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Preparation and Characterization of Cobalt Oxide by Electrochemical Technique

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Abstract

Cobalt oxide was prepared from synthetic cobalt nitrate solutions through two step process; electrolysis of cobalt nitrate solution to produce cobalt hydroxide and then preparation of cobalt oxide by calcination of cobalt hydroxide. Cathodic reduction of cobalt nitrate solution at pH ~4 with a cobalt concentration of 28g/L at a current density of 200A/m² lead to formation of β -Co(OH)₂ with a current efficiency of 41%. On increasing current density, the current efficiency has increased and reached a maxima of 59% at an applied current density of 500 A/m². The effect of Co(II) concentration was studied and found that with increase in Co(II) concentration from 28g/L to 42 g/L the current efficiency increased to 59% at an applied current density of 200 A/m². The β -cobalt hydroxide when calcined at 300°C the corresponding β -Co₃O₄ was obtained. The morphology and structure of both the cobalt hydroxide and oxide were characterized by scanning electron microscope (SEM) and X-ray diffractometer (XRD) and the discharge capacity of cobalt oxide was measured.

Keywords: Cobalt nitrate, Cobalt hydroxide, Cobalt oxide, Electrochemical preparation

1. Introduction

Electrodeposition of metals and its oxides are the oldest themes in electrochemical science (Conways, 1952a, 1965b; Parson, 1959; Bockris and Reddy, 1970; Freitas and Garcia 2007; Chuan-li et al. 2009). The initial studies on this topic are dated from early nineteenth century, using galvanic cells as a power source (Parson, 1959; Bockris and Reddy, 1970; Freitas and Garcia 2007; Chuan-li et al. 2009). Despite the

antiquity, electrodeposition is still a much studied topic. Themes such as supercapacitors or electrochemical cell devices have raised considerable attention (Wang et al. 2013, Zhang et al. 2012; Yousefi et al. 2012; Wu et al. 2011; Pan et al. 2012; Kung et al. 2012; Zhou et al. 2009; Asano et al. 2009; Feng et al. 2009; Chou et al. 2006; Nan et al. 2006). In this case, the electrodeposition technique is of great interest due to their unique principles and flexibility in the control of the structure and morphology of the oxide electrodes. Cobalt oxides demonstrated the best electrochemical properties as lithium storage material in Li-ion

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cells among a class of new anode materials composed of nano-sized transition-metal oxides, such as nickel oxides, cobalt oxides and iron oxides (Poizot et al. 2000). Li/CoO (Co_3O_4) half-cells can exhibit a reversible capacity of 750–1000 mAhg^{-1} range (Badway et al. 2002) while CoO electrode can go for 300 mAhg^{-1} after 30 cycles (Wang et al. 2002).

The present investigation attempts to evaluate the effects of different parameters such as current density, concentration of cobalt on the cathodic deposition of cobalt hydroxide and ultimately cobalt oxide. The specimen powders were characterized by XRD, FE-SEM, and charge/discharge tests.

2. Experimental

Apparatus and material

Galvanostatic electrodeposition of cobalt hydroxide was carried out in an electrolytic cell made of perspex sheet with distinct cathodic and anodic chambers separated by means of a polypropylene diaphragm. Cathode and anode used for the electrolysis were made of SS 304 grade and Ir-coated Ti respectively and the inter-electrode spacing was 4 cm. DC current was supplied from a rectifier [Aplab, India] for carrying out the electrolysis under galvanostatic mode.

Reagents

All the solutions were prepared by using double distilled water and analytical grade reagents (Merck Chem. Ltd., India) of cobalt nitrate [$\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$], sodium hydroxide and nitric acid were used for preparation of electrolytic solutions having desired cobalt concentration and pH.

Electrode preparation

Cathodes were polished with 400 and 1200 grid sand paper respectively to mirror finish followed by washing with de-ionised water.

The cathodes were then dipped in dilute nitric acid for 30 minutes, followed by its washing with water. It was then allowed to air dry. The dried cathode was then weighed prior to electrodeposition.

Electrolysis and calcination

The electrodeposition of cobalt hydroxide was carried out for 6h. The concentration of cobalt in both catholyte and anolyte was 28 g/L, except the case where the concentration was varied. The cell voltage was recorded at an interval of 30 min. After the electrolysis, the cathode and anode were removed and the catholyte was filtered. The electrodeposited cobalt hydroxide material was washed with distilled water upto the filtrate pH reached to ~7 and air dried. The current efficiency (CE) was calculated from the weight of cobalt hydroxide deposited as given in equation (1). The electrodeposited cobalt hydroxide was calcined at a temperature of 300°C for 2h in a muffle furnace.

$$\text{CE (\%)} = \left(\frac{\text{Wt. of cobalt hydroxide deposited}}{\text{Theoretical wt. predicted from Faraday's law}} \right) \times 100 \dots\dots(1)$$

Characterization

An X-ray diffractometer (PANalytical PW 1830; Philips, Japan) with Mo K α radiation, $\lambda = 0.70932\text{\AA}$ was used to determine the preferred crystal orientation and phase of the deposited cobalt hydroxide. The deposits were also analysed by scanning electron microscope (SEM, JEOL JSM 6510, Japan) to view the deposit morphology of the electrodeposited metal hydroxides prepared under various deposition conditions.

Charge-Discharge measurement

A floated cell arrangement was employed to study the electrochemical behaviour of the prepared cobalt oxide sample. The charge-discharge profile was measured at room temperature ($27 \pm 2^\circ\text{C}$) while imposing constant

charge and discharge currents in 1 M LiOH electrolyte solution. The experimental cell consisted of a zinc anode, with Co_3O_4 pellet as cathode and another zinc sheet was used as reference electrode. The cathode was made in the form of a pellet, consisting of a mixture of cobalt oxide and graphite powder (4:1), with 2–3 drops of 5 % polyvinyl alcohol used as a binder. The mixture was placed in a stainless steel mesh meant for electrical contact and then subjected to a pressure of 12 ton for 3 min by means of a pelletiser (KBr press) in a 20 mm die. The pellet was put into a cell assembly and allowed to equilibrate for 1 h at its open circuit potential. Charging and discharging were carried out at a current of 80 mA. Discharging was done till a cutoff voltage of 0.1V. The total system was operated by a computer controlled deep cycle battery tester (Bitrode, LCN1-25-24, USA)

3. Results and Discussion

Effect of current density

The effect of current density on the current efficiency is shown in Fig.1. With increase in current density, the current efficiency has increased and more or less stabilised at 500 A/m^2 . There is only a marginal effect of current density beyond this point on the current efficiency.

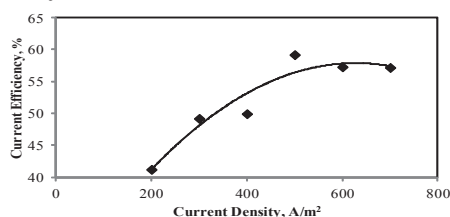


Fig. 1: Effect of current density on current efficiency during electrodeposition of cobalt hydroxide, [Co]: 28g/L, pH:~4, time: 6h
Effect of cobalt concentration

The effect of cobalt concentration on the current efficiency during electrodeposition of cobalt hydroxide at a current density of 200 A/m^2 and ~4 pH is shown in Table 1. Doubling the concentration of cobalt from 28 to 42 g/L, the current efficiency increased from 41 to 59%.

Table 1: The effect of cobalt concentration on current efficiency during electrodeposition of cobalt hydroxide, Current density: 200A/m²,

[Co], g/L	Current efficiency, %
28	41.23
42	59.38

The XRD patterns of the as obtained $\hat{\alpha}$ -cobalt hydroxide and $\hat{\alpha}$ - Co_3O_4 are presented in Fig.2. The corresponding FESEM images of the samples are given in Figs. 3 and 4 respectively. The morphological studies reveal that the particle size has decreased after the transformation of cobalt hydroxide to oxide but the structure remained similar which has been confirmed from the beta configuration of both hydroxide and oxide.

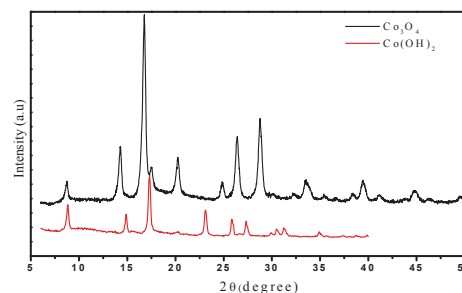


Fig.2: XRD patterns of $\text{Co}(\text{OH})_2$ and Co_3O_4

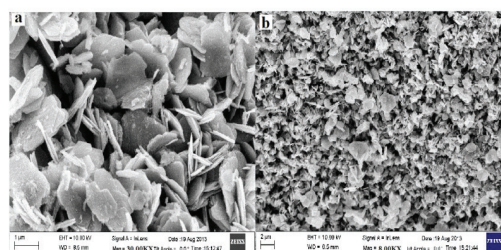


Fig. 3: FESEM images of $\text{Co}(\text{OH})_2$

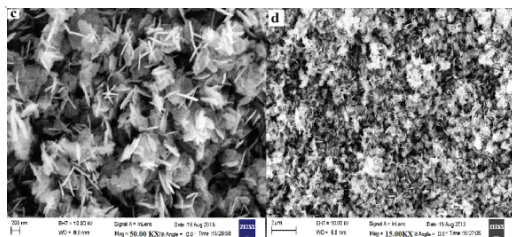


Fig.4: FESEM images of Co_3O_4

Charge-Discharge study

The suitability of the Co_3O_4 as a battery material was assessed from its discharge behaviour through imposing a constant current over a period of time. The sample prepared was subjected to charge-discharge studies in 1 M LiOH aqueous solutions. The Co_3O_4 sample synthesised in this work showed a discharge capacity of 1738 mAhg^{-1} with a cut of voltage of 0.1 V.

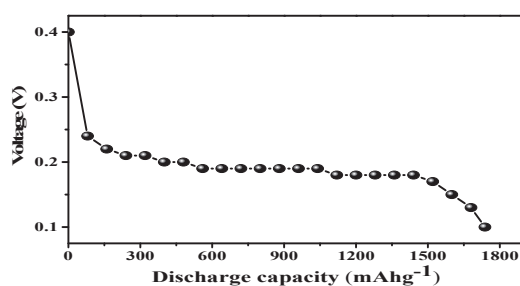


Fig. 5: Discharge capacity plot of cobalt oxide material in LiOH electrolyte.

4. Conclusions

Electrodeposition of cobalt hydroxide was carried out with 28g/L of cobalt nitrate. The parametric variations such as concentration of cobalt and current density lead to optimization condition of 42 g/L cobalt concentration and current density of 500 A/m^2 . The electrochemically prepared beta cobalt hydroxide was calcined at 300°C for 2h to

obtain beta cobalt oxide (Co_3O_4). The Co_3O_4 was tested for its suitability as a cathode material against zinc anode that showed a discharge capacity of 1738 mAhg^{-1} .

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