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In-situ and ex-situ characterization of surface oxide films on AB_5-type metal hydride electrodes

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Abstract

The surface oxide films on AB_5-type metal hydride electrodes have been investigated by means of in-situ and ex-situ techniques such as in-situ laser scanning photoelectrochemical microscopy (PEM), ex-situ scanning tunneling microscopy (STM) and in-situ confocal Raman spectroscopy. The results indicated that the growth of surface oxide films can be monitored by using in-situ photoelectrochemical methods. Both laser-scanning photoelectrochemical microscopic and confocal Raman microscopic results showed that crack sites on the electrode surface are more feasible to be oxidized than other smooth sites under electrochemical conditions. In addition, the primary surface oxide layer on fresh metal hydride electrode was found to be composite metal oxides with nickel oxide as its main component.

Keywords: Metal-hydride electrodes; Surface properties; Surface oxide film; In-situ spectroscopic characterization

1. Introduction

It is well known that the surface oxide film formed on AB_5-type metal hydride electrodes, used in commercial MH/Ni batteries is a key factor affecting its performance [1]. But up to now, little work has been done on the characterization of the surface morphology and surface oxide film on the metal hydride electrodes [2–5]. It is necessary to understand more about the mechanism of formation, growth and properties of the surface oxide film for adopting proper methods to improve the electrochemical activity and stability of the electrodes. In our previous work [4,5], we have reported the results of characterization of the surface oxide film on the metal hydride electrodes by using ex-situ scanning tunneling microscopy (STM) and in-situ laser scanning photoelectrochemical microscopy (PEM) techniques. In this paper, we will report some new results about the studies of surface oxide films on the metal hydride electrodes in 30% KOH+1% LiOH solution by using ex-situ STM, and in-situ PEM and in-situ confocal microprobe Raman spectroscopy.

2. Experimental

AB_5-type hydrogen-storage alloy ($La_{0.54}Ce_{0.32}Pr_{0.03}Nd_{0.11}Ni_{3.5}Co_{0.8}Mn_{0.4}Al_{0.3}$) ingots were machined to cylinder rods with a diameter of 1 mm, which were sealed into Teflon sheaths and used as working electrodes. One end of the electrodes was abraded with successively finer grades of silicon carbide paper, and finally polished to a mirror finish with 0.05 μm aluminum oxide. Electrodes used in the PEM experiments were not polished with aluminum oxide. The surface of the electrodes were thoroughly rinsed with distilled deionized water, and dried by high purity nitrogen gas before STM experiments. A slice of platinum wire and Hg/HgO (30% KOH) were used as counter electrode and reference electrode, respectively. The electrolyte of the cell was 30% KOH+1% LiOH solution. The STM measurements were carried out using a Nanoscope IIIa (Digital Instruments, USA). The PEM measurement system was built in the lab, the details of the system and experiments were described in the previous publications [6,7]. The excitation light was provided by a Model 2017 Argon ion laser (514.5 nm, Spectra Physics Co., USA), the power of the focused laser spot was 10 mW with a diameter of about 10 μm during the laser-scanning process (step-length of laser-scanning is 20 μm) on the electrode surface. Raman spectra were obtained by using a confocal microprobe Raman system

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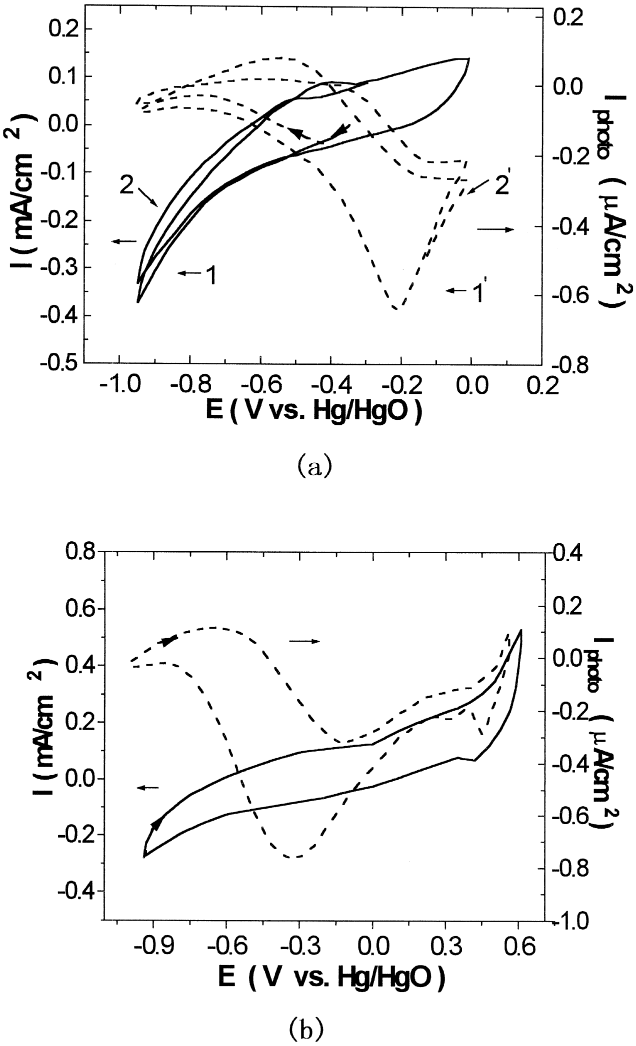
(LabRam I from Dilor, France). The excitation light was from an air cooled He–Ne laser (632.8 nm) with the power of 13 mW and a spot of diameter at about 3 μm.

3. Results and discussion

3.1. Photoelectrochemical behaviour of surface oxide films on AB_5-type metal hydride electrodes

Since most metal oxides are semiconductors, it is interesting to investigate the semiconducting properties of the surface oxide film formed on the metal hydride electrode by using in-situ photoelectrochemical methods [5,6].

Fig. 1 shows potential–current curves and simultaneous recorded photocurrent–potential curves of the electrodes in different potential regions in 30% KOH+1% LiOH solution at potential scanning rate of 3 mV/s. In Fig. 1a, when the anodic limit of the potential-sweeping region was set at 0.0 V, we observed a couple of photocurrent peaks where anodic and cathodic photocurrent peaks were located at −0.55 V and −0.18 V in the second potential cycles, respectively. In addition, besides the cathodic photocurrent being shifted to −0.3 V, another anodic photocurrent peak and a small cathodic photocurrent peak appeared at about +0.33 V and +0.5 V, respectively, when the anodic limit of the potential-sweeping region was extended to +0.65 V (Fig. 1b). As a comparison, a set of experiments was done using pure manganese, cobalt and nickel electrodes. Though the properties of surface oxides formed on the metal hydride electrodes may not be due to direct addition of the contribution from single manganese oxides, cobalt oxides and nickel oxides, it is still reasonable to assume that the photocurrent peaks appearing at −0.55 V and −0.18 V arising from the photoelectrochemical reaction on the semiconducting manganese and/or cobalt oxides based on our results (detailed photoelectrochemical results will be reported later). In our previous work [5], the photoelectrochemical reactions were proposed as the photo-reduction of oxygen (~−0.3 V) and the photo-oxidation of adsorbed hydrogen in the electrodes (−0.55 V). In addition, oxidation and reduction of nickel and/or manganese into different valent oxides are tentatively attributed to the origins of anodic and cathodic photocurrent peaks at about +0.33 V and +0.5 V, respectively. Anyway, the above results showed that the in-situ photoelectrochemical method is very sensitive to the formation and growth/transformation of surface oxide films on metal hydride electrodes.



(a)

(b)

Fig. 1. Potential–current curves and simultaneous recorded photocurrent–potential curves of the metal hydride electrode in the different potential regions in 30% KOH+1% LiOH solution, potential sweeping rate is 3 mV/s. (a) −0.9–0.0 V; (b) −0.9–0.6 V.

3.2. Measurements of surface morphological changes and formation of oxide films on crack sites

During long charge–discharge cycles, the metal hydride electrodes (i.e. large hydrogen-storage powders) are often cracked and pulverized into smaller powder electrodes due to mechanical tensile formed in the adsorption/desorption processes of hydrogen into/from crystal lattice of the alloys. Fig. 2a shows an STM image of the freshly polished surface of the metal hydride electrode. It shows clearly that the polished electrode's surface was composed of crystalline particles with diameter between 4 and 10 nm. For the investigation of surface morphology in the initial charge–discharge cycles, the electrode was cathodically polarized at −0.95 V (vs. Hg/HgO) for 20 min at first and then potentially-cycled in the potential region of −0.95 to −0.6 V in 30% KOH+1% LiOH solution at potential sweeping rate of 25 mV/s. From the increase in peak current in the cyclic voltammogram after the cathodic polarization, it is inferred that the surface of the electrode was activated. It can be seen from the STM image (Fig. 2b) that the crystalline particles agglomerate together on the electrode surface. In addition, some cracks appeared on

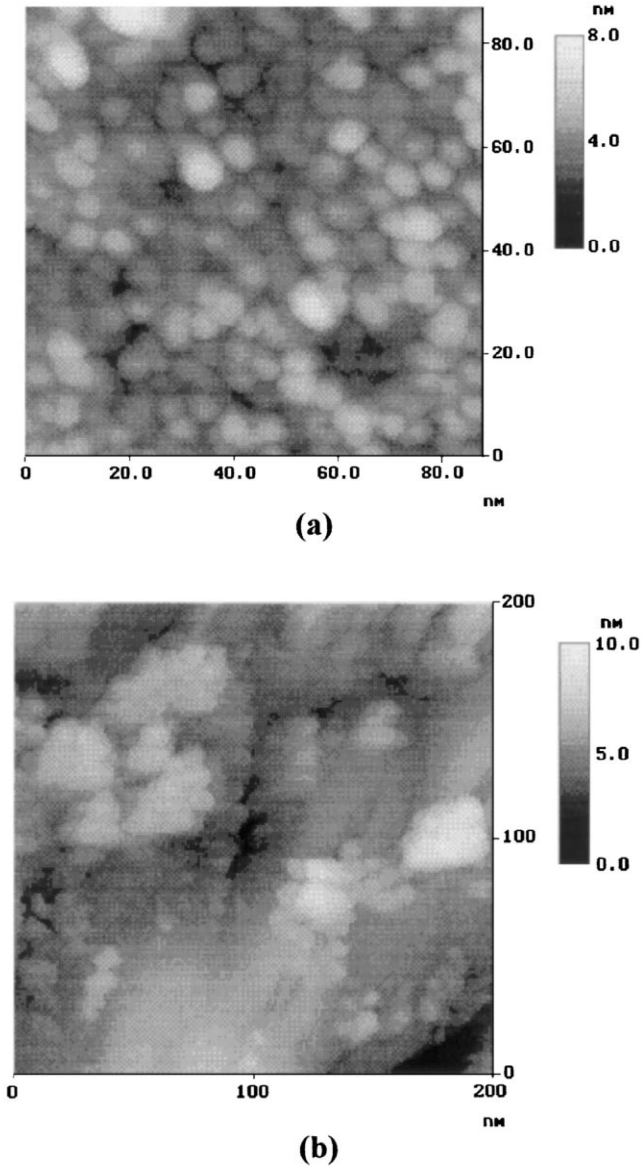


Fig. 2. Ex-situ STM images of the metal hydride electrode surface. (a) Polished surface of the metal hydride electrode, (b) after cathodic polarization at −0.95 V (vs. Hg/HgO) for 20 min and then cycled in the potential region of −0.95–0.6 V at a sweeping rate of 25 mV/s.

the electrode surface after more cathodic polarization and charge discharge cycles. Apparently, the generation of cracks on the surface not only increases the activation performance of the electrodes but may also affect the formation of oxide films.

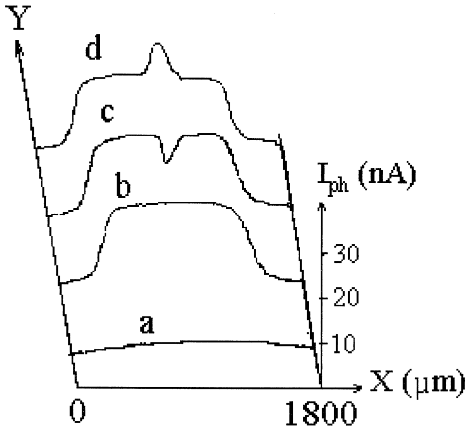


Fig. 3. In-situ line-scan PEM graphs of the metal hydride electrode in 30% KOH+1% LiOH solution, the photocurrent profile curves were measured at −0.55 V. (a) Polished electrode, (b) after five cycles of potential sweeping, (c) just after making artificial-crack, (d) after further potential cycles.

Although it can be easily imagined that more oxides will be formed on the crack sites, it is certainly interesting to do in-situ monitoring of the formation and growth of oxides on the crack sites on the electrode surface. Fig. 3 shows the line-scan PEM graph at −0.55 V. In the figure, it can be observed that the photocurrent is nearly zero before the formation of surface oxide film (curve a). When a stable oxide film was formed on the electrode surface (i.e. the electrodes were potentially-cycled in the potential region between −1.0 and +0.55 V at a scanning rate of 3 mV/s, the photocurrent became quite stable with further increasing cycle numbers), a big photocurrent was observed in the electrode area (curve b), indicating a thick oxide film was formed on the electrode surface. Curve c is obtained after making an artificial-crack on the surface of the electrode using a needle; it can be seen that a smaller photocurrent dip appeared at the crack site. The decrease of the photocurrent could be attributed to the thin oxide film formed on the fresh crack site since the photocurrent is proportional to the thickness of the oxide film under suitable conditions [7]. After that, if the electrodes were cycled between −1.0 and +0.55 V for several times, it can be observed that a higher photocurrent peak appeared in the crack site (curve d), indicating more oxides were formed on the crack site due to higher current density on the crack site when the passive film was abruptly broken in the local area [7]. Although photoelectrochemical methods could not provide directly the composition of the oxide films, the above results showed again that in-situ laser-scanning photoelectrochemical microscopic method is very sensitive to the local changes of surface oxide films on the metal-hydride electrodes.

3.3. Analysis of composition of surface oxide films by using in-situ Raman spectroscopy

In order to understand and analyze the composition of surface oxide films on metal hydride electrodes, in-situ Raman spectroscopy has been explored for this aim. Fig. 4 shows typical Raman spectra of primary oxide films formed on the surface of the metal hydride electrode. From the spectra (Fig. 4a), two strong peaks appeared at 475 and 556 cm^{-1}, respectively after the potential was more positive than 0.35 V. These two peaks can be attributed to β-NiOOH and γ-NiOOH [8,9]. If the electrode potential

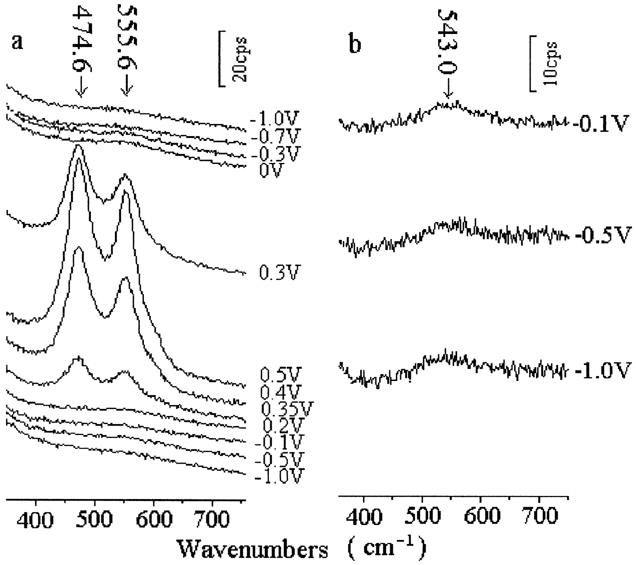


Fig. 4. In-situ Raman spectra of surface oxide film on the metal hydride electrode in 30% KOH+1% LiOH solution, (a) polished electrode, (b) after five potential cycles in the potential region between −1.0 and 0.55 V.

was reversed after reaching +0.5 V, it was observed that two peaks decreased and disappeared after potentials were more negative than 0.0 V. In addition, when the electrodes were cycled between −0.95 and 0.55 V for 5 times, it can be inferred that a quite stable oxide film is formed on the electrode surface based on photoelectrochemical results [10]. At this time, if we took Raman spectra for the electrodes, we observed a wide spectral peak appearing at 543 cm^{-1} even in the negative potential (Fig. 4b). It is attributed to the contribution of $Ni(OH)_2$ and NiO mixture at this stage. In addition, our other Raman results [11] also showed that more oxides (i.e. more manganese and cobalt oxides) are formed on the crack sites after 100 potential-cycles, and the composition of the oxides on the crack area is also quite different from the smooth area on the electrode surface.

4. Conclusions

In this work, in-situ laser-scanning photoelectrochemical microscopy, in-situ confocal microscopy and ex-situ STM techniques have been explored to study surface oxide film on AB_5-type metal hydride electrodes for the first time. The results demonstrated that photoelectrochemical method is a powerful method to study the formation and growth/transformation of surface oxide films on metal hydride electrodes. Both laser-scanning photoelectrochemical microscopic and confocal Raman microscopic results showed that crack sites on the electrode surface are more feasible to be oxidized than other smooth sites under electrochemical conditions. The composition and thickness of surface oxides formed on the crack sites also seems different from that of oxides on the smooth sites. The primary surface oxide layer on fresh metal hydride electrode was found to be composite metal oxides with nickel oxide as its main component by in-situ Raman spectroscopy. However, since the surface oxide film is a complex system, which may include different valent oxides, further detailed studies of surface oxides by using various in-situ spectroscopic techniques are planned in the lab.

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References

[1] J.J.G. Willems, Philips J. Res. 39 (Suppl. 1) (1984) 1.
[2] D. Chartouni, A. Zuttel, C. Nutzenadel, L. Schapbach, J. Alloys Comp. 261 (1997) 273.
[3] M.E. Fiorino, R.L. Opila, K. Konstadinidas, W.C. Fang, J. Electrochem. Soc. 143 (1996) 2422.
[4] Y. Yang, J. Li, J.M. Nan, Z.G. Lin, J. Power Sources 65 (1997) 15.
[5] Y. Yang, J.M. Nan, J. Li, Z.G. Lin, in: Proceedings of Symposium On ‘Batteries For Portable Applications and Electric Vehicles’, Proceedings Series, Vol. PV97–18, The Electrochemical Society, Pennington, NJ, 1997, p. 750.
[6] Z.G. Lin, J.K. You, X.D. Zhuo, C. Zhang, Y. Yang, Electrochemistry (Chinese) 1 (1995) 166.
[7] X.G. Chen, Y. Yang, Z.G. Lin, W. Chu, Y.X. Shi, B.M. Wei, Appl. Surf. Sci. 103 (1996) 189.
[8] L.J. Oblonsky, T.M. Devine, J. Electrochem. Soc. 142 (1995) 3677.
[9] C. Johnson, P.R. Graves, Appl. Spectrosc. 44 (1990) 105.
[10] J.M. Nan, Ph.D Thesis, Xiamen University, China, 1998.
[11] J.M. Nan, Y. Yang, J.K. You, Z.G. Lin, in preparation.