Article ID: 1003-6326(2003)01-0020-05

Crystal structure and electrochemical behaviors of Pt/mischmetal film electrodes①

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Abstract: The Ml(La-rich mischmetal) films with a thin Pt layer on the substrate of chemically coarsen ITO glass or silicon slices were prepared by magnetic sputtering technique. The crystal structure and surface morphology of the films were investigated by X-ray diffraction(XRD) analysis and atomic force microscopy(AFM), respectively. The electrochemical hydridation/dehydridation behaviors of the films in KOH solution were studied by using cyclic voltammagraph and electrochemical impedance spectrum (EIS) as well. The AFM results show that the Pt cover layer on the Ml films is of island structure with a grain of 150-200 nm in size. The presence of a thin Pt layer can provide sufficient high electrocatalytic activity for the electrochemical charge-transfer reaction. The electrochemical reduction and oxidation reaction occur on the Pt layer, and the diffusion of H into the Ml film is the rate-controlled step. The Pt coatings also act as protective layers, preventing oxidation and/or poisoning of the underlying Ml films in air.

Key words: rare earth films; electrochemical behaviors; cyclic voltamagraph

CLC number: TG 139.7 **Document code:** A

1 INTRODUCTION

In recent years, more and more functional materials based on rare-earth(RE) have been developed, especially the extensive researches of RE-H system have resulted in the discovery of the hydrogen storage alloys and their applications in nickel-metal hydride secondary battery[1, 2]. In 1996, Huiberts et al[3, 4] first reported the dramatic reversible change in the optical property of metal/hydride films of yttrium during hydrogen adsorption/desorption. By changing the hydrogen concentration within the rare-earth films, the optical appearance of the film changes from mirrorlike for the dihydride composition to highly transparent for the trihydride compound. The studies of Sluis et al[5] disclosed that most other rare-earth films, such as lanthanum and cerium can also exhibit the reversible changes in optical properties during gas hydrogen absoroption/desorption process. Besides the gas-phase hydrogen loading, electrochemical charging was also reported by Notten et al[6] to much more rapidly and conveniently achieve the reversible optical switching characteristics of yttrium, lanthanum and magnesium-lanthanum films. Compared with the normal electrochromic materials, such as WO_3 and V_2O_5, the novel rare-earth films show the wider range of the transparent amplitude[3-8]. The corresponding theory for metal hydrides with switchable optical properties was put forward by Ng et al[9]. Among these studies, the reports on the electrochemical behaviors of the rare-earth films was rare, especially the investigation on the rare earth films by electrochemical impedance spectrum technology. The previous works[3, 6] have shown that a thin Pd top coating is essential for loading and unloading the Y films with hydrogen gas. These Pd coatings act as the protective layers against Y oxidation, and also provide the sufficient catalytic activity for hydrogen molecules dissociative adsorption and associative desorption. In this paper, we select Pt as the protective layer and prepare Pt/Ml La-rich mischmetal films on the ITO glass and silicon slice substrate by magnetron sputtering technology, and studies the crystal structure and the electrochemical behaviors of the prepared films.

2 EXPERIMENTAL

Pt-coated La-rich mischmetal(Ml) films were prepared by magnetically sputtering coating techniques on the chemically pretreated ITO glass and the silicon slice substrates. Before sputtering, the chamber was first evacuat-

① **Foundation item:** Project(59971046) supported by the National Natural Science Foundation of China
Received date: 2001-12-20; **Accepted date:** 2002-05-08
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ed to 2.0×10^{-4} Pa, then filled with pure Ar up to 0.25 Pa. The compositions of raw materials are as follows. Palladium 99.9% (Institute of Yunnan Precious Metals); La-rich mischmetal (Shanghai Yuelong Nonferrous Metals Company): 77.7 %La, 3.2 %Ce, 17.4 %Pr, 1.7 % Nd (in mass fraction). Two Pt/Ml films with different thickness, ie, Pt(5 nm)/Ml(189 nm) and Pt(20 nm)/Ml(945 nm), were prepared. The thickness of the films was calibrated by optical method. The as-prepared films were kept in air without any protection.

The Pt/mischmetal film electrodes were tested in a conventional three-electrode electrolysis cell in which the counter electrode was NiOOH (with a much larger capacity than that of the working electrodes), the reference electrode was Hg/HgO/KOH (6 mol/L), and the electrolyte was 6 mol/L KOH solution. All of the electrochemical charging/discharging tests were performed with an EG&G 273A potentiostat/galvanostat at room temperature. And the electrochemical impedance spectrum (EIS) measurements were carried out by using an EG&G 273A potentiostat/galvanostat along with a 5210 lock-in amplifier. The frequency is ranged from 0.01 Hz to 100 kHz at various DC potentials from zero to − 200 mV vs Hg/HgO/KOH (6 mol/L). A small AC signal of 10 mV in amplitude was used to perturb the electrochemical systems.

The XRD analyses were conducted by a Rigaku D/max-IIIB diffractometer, using Cu K_α radiation in the 2θ range from 20° to 90° with a scan rate of 4°/min. The morphologies of the rare earth films were observed by an atomic force microscopy (AFM). The scan time was 2 s, brightness threshold was 0.71, scan range was 2.0 μm × 2.0 μm, image size was 400 × 400 dots, and three-dimensional range was 1.0 μm × 1.0 μm × 0.1 μm.

3 RESULTS AND DISCUSSION

3.1 Crystal structure and morphologies of Pt/Ml films

Fig. 1 shows the XRD patterns of the as-prepared Pt/Ml films deposited on ITO and silicon slice substrate. As shown in Fig. 1(a), for Pt(5 nm)/Ml(189 nm)/ITO film, the intensity of Pt diffraction peak is very low due to the thin Pt layer (about 5 nm). No diffraction peak from the pure rare-earth elements is observed. However, the peak of La_2O_3(101) is very high. It indicates that too thin layer of Pt cannot provide enough protection against oxidation for the underlying Ml films. When the Pt layer is increased up to 20 nm, the oxidation of the underlying Ml film is reduced remarkably. For Pt(20 nm)/Ml(945 nm)/ITO film as shown in Fig. 1(b), only a weak diffraction peak of lanthanum oxide La_2O_3 is observed. For the case of Pt(20 nm)/Ml(945 nm)/silicon film as shown in Fig. 1(c), the peak of lanthanum oxide disappears. The results mean that a Pt layer of 20 nm thickness can provide enough protection against oxidation in air. However, the protective layer of Pt is thicker than that of Pt(5 nm) which was reported to provide sufficient protection and electrochemical catalytic activity[3].

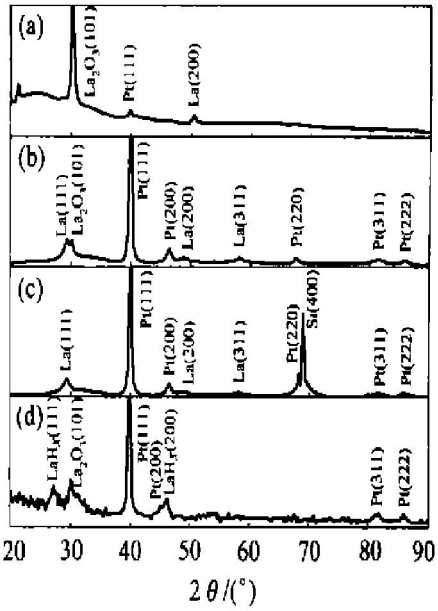

Fig. 1 XRD patterns of different Pt/Ml films deposited on ITO and silicon slice substrate
(a) —ITO substrate, Pt(5 nm)/Ml(189 nm);
(b) —ITO substrate, Pt(20 nm)/Ml(945 nm);
(c) —Silicon slice substrate, Pt(20nm)/Ml(945 nm);
(d) —ITO substrate, Pt(20 nm)/Ml(945 nm), after electrochemical charging/discharging

At room temperature, α-La with an HCP structure is stable. However, in our experiment, La was found to be the β-La with a cubic structure. As the transformation enthalpy $\Delta H_{\alpha \rightarrow \beta}$ of α-La to β-La is only 0.36 kJ/mol La, the formation of β-La is available.

Based on the XRD, the crystal structures and lattice parameters of both Pt and La are calculated and presented in Table 1.

Table 1 Lattice parameters of Pt and La in different films (10^{-10} m)

Film	La (FCC)	Pt (FCC)
Pt(5 nm)/Ml(945 nm)/ITO	–	a= 3.915 8
Pt(20 nm)/Ml(945 nm)/ITO	a= 5.263 8	a= 3.915 8
Pt(20 nm)/Ml(945 nm)/Si	a= 5.262 7	a= 3.912 2
Pt(20 nm)/Ml(945 nm)/ITO (after charging/discharging)	a= 5.594 6	a= 3.917 7

The lattice parameter of Pt is almost the same for the different film electrodes. The lattice parameters of both Pt and La in Pt/Ml/ITO and Pt/Ml/Si films are also similar. The different substrate materials have no evident impact on the crystalline properties of the films.

However, after several electrochemical charging/discharging cycles, the film electrode was discharged to the cutoff potential at a discharge current of 1.25 mA/cm^2, then the electrode was rinsed with water and dried in air for further XRD test. The lattice parameter of La(111) increases from $5.263\ 8 \times 10^{-10}$ m for the untested sample to $5.594\ 6 \times 10^{-10}$ m. The corresponding expansion ratio of 5.59% in *a*-axis direction indicates the existence of residual hydrogen in films. A little expansion in *a*-axis direction is also observed for Pt layer after charging/discharging.

The morphology of the Pt/Ml/ITO film was observed by AFM analysis. As shown in Fig. 2, the top Pt coatings of the as-prepared films do not form a flat and smooth coating like the Pd/Y film reported by Notten et al[10]. The Pt coatings were of island structure, and Pt particles with an average size of 100 – 200 nm were piled up each other with the clear boundary. After electrochemical charging/discharging process, Pt particle sizes of Pt grains have a slight decrease to 100 – 150 nm due to the corrosion of rare earth element in KOH solution. As shown in Fig. 2(b), an obvious corrosion phenomenon can be observed.

3.2 Electrochemical behaviors

Fig. 3 plots the electrode potential of the Pt(20 nm)/Ml(945 nm)/ITO film during the first galvanostatic charging. Before charging, the electrode potential is near to zero. Immediately after applying a charging current of 0.6 mA (the current density is 1.25 mA/cm^2), the potential shifts negatively to about – 0.35 V, then decreases with the charging time. In the region of α+β, the electrode potential only decreases slightly with the charging time, and an obvious α+β potential plateau occurs. When the charging time is above 25 min, the potential electrode has a remarkable significant drop.

In the gas hydrogen loading process[6], at first, the hydrogen molecules on the surface decomposes and forms adsorbed hydrogen atom(H_{ad}) via the electro catalytic effect of Pd or Pt. Subsequently, the adsorbed hydrogen atoms can be transported into the bulk of the solid via solid-state diffusion, which results in the absorbed hydrogen (H_{ob}). The reactions can be represented by

$$H_2 \leftrightarrow 2H_{ad} \quad (1)$$

$$H_{ad} \leftrightarrow H_{ab} \quad (2)$$

If the hydrogen loading/unloading process is accomplished by electrochemical method, the following electrochemical reactions will take place:

1) Electrochemical charging

(1) The adsorbing hydrogen formed at Pt surface:

$$Pt + H_2O + e \rightarrow H_{ad}(Pt) + OH^- \quad (3)$$

(2) The absorbing hydrogen on Pt surface diffuse to the interface of Ml:

$$H_{ad}(Pt) \rightarrow H_{ab}(Pt) \quad (4)$$

(3) The bulk hydrogen reacts with the bulk Ml to form the hydride:

$$Ml + H_{ab}(Pt) \rightarrow MlH_x(\alpha) \xrightarrow{+H} MlH_2 \xrightarrow{+H} MlH_y \quad (5)$$

2) Accordingly, the corresponding discharging process can be expressed as follows.

$$MlH_y \xrightarrow{-H} MlH_2 + H_{ab}(Pt) \quad (6)$$

$$H_{ab}(Pt) \longrightarrow H_{ad}(Pt) \quad (7)$$

$$H_{ad}(Pt) + OH \xrightarrow{-e} Pt + H_2O \quad (8)$$

It was reported[5] that the dihydrides of rare earth metals(RE) are electronically conductive, and the electrochemical reaction can easily occur on the surface of RE

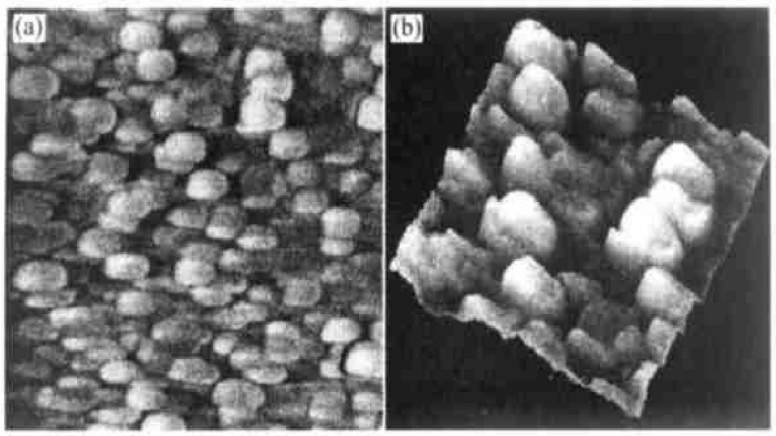

Fig. 2 AFM photographs of Pt/Ml/ITO film electrodes
(a) —As-deposited(2.0 μm × 2.0 μm);
(b) —Three dimensional photo of Pt/Ml/ITO film after charging/discharging(1.0 μm × 1.0 μm × 0.1 μm)

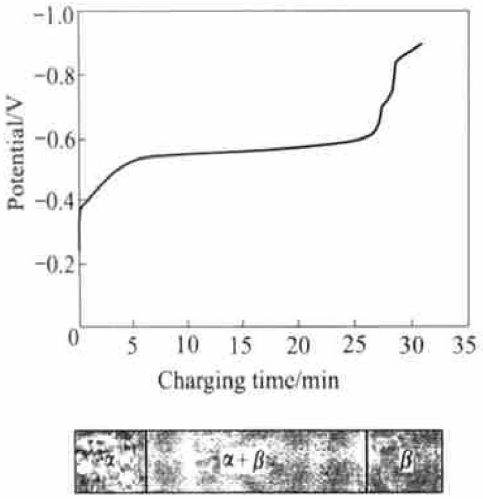

Fig. 3 Dependence of electrode potential on charging time of Pt/Ml/ITO films (Pt layer 20 nm, Ml layer 945 nm, specimen size 0.8 cm × 0.6 cm; charging current density 1.25 mA/cm^2, temperature 15 ℃. α phase corresponds to soluble hydrogen in Ml bulk, and β phase to La dehydride and trihydride)

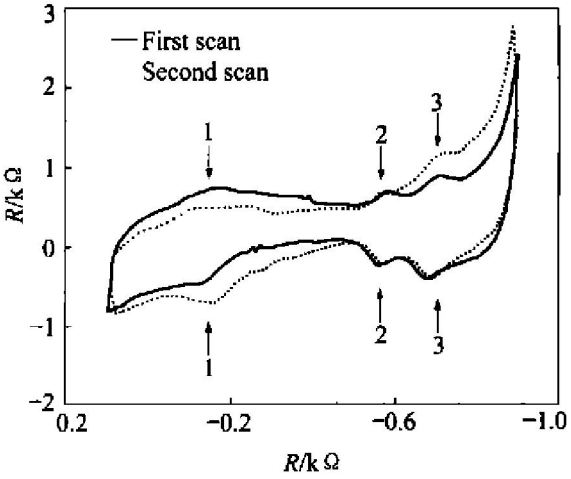

Fig. 4 Cyclic voltammagraph curve of Pt/Ml/ITO film (Pt layer 20 nm, Ml layer 945 nm, scan rate 100 mV/s, temperature 15 ℃)

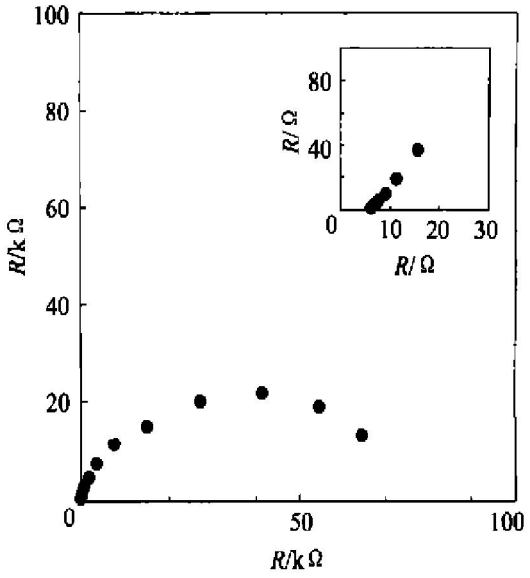

Fig. 5 Electrochemical impedance spectrum of Pt/Ml/ITO film (surface area of film electrode: 0.5 cm^2)

dihydride. So the extra electrochemical reaction will take place, which provided that the thin Pt cover layers do not form a fully closed coating.

$$MlH_2 + xH_2O \leftrightarrow MlH_{2+x} + xOH^- \quad (9)$$

Among the above-hypothesized step-by-step reactions, the slow diffusion of hydrogen atom in the bulk of Ml films is believed to be the rate-controlled step. Fig. 4 depicts the cyclic voltammagraph curves of the Pt(20 nm)/Ml(945 nm)/ITO film. The obvious oxidation/reduction current peaks indicate the sufficient electrocatalytic activity for the electrochemical reactions with the Pt layer. Three pairs of current peaks occurred during the cyclic voltammagraph measurements. The first pair of current peaks(1 and 1′) around − 0.15 V may be ascribed to the reduction/oxidation of Pt on the top layer of the film. The second set of peaks(2 and 2′) appeared near to − 0.55 V is corresponded to reaction(3) and (8), respectively. The third pair of peaks(3 and 3′) may be ascribed to reaction(9).

Fig. 5 shows the electrochemical impedance spectrum of the Pt(20 nm)/Ml(945 nm)/ITO film electrode. As shown in Fig. 5, the electrochemical impedance spectrum of the Pt/Ml/ITO film electrode is composed of two semicircles, of which the high frequency zone is negligible(as shown in the enlargement picture in Fig. 5) and the low frequency zone is very large. Based on the analysis of the electrochemical reaction occurred on the Ml films, the high frequency zone is corresponded to reaction(3) and the low one to reaction (5). According to the previous EIS theory[9], the semi-circle appeared in the low frequency indicates the Warburg impedance with the semi-infinite characteristic. The solid diffusion process, i.e., the diffusion of hydrogen atom, is the rate-controlled step.

4 CONCLUSIONS

Ml films capped with a thin Pt layer are prepared by magnetic sputtering coating technique on ITO and Si slice substrates. The Pt layer on the as-prepared films is of island structure with the grain size of 150 − 200 nm. The presence of 20nm Pt layer can effectively protect the rare earth metal sub-layer against oxidation in both air and electrochemical environments and provide the necessary

electro-catalytic activity for the electrochemical charge-transfer reaction. The electrochemical reduction and oxidation reaction occurs on the Pt layer, and the diffusion of H in the Ml film is the rate-controlled step.

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(Edited by HUANG Jin-song)