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Electrodeposition and Characterization of Mesoporous Nanostructured Cobalt Films using Brij78 Templated

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Abstract: *In this manuscript the preparation of highly ordered mesoporous cobalt films containing close packed arrays of spherical holes of uniform size was demonstrated by electrochemical deposition using the hexagonal liquid crystal template (H_{1}-e Co). The template used was Brij®78 surfactant. Transmission electron microscopy (TEM), scanning electron microscopy (SEM), voltammetric methods, and low angle X-ray diffraction (XRD) were used to characterize the electrodeposited mesopores films. Cyclic voltammetry (CV) technique are used to show the mesoporous thin films are promising to be used as electrode materials of high - performance super capacitors.*

Keywords:Nanostructured, mesoporous, Electrodeposition, Brij 78, Cyclic voltammetry

1. INTRODUCTION

Mesoporous materials exhibits very interesting properties such as electrical, magnetic, chemical, and optical that could not be reach by the corresponding bulk equivalents [1]. Currently, many of merging applications such as medical diagnostic, drug delivery, catalysis and variety of biological applications use nanostructured materials [2].

It was found that, in recent years, the electrochemical capacitors (ECs) is highly efficient and longer cycle life in comparison with batteries of the secondary type and higher energy density than conventional electrical double-layer capacitors [3-5]. Some of its applications is the supplementary power supply for new electrical equipment such as mobile, *etc*. [6,7]. For energy storage at an electrode/ electrolyte interface, electrochemical capacitors utilize both interfacial redox processes and electrical double layer. Accordingly, for supercapacitors the electrochemical behavior of Co films is strongly affected by the structural properties of the deposited films. The pore size (mesopores) in the range 2 - 50 nm is highly desirable for the supercapacitors fabricated via electrochemical deposition[8].

According to the constructed phase diagram demonstrated in literature [9-11], the composition of the components of hexagonal phase was determined. The uses of surfactant molecules as templates in construction of nanostructured materials was found to be a very promising area of the field of research [11,12].

The molecules of surfactant aggregate into micelles with long cylindrical in the hexagonal phase and these molecules of micelles pack again into a hexagonal arrangements (Figure 1) with the distance between the micelles species is equivalent to their radius (more or less than 1 nm) [13].

In electrochemical deposition of cobalt films, the dissolution of electrolyte and cobalt salt are occurs in aqueous domain of the mixture and metal electrodeposition takes place on the electrode surface, through the aqueous domain of the surfactant micelles. After completion the electrodeposition process, the molecules of

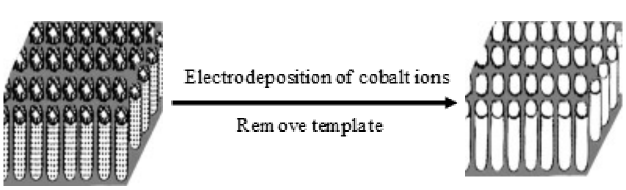

Figure 1. Schematic mechanism of electrodeposition process of the mesoporousH1-e Co films in the presence of hexagonal liquid crystal template.

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surfactant is washed away to leave a metal film with replica of arranged hexagonal arrays of uniform pores. The film thickness can be controlled by the amount of coulomb passed during the electrodeposition process.

In this manuscript, the electrochemical deposition of cobalt film was performed from the aqueous zone of the hexagonal liquid crystal template of Brij®78 to fabricate the nanostructured mesoporous cobalt films (H1-eCo) were described . The structure of H_1-eCo films was characterized by Scanning electron microscopy (SEM), transmission electron microscopy (TEM) and X-ray diffraction. Cyclic voltammetry technique (CV) was adapted to study the performance of electrochemical and capacitance behavior of the electrodeposited films.

2. EXPERIMENTAL

Brij®78 is a trade name of polyoxyethyleneglycol dodecyl ether copolymer ($C_{18}EO_{20.}$). The chemical structure of Brij 78 is indicated in scheme 1. It is purchased from Aldrich. Reagent grade (18 MΩ cm) was used to prepare the solutions and the materials used.

Scheme 1: Chemical structure of Brij 78.

$C_{18}H_{37}$ - [O.CH_2 - CH_2-]$_n$- OH

The glassware were cleaned by soaking in 5% solution of Decon 90 (Aldrich solution) for few days followed by rinsing with triple distilled water and using an oven for drying (50°C). P-xylene with percentage 99%, 99.5% percentage of cobalt acetate ($CoAc_2.4H_2O$). potassium acetate (KAc) with percentage 99% and boric acid (H_3BO_3) were purchased from Aldrich. Ternary system consisting, aqueous solution of $CoAc_2.4H_2O$, Brij 78 non-ionic surfactant ($C_{18}EO_{20.}$, p-xylene and H_3BO_3 were used as plating mixture. The used ternary template mixture containing 44.6% weight of Brij 78, 53.13 wt % aqueous $CoAc_{2.}$4H2O, and H_3BO_3, and 2.23% weight of p-xylene. The template mixture mixed together using glass rod at room temperature and remains chemically stable for more than thirty days. Electrodeposition of Co from electrochemical cell containing the plating materials on polished gold electrode was carried out at room temperature. In order to remove the surfactant from the deposited film, the electrodes are rinsed with excess amounts of deionized water. For cleaning the gold electrode used in electrodeposition, propanol (BDH) are used in sonication the electrode for 1 h followed by rinsing with very pure water [14].

2.1. Instrumentation

Potentiostat supplied from EG & G 283 and a conventional electrochemical cell with three electrodes and volume 15 cm^3 were used to perform the electrochemical. In electrochemical cell, 1 mm diameter gold disk electrode is the polarized electrode, while 1 cm^2 flat polarized electrode is used for structural characterization of the produced Co films. 1 cm^2 area of platinum gauze was used as counter electrode and saturated calomel electrode (SCE) as the reference electrode. Polishing paper (grade 1200) was used to polish the polarized disk electrode followed by alumina (Buehler) of two grades: 1.0 and 0.3 μm then rinsed with deionized water. The morphology and thickness of the electrodeposited cobalt films were investigated using analytical electron microscope (JOEL 6400) of type SEM. Electroplated Co film from the template mixture on evaporated gold electrodes (area 1 cm^2) was used for SEM analysis. The primary test for the fabrication of a nanostructured films is performed via XRD with Cu Kα radiation. JEOL 2000FX transmission electron microscope operating at an accelerating voltage of 200 KV was used to investigate the regularity of the nanostructure film.

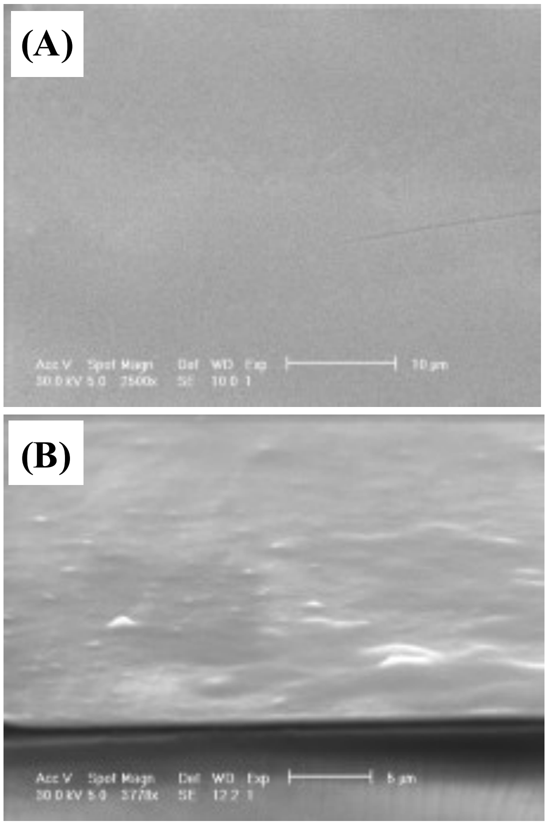

Figure 2. SEM images of the H1-eCo films deposited at –0.91 V *vs* SCE (A) surface image and (B) cross-section image.

3. RESULTS AND DISCUSSION

3.1 SEM and TEM of cobalt /Brij 78 films

The components of the phase in lyotropic form used in deposition process is used for determination of the final film deposited electrochemically with nanostructured properties [9 – 11, 15]. The electrochemically deposited cobalt films at –0.91 V *vs*. SCE from template mixture with phase in hexagonal form was stable and adhering well to evaporated slide of gold electrodes and have a silvery metallic luster. The featureless character of H_1 – Co film indicated via scanning electron micrograph is shown in Figure 2A. The view of cross-sectional (Figure 2B) clarifies smoothing of the film which is uniform and compact. The thickness of the formed film is about 221 nm. As shown in Figure 2B, the SEM image is unable to indicates the nanostructured properties of the deposited film. So, TEM is necessary to describes the electrochemically deposited cobalt films in form of nanostructured material. Figure 3 shows the image of cobalt metal deposited at potential -0.91 V performed using TEM technique. It is apparent that the TEM imag-

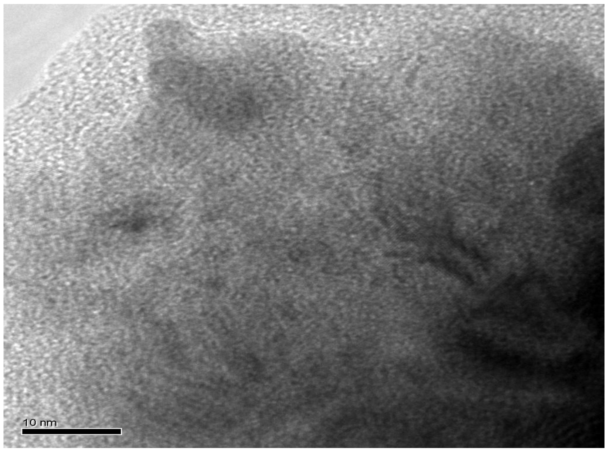

Figure 3. TEM image of the H1-eCo films electrodeposited at deposition potential -0.91V.

es have well ordered hexagonal and uniform arrays of mesoporous structure. After removing the surfactant template from the deposited Co metal the left pores exhibit bright regions. The electrodeposited cobalt metal produces dark regions. It was observed that the pores are ordered in hexagonal form over length scales. It is clear that, although some defects are evident, the indicated pores are continuous and nearly straight over their whole length. When the cobalt is deposited in the hexagonal crystalline phase electrolyte which is soft template, the presence of defects and the slight damage from the normal behavior are expected [16,17]. The distance between the pores centers of cobalt film are estimated to have 11.2 nm, with deposited cobalt thickness of about 5.6 nm and a uniform pore diameter of about 8.9 nm . Under different deposition potentials, the TEM results indicated that, the H_1-eCo film with meso-character structure almost remain unchanged which is consistent with the results reported in literature [18,19]. A large surface area of the pores are affected by pore size and wall thickness.

3.2. X-ray investigation of H_1-eCo films

The existence of one peak of nanoporosity size of Co metal film deposited from Brij®78 hexagonal (H_1) template is investigated using low-angle XRD spectra. An example response of the recorded low angle XRD pattern is shown in Figure 4. The presence of diffraction peak at about $2\theta = 1.49^{o}$ is attributed to the formation of the hexagonal H_1-eCo film and indicated from low angle XRD. In hexagonal arrays the distance between the pores (R) is given by the following equation:

$$R = d_{110}/\cos 30 \qquad (1)$$

and found to be 10.27 nm. The following equation (2) is used to calculate the basic vector length (lattice parameter), a_h of the hexagonal phases [20]:

$$a_h = (2d/\sqrt{3}) \qquad (2)$$

For the pure hexagonal phase, the distance between the pore centers, a_h is calculated from Eq. (2) and found to be 10.27 nm which compare well with the value obtained via Eq. (1). The order of mesoscopic in the template of liquid crystalline exhibited in the nanopores Co films is indicated from the appearance of low angle peal. It was noted that the long-range order during electrodeposition which partially destruct causes broaden of the diffraction peak of single films.

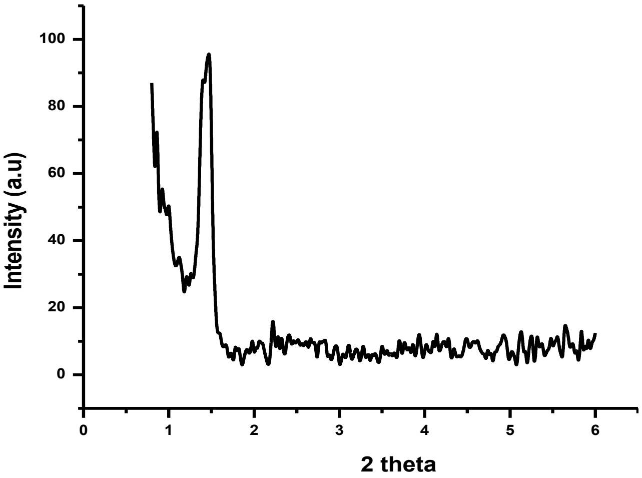

Figure 4. Low -angle XRD for the H1-eCo film electrodeposited on gold substrate from the hexagonal liquid crystal template (Brij 78).

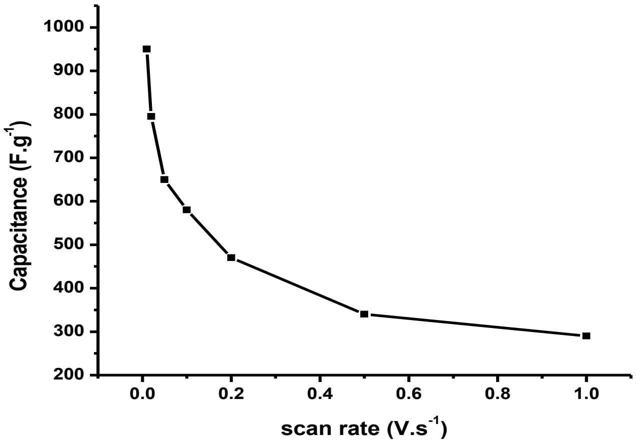

Figure 5. Indicates the variation of specific capacitance of the electrodeposited films versus the scan rates.

The cyclic voltammogram curve represent a simple way to calculate the specific capacitance of the Co film deposited from nonionic surfactant Brij 78 using the following equation [21]:

$$C_{sp} = i / v \times M \qquad (3)$$

the symbol, i, is the average cathodic current, v is the scan rate, and M is the mass of the active electrode. The specific capacitance values were found to be in the range 290 - 950 Fg^{-1} for the electrodeposited films. It was found that the capacitors depends on many factors, such as the mass of the active electrode surface, the conductivity of the active electrode, the electrolyte concentration, and the morphology of the electrode. Electrochemical stability is one of the important indicators of device quality.

The variation of capacitance and peak current of the deposited film with sweep speed were summarized in table 1. Figure 5 shows the specific capacitance values calculated from the CV measurements as a function of sweep speed. The decrease in the capacitance values is described according to the Randles-Sevcik relationship (Eq. 4), in which the current is a measure of the supercapacitive properties of the electro- chemical redox reaction is linearly proportional to the concentration of the electroactive species and the square root of the sweep speed.

$$ip = 0.4463nF\ (nFD/RT)^{1/2}\ AC\ v^{1/2} \qquad (4)$$

4. CONCLUSION

The electrodeposition of mesoporous H_1-eCo films is carried out via simple method on the slide of gold substrate from lyotropic liquid crystalline of hexagonal phase using cheap Brij®78 as nonionic micelle.

The obtained results indicated that the electrochemical capacitance and the structure of the prepared H_1-eCo films are affected by experimental conditions. The exhibited results from low angle XRD and TEM clarify the existence of nanostructured and confirm the direct electrodepostion of mesoporous Co films using hexagonal template of Brij®78, which means that the deposited films of Co metal have higher aspect percentage and excellent mesoporous films. The mesoporous H_1-eCo films show superior specific capacitance, which may be attributed to a larger electroactive surface area due to the formation of mesopores.

5. ACKNOWLEDGEMENT

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Table 1. Capacitance values derived from cyclic voltammograms of electrodeposited nanostructured cobalt films at various sweep rates.

Scan rate ($V.s^{-1}$)	Capacitance ($F.g^{-1}$)
0.01	950
0.02	695
0.05	510
0.1	460
0.2	390
0.5	320
1	290