A, immediately after the electrode had reached -0.9 V; B, after the electrode had been charged at -0.9 V for 2 h.

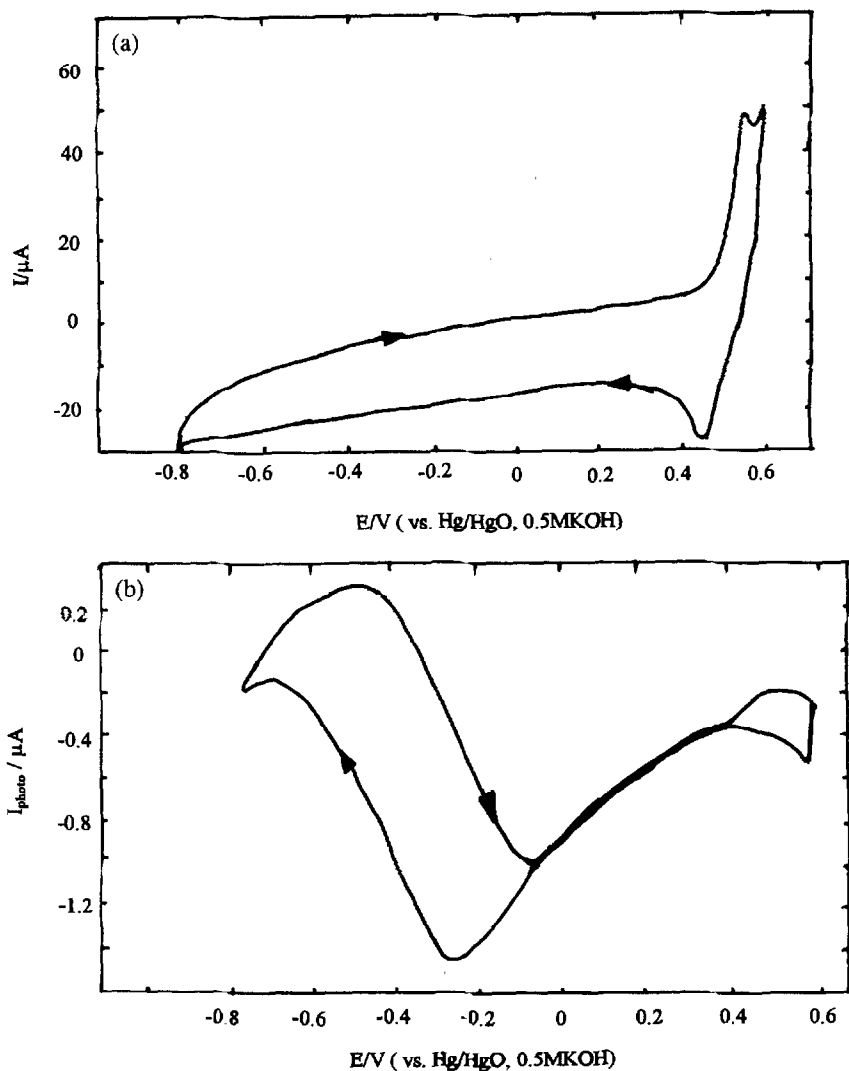


Fig. 6. Cyclic voltammogram (a) and a simultaneously recorded photocurrent/potential curve (b) of the ABS-type solid electrode in 0.5 M KOH solution. The potential scan rate is 5 mV s^{-1} .

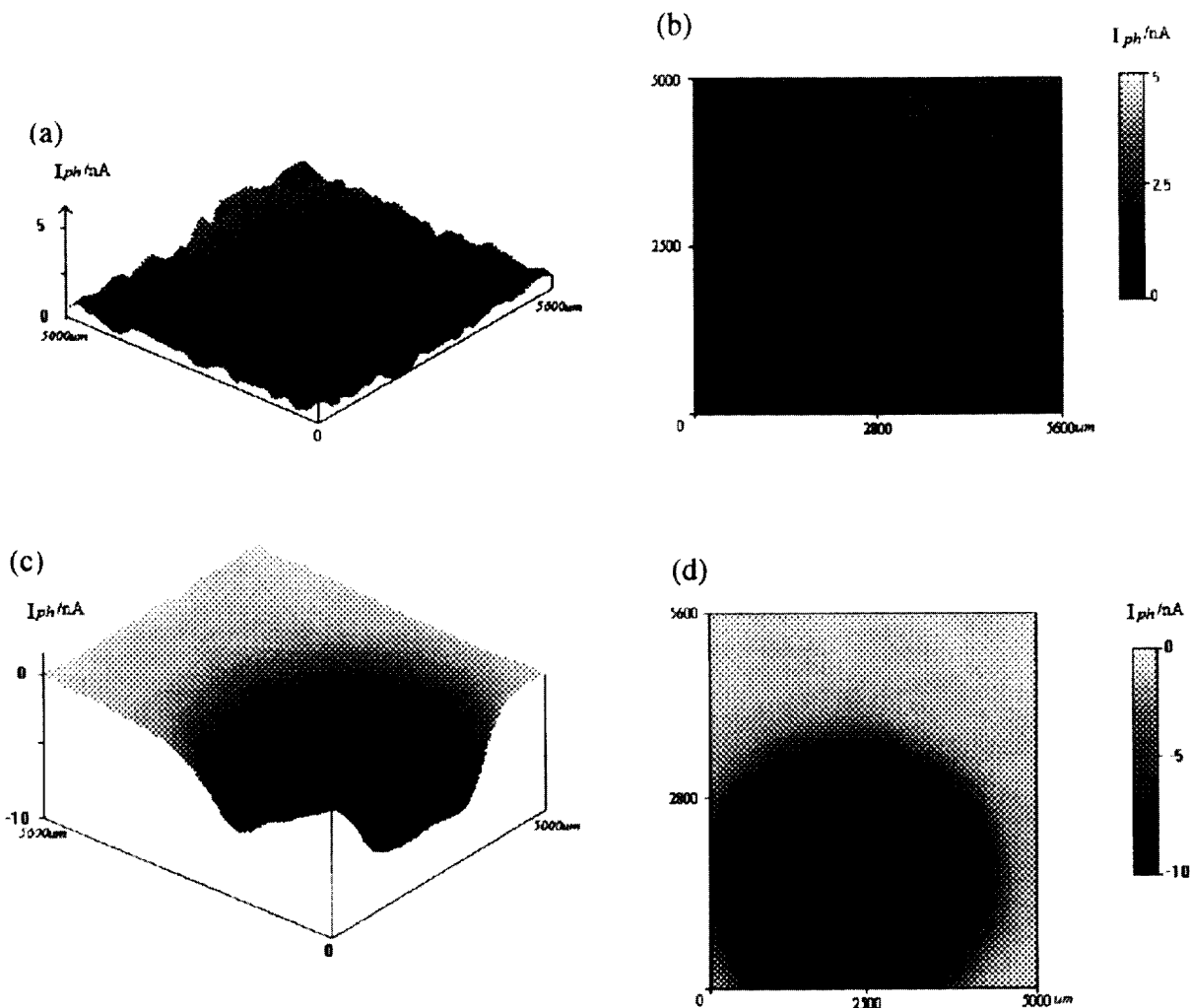


Fig. 7. In situ laser-scanning photo-electrochemical microscopic graphs (a, c) and images (b, d) of AB5-type solid electrodes. The potential was held at -0.3 V before charging (a and b). (c) and (d) were obtained after charging at -0.85 V for 15 min.

were also tested. Fig. 2 shows a set of discharge capacity versus cyclic times for alloy powders with and without surface treatment within an open-to-the-air test battery. The figure shows that surface treatment has a great effect on the performance of the electrodes, especially on the initial discharge capacity and on capacity maintenance.

In addition, the effects of surface pre-treatment on the performance of the electrodes have also been evaluated and analyzed using Tafel curves and electrochemical impedance spectra (EIS), respectively. Fig. 3 shows Tafel curves of the electrodes with and without surface treatment. Table 1 shows calculated kinetic parameters such as the exchange current density and symmetry factor α .

From Table 1, it can be observed that after surface treatment, the exchange current density (i_0) of the electrodes becomes larger and the symmetry factor decreases. These results indicate an improvement of electrocatalytic activity in the treated electrode. Fig. 4 shows a comparison of the electrochemical impedance spectra of surface treated, anodized and untreated electrodes. It is observed that the charge-transfer impedance of the untreated electrodes is higher than that of treated electrodes. This suggests that the passivation of the

alloy impedes the electrochemical reaction of hydrogen formation. If the electrode is anodized at 0.0 V for 10 min, the charge-transfer impedance is even higher than that of the untreated electrode, indicating that the anodic film determines the amount of charge-transfer impedance in this case.

In addition, if the time-dependent impedance is measured (Fig. 5), then it is found that the imaginary part of the impedance becomes higher, accompanied by an increase in the amount of hydrogen stored.

Whether it is possible to use the capacitance change of the metal hydride electrode during charging as a measurement of the amount of hydrogen stored in the alloy will be an interesting subject to investigate.

3.2. In situ characterization of surface films on metal hydride electrodes

In order to get more insight into the surface properties of the electrode, the AB5 alloy electrodes have also been investigated using in situ scanning probe microscopic techniques such as laser-scanning photo-electrochemical microscopy (PEM) as well as STM methods.

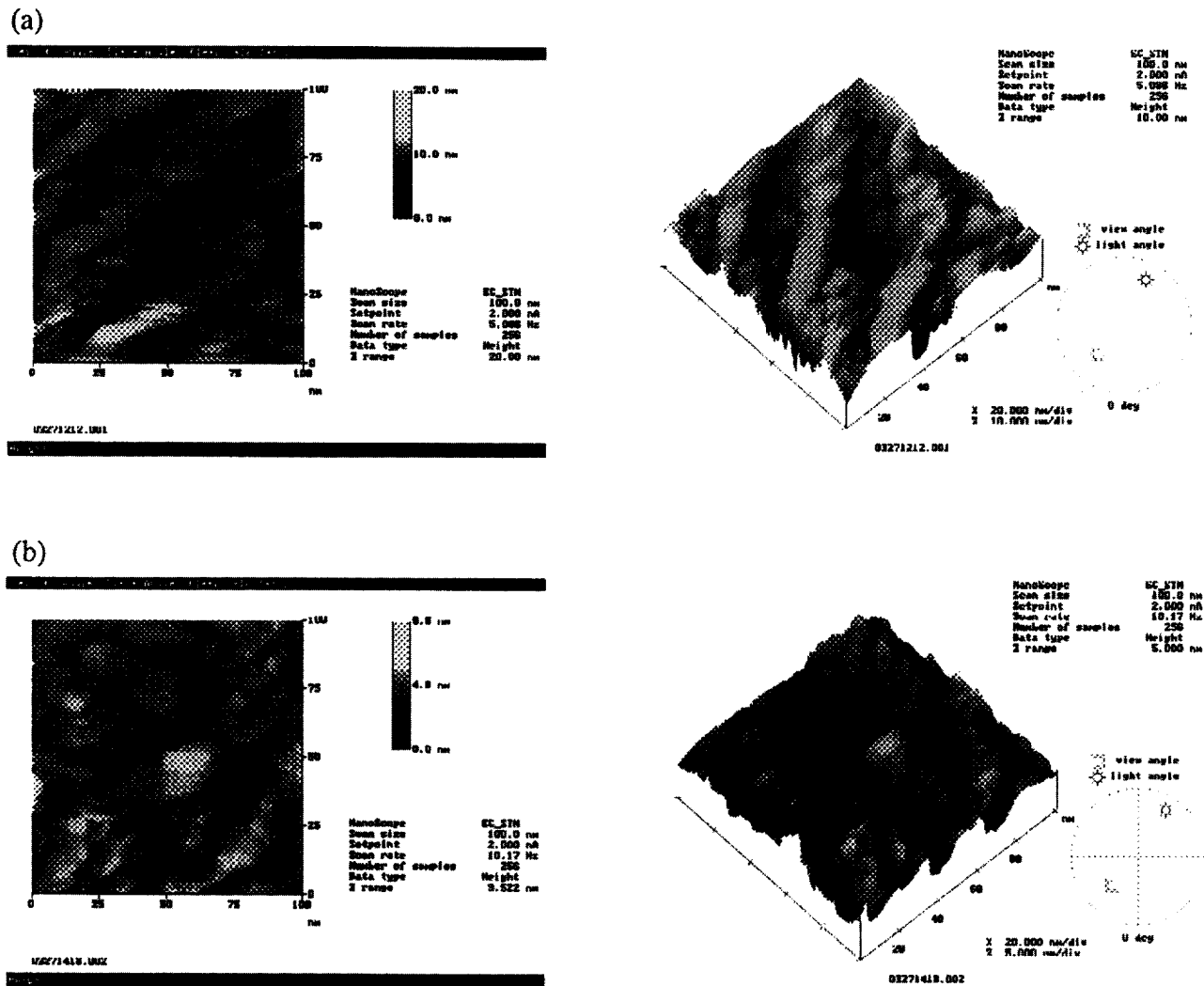


Fig. 8. Ex situ scanning tunnelling microscopic (STM) images of AB5-type solid electrodes before and after treatment in 1% HF solution for 10 min. (a) Before treatment; (b) after treatment.

At first, the photo-electrochemical behaviour of the alloy electrodes was investigated. Although some results have been reported about the photo-electrochemical behaviour of passive films on pure nickel electrodes in alkaline solution [5,6] and on pure NiO film in acid solution, the semiconducting properties of nickel oxides or hydroxides have not been totally clarified. Fig. 6 shows a cyclic voltammogram (a) and a simultaneously recorded photocurrent–potential curve (b) of an AB5 electrode in 0.5 M KOH solution. From the figure, it can be observed that a cathodic photocurrent peak appeared at about -0.3 V. However, when the potential was reversed at -0.8 V, an anodic photocurrent peak appeared at about -0.6 V. Apparently, besides the macro photocurrent of the total electrode, the micro-activity of the electrodes is also worth investigating. Fig. 7 shows two photo-electrochemical microscopic (PEM) images for original electrodes before and after hydrogen storage. It can be observed that the photocurrent is cathodic at -0.3 V before hydrogen storage, however, the photocurrent changes its sign to anodic after charging for 15 min at -0.85 V. Some spatial variations can

be observed from the PEM graphs, reflecting the heterogeneous photo-electrochemical activity of the electrode surface.

At this stage, it is tentatively considered that the cathodic photo-reaction (cathodic photocurrent) corresponds to hydrogen–hydride formation, and that the anodic photo-reaction may be attributed to a photo-assisted oxidation reaction of hydrogen stored in the alloy, i.e. oxidation of hydride.

However, we did not observe an anodic photocurrent on the oxidized form of the passive films on alloy electrodes at potentials higher than $+0.3$ V (versus Hg/HgO, 6 M KOH) as found by other people [6] on pure nickel electrodes, because of the strong noise accompanying the evolution of oxygen.

We have also done similar PEM experiments in 6 M MOH solution. However, the signal to noise ratio is not good enough for resolution, due to a weak signal. The details of the different sign of the photocurrent and an analysis will be investigated and reported later.

In addition, the changes in microstructure of the alloy electrode surface with and without treatment with 1% HF solution

were also investigated using ex situ STM techniques (Fig. 8). It was found that the surface state of the electrodes is quite different for treated and untreated examples. For example, only mechanical damage on the electrode surface is seen before treatment, however, some Ni cluster-like compounds can be distinguished. It is thought that these cluster-like compounds may play an important role in the activation of the electrodes.

4. Conclusions

In conclusion, it has been demonstrated that the surface state of metal hydride electrodes can be improved by using several surface treatment techniques. In order to do this, we may need to:

(i) remove the passive film on the alloy powders which is formed in storage or during production;

(b) put some active components and a protection layer on the alloys.

An investigation of passive films on AB5 alloy using in situ laser-scanning photo-electrochemical microscopy has been carried out for the first time in this work. Some cathodic and anodic photocurrents have been observed in the potential

regions of hydride formation and hydride oxidation. Ex situ STM results showed that some Ni cluster-like compounds are formed on the electrode surface after treatment with hydrofluoric acid.

Acknowledgements

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