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Charge/discharge characteristics of electroless CoB films

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ABSTRACT

CoB thin films were obtained by the electroless coating technique and their charge/discharge cyclic characteristics were investigated. The effect of heat-treatment on the structure and the discharging behavior of CoB films was also investigated. It was observed that both the amorphous/nano-crystalline and crystallized CoB films had very limited hydrogen storage capacity. Upon heat treatment at 550 °C the electrode performance of the CoB film deteriorated significantly due to Co_3B phase formation in the film structure. The discharging process yielded $Co(OH)_2$ and CoOOH formations on the electrode surface. After activation, the charge/discharge process was mainly controlled by the reversible oxidation/reduction reactions of Co. The surface of the crystallized CoB films was observed to be more catalytic than that of the as-deposited amorphous/nano-crystalline CoB films.

1. Introduction

Nickel-cathode rechargeable batteries have recently attracted great attention [1–3]. Cobalt-based alloys are considered as very promising anode materials for the nickel-cathode rechargeable batteries [4–6]. Recently, focus has been addressed on CoB alloy as the energy storage anode material [7–13].

Electrode materials are generally synthesized in the form of powders by various methods like chemical reduction [8–10,12,13], mechanical alloying [11,14–19] and arc melting (and then mechanical crushing) [7,20,21]. Preparation of the electrode from powders has some disadvantages like necessity to the use of binder or pulverization of the electrode material during the handling. From practical point of view these disadvantages can be eliminated if the electrode materials are synthesized in the form of thin films. Cobalt or CoB thin films are produced by the electroless coating technique for various purposes [22–24].

In this work CoB thin films were obtained by the electroless coating method to investigate their charge/discharge cyclic characteristics. Effect of the heat treatment on the structure and the electrode performance of these films was also investigated and possible discharging mechanism was proposed.

2. Materials and methods

Nickel foil was used as substrate material (10×15×0.1 mm) for the deposition of CoB films. The substrate was pre-cleaned by ultrasonic degreasing in acetone for 10 min, rinsing in 10% KOH at 60 °C for 5 min and pickling in 10% sulfuric acid for 30 s. The volume of the coating bath was 200 ml. The composition of the coating bath (each chemical constituent was purchased from Aldrich) and the coating parameters are given in Table 1. For the electrochemical quartz crystal microbalance (EQCM) experiments, Pt crystals (total area was 0.2 cm^2) were coated in a bath given in Table 1 at 45 °C in 50 ml micro cell without any pre-cleaning. The thicknesses of CoB films used in the characterizations and EQCM experiments were approximately 30 μm and 0.3 μm, respectively. The film thicknesses were estimated from the deposited film densities and the weights which are determined by the precision balance for 30 micron films and by the observed frequencies (EQCM supplies frequencies very sensitively) for 0.3 μm films.

The phase structure of the films was examined by the X-ray diffractometry (Bruker AXS D8) using Cu Kα radiation (the measurement configuration was Bragg–Brentano (θ–2θ)). The surface morphologies were observed by ZEISS SUPRATM 50 VP Scanning Electron Microscope (SEM) with the operating voltage of 20 kV and Veeco Multimode V Model Atomic Force Microscope (AFM) at tapping mode with 360 kHz Cantilever. The heat treatment of the films was conducted in a vacuum furnace.

$NiOOH/Ni(OH)_2$ counter electrode and a Hg/HgO reference electrode were used to set up a three-electrode cell in 6 M KOH solution. Tests were performed with PARSTAT Model 2273 potentiostat/galvanostat unit. The charge current density was 100 mA g^{-1} and the charging was carried out down to the severe gassing potential. The discharge current density was 25 mA g^{-1} and the discharge cut-off potential was −0.72 $V_{Hg/HgO}$. The excitation voltage was 10 mV (peak to peak) and the applied frequency varied from 100 kHz to 0.01 Hz in the electrochemical impedance spectroscopy (EIS) measurements. The cyclic voltammetry (CV) experiments were carried out by sweeping the potential from open circuit potential to −1.2 $V_{Hg/HgO}$ in the negative direction, then from −1.2 $V_{Hg/HgO}$ to −0.4 $V_{Hg/HgO}$ in the

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Table 1
Composition of the coating bath and the coating parameters.

Bath constituents and coating parameters	Quantity
$CoSO_4 \cdot 7H_2O$	0.1 M
$Na_2C_4H_4O_4 \cdot 6H_2O$	0.1 M
$(CH_3)_2NHBH_3$	0.1 M
Temperature	55 ± 1 °C
pH	4.5
Time	3 h

positive direction and then from -0.4 $V_{Hg/HgO}$ back to open circuit potential in the negative direction at a scan rate of 1 mV s^{-1}. QCA922 Model Quartz Crystal Microbalance was used with Pt substrate (9 MHz) to observe the mass change in the deposited CoB thin films during CV experiments.

3. Experimental results and discussion

3.1. The structural and morphological characteristics of the as-synthesized and heat-treated CoB films

According to the previously reported differential scanning calorimetry analysis, the amorphous CoB structure crystallizes at around 490 °C [12]. By taking into account this report, the heat treatment temperatures were selected as 350 °C (HT-350) and 550 °C (HT-550) to observe the effect of change in the film structure on the CoB electrode performance. The duration for the heat treatments was fixed as 3 h.

The X-ray diffraction (XRD) patterns of the as-deposited and heat-treated CoB films are compared in Fig. 1. As-deposited film exhibits a single broad peak at around 45° indicative of amorphous/nano-crystalline structure [8,9,12]. In addition to the broad peak, Co peaks are also observable in the XRD pattern of HT-350 film [8,9]. The broad peak disappears and Co peaks become more apparent in the XRD patterns of HT-550 film in Fig. 1 [8,9]. Obviously the film structure crystallizes more efficiently as the heat treatment temperature increases. Besides the crystallization, Co_3B phase also forms [7] in CoB film heat-treated at 550 °C according to the XRD pattern of HT-550 film in Fig. 1.

Scanning electron micrographs (SEM) of the as-deposited, HT-350 and HT-550 films are given in Fig. 2a, b and c, respectively. Since the surface morphology of the films is not very observable in these figures, AFM images of the as-deposited, HT-350 and HT-550 films

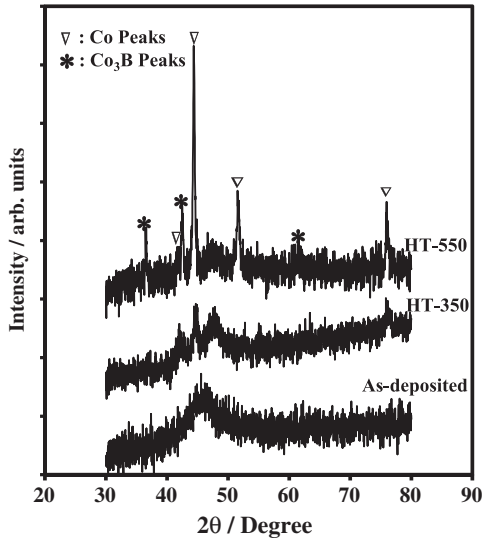

Fig. 1. XRD patterns of the as-deposited and heat-treated CoB electroless films.

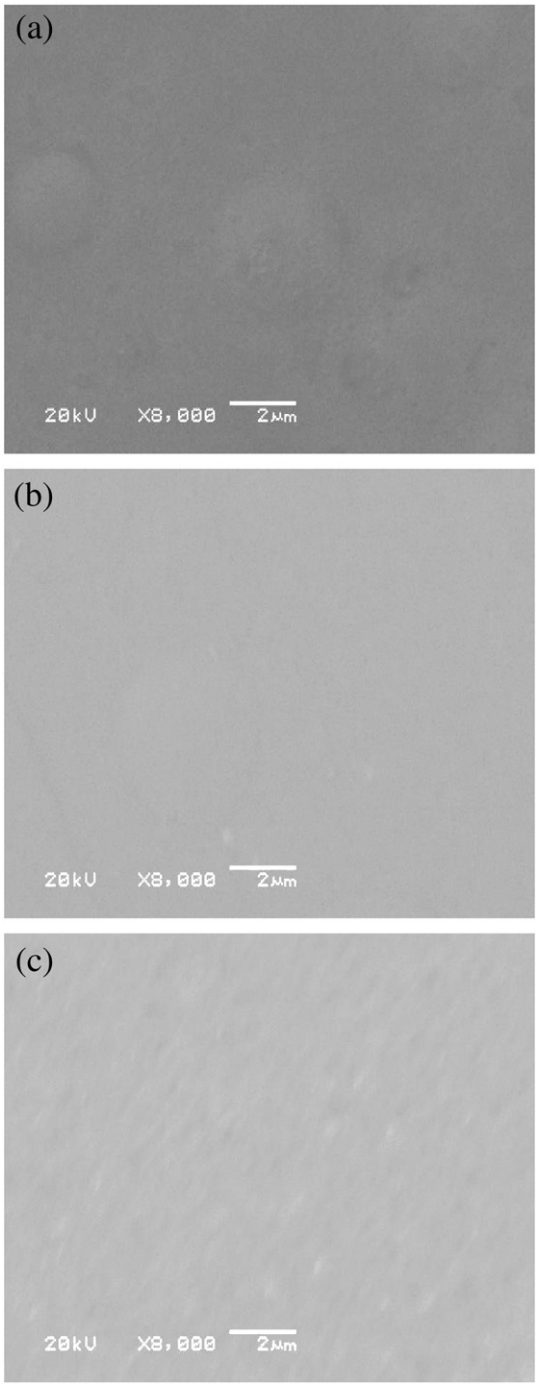

Fig. 2. SEM micrographs of (a) the as-synthesized, (b) HT-350 and (c) HT-550 CoB films.

are given in Fig. 3a, b and c, respectively. While the approximate surface grain size in the as-deposited film is 200 nm, that in HT-350 film is 3.5 μm. The surface morphology of HT-550 alloy in Fig. 3c looks totally different probably due to the Co_3B phase formations at 550 °C (Fig. 1).

3.2. The cyclic stabilities of the as-deposited and heat-treated CoB films

The variations in the discharge capacities of the as-deposited and heat-treated CoB films depending on the charge/discharge cycle numbers are indicated in Fig. 4. For the as-deposited and HT-350 films there is need to at least 10 cycles to activate the films and to reach a stable discharge capacity. The activation process looks longer in HT-550 alloy in Fig. 4. The stable discharge capacities of the