Electrochemical and SEM properties of Co^{2+} ion in hexagonal mesophase of pluronic lyotropic liquid crystal template

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Abstract. The electrochemical and SEM properties of Co^{2+} ion in hexagonal mesophase of the pluronic lyotropic liquid crystal template are reported. The cyclic voltammetric studies evidenced the occurrence of two slow electron transfer reduction processes. Such a reaction presumably related to the reduction of Co^{2+} ion to Co metal. The hexagonal (H_1) lyotropic liquid crystalline phases of P_{84} surfactant have been used to template the electrochemical deposition of nanostructured cobalt films as well as its uses as background electrolyte. Electrochemical studies show that these films have very high surface areas, which reveals that the deposited film exhibits promising properties. The electrode parameters of Co(II) ion in hexagonal meso phase of the lyotropic liquid crystal ternary system (pluronic P_{84} /cobalt/*p*-xylene) is determined using cyclic voltammetry, deduced convolutive voltammetry and chronoamperometry techniques. The morphology of nanostructured deposited films of Co^{2+} ion in pluronic lyotropic liquid crystal template was investigated via scanning electron microscopy (SEM) technique.

Keywords. Electrochemical properties; hexagonal mesophase; liquid crystal; deduced convolutive voltammetry; chronoamperometry.

1. Introduction

Liquid crystals (LC) have become the basis of many advanced technologies. They are used in displays of wristwatches, calculators, laptop computers, aircraft and have newer applications in flat-panel television, large switchable privacy windows, optical computing and optical devices for communication networks (Zhang and Schuster 1994; Deschenaux *et al* 1996). The hexagonal phase composition of the $\text{P}_{84}/\text{Co}/p$ -xylene system was determined according to the phase diagram established in the literature (Raman *et al* 1996; Paavola *et al* 1998; Liu *et al* 2000; Yang and Alexandridis 2000).

The construction of nanostructured materials using surfactant molecules as templates was found to be a very productive area of research (Raman *et al* 1996; Raimondi and Seldon 1999; Liu *et al* 2000). Bartlett *et al* have shown that the possibility of electrochemical deposition of a range of metals with regular mesoporous architectures by using lyotropic liquid-crystalline phases as template (Attard *et al* 1997; Bartlett *et al* 2002). The idea of using the lyotropic liquid crystalline phases of nonionic surfactants to template the deposition of inorganic materials was first introduced by Attard who demonstrated the formation of nanostructured silica by hydrolysis of tetra-

methyl orthosilicate (Attard *et al* 1995) and platinum by chemical reduction of hexachloroplatinic acid (Attard *et al* 1997). In this case a high concentration of the non surfactant, typically 40–60 wt% is employed and the nanostructure is a direct cast of the structure of the lyotropic phase used to template the deposition.

In the hexagonal phase the surfactant molecules assemble into long cylindrical micelles and these micelles then pack into a hexagonal array in which the separation between the micelles is comparable to their diameter (around 2 nm) (Mitchell *et al* 1983). When these phases are used to template the electrochemical deposition of metal films, the metal salt and electrolyte are dissolved into the aqueous component of the mixture and metal deposition occurs from the electrode surface, around the surfactant micelles. When deposition is complete, the surfactant is removed by washing to leave a metal film punctured by a regular hexagonal array of uniform pores. The thickness of the film is directly controlled by the total charge passed. In spite of the synthesis of nanostructured mesopore material using surfactant for coassembly was first reported in 1992 (Beck *et al* 1992; Kresge *et al* 1992), to date there have been no reports of the determination of the electrochemical parameters of nanostructured mesoporous films. In this work, we describe the fabrication of nanostructured cobalt films (H_1 -e Co) by the electrodeposition of cobalt from the aqueous domain of the hexagonal liquid crystal phase of P_{84} . The electroche-

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mical properties of the liquid crystal template and the morphology of the deposited film was studied via cyclic voltammetry, deduced convolutive voltammetry, chronoamperometry and scanning electron microscopy.

2. Experimental

2.1 Material and methods

The pluronic P₈₄ poly (ethylene oxide)-block-poly-(propylene oxide)-block-poly (ethylene oxide) copolymer was obtained from Bartlett. P₈₄ can be represented by the formula (EO)₁₉(PO)₄₃(EO)₁₉ based on its nominal molecular weight of 4200 and 40% PEO content. All solutions and liquid crystalline template (LCT) were prepared using reagent grade water (18 MΩ cm). All glassware was cleaned by soaking in a 5% Decon 90 (Aldrich solution for few days followed by rinsing with deionized water and dried in an oven at 50°C. *p*-xylene (99%), cobalt acetate (CoAc₂·4H₂O 99.5%), potassium acetate (kAc) (99.4%) and boric acid (≥ 99.5%) were obtained from Aldrich.

The plating mixtures used in this work were ternary system consisting of P₈₄ non-ionic surfactant [(EO)₁₉(PO)₄₃(EO)₁₉], aqueous solution of CoAc₂·4H₂O, H₃BO₃ and *p*-xylene. The H₁ phase of ternary mixture containing 53.13 wt% aqueous Co salts and boric acid, 44.64% weight of P₈₄ and 2.23 weight of *p*-xylene which is stable at room temperature and remains chemically stable for more than a month. Electrodeposition of cobalt from the liquid crystalline plating mixture onto polished gold electrode was conducted at room temperature. After deposition the electrodes were rinsed with excess amounts of deionized water to remove the surfactant. The gold electrode used as substrate was prepared by evaporating 10 nm of a chromium adhesion layer, followed by 200 nm of gold, onto 1 mm thick glass microscope slides (Bartlett *et al* 2001). The gold electrode was cleaned by sonication in propanol (BDH) for 1 h followed by rinsing with deionized water.

2.2 Instrumentation

The electrochemical experiments were carried out using an EG & G 283 potentiostat and a conventional three electrode cell (15 ml volume capacity). In electrochemical measurements, the working electrode was a 1 mm diameter gold disk electrode, while for the structural characterization of the produced material films, the working electrode was 1 cm² area flat electrode (made by evaporating 10 nm of a chromium adhesion layer followed by 200 nm thick of gold onto thin glass microscope slides). Platinum gauze of area 1 cm² was used as counter electrode and a saturated calomel electrode (SCE) as the reference electrode. 1 mm disk electrode was polished by polishing

paper (grade 1200) followed by alumina (Buchler) of two grades: 1.0 and 0.3 μm then rinsed with deionized water. The 1 cm² flat gold working electrode were cleaned by sonication using ultrasonic bath (decon F5 1006) in propanol for 1 h, then kept in deionized water until used.

The morphology and structure of the deposited films were characterized via scanning electron microscopy (JEEOL 6400).

3. Results and discussion

Figure 1 shows cyclic voltammogram of 0.2 M CoAc obtained in template mixture on gold electrode at a scan rate of 0.02 V/s. As shown, on the forward scan almost no current was observed until the potential reached -0.88 V. Thereafter, the cathodic current increased rapidly once the nucleation process began. The *i*-*E* responses from figure 1 also shows, as common feature, one stripping peak on the reverse scan at -0.4 V. The shape of the cyclic voltammogram corresponds to a slow rate of two charge transfer. This is illustrated from the non-broad peak of the reduction peak which clearly supports the rapidity of the second electron transfer than the first one. The dependence of the electrochemical parameters, estimated from the recorded cyclic voltammograms, on the potential scan rate, gives important indications about the kinetic of the electrode process (Nicholson and Shain 1964; Bard and Faulkner 1986). Table 1 shows the variation of potential scan rate with the peak characteristics of the electrochemical reduction of Co²⁺ ion on gold electrode in lyotropic liquid crystal. It was found that the cathodic peak potential, $-E_p$, peak separation, ΔE_p , is dependent on the sweep rate in the cyclic voltammogram, and the cathodic peak current, i_p , is proportional to the square root of the potential sweep rate. This behaviour

Figure 1. Cyclic voltammetry of 0.2 M CoAc in pluronic lyotropic liquid crystal, $\nu = 0.02$ V/s and $T = 298$ K.

indicates that the rate of electrode reaction for the reduction of Co^{2+} ion in the liquid crystal template is a slow electron transfer process.

The relationship of peak potential and peak current with sweep rate of the forward sweep was analysed by using the following relationships (Nicholson and Shain 1964):

$$E_p = \text{const} + (RT/2.3\alpha n_a F) \ln \nu, \quad (1)$$

$$i_p = 2.99 \times 10^5 n(\alpha n_a)^{1/2} C^b D^{1/2} A \nu^{1/2}, \quad (2)$$

where E_p is the peak potential, α the transfer coefficient, n_a the number of electrons involved in the rate determining step, ν (mV/s) is the potential scan rate, i_p (μA) the peak current, n the Faradays per mole of the substrate electrolyzed, C^b (mM) the bulk concentration of electroactive species and D (cm^2/s) the diffusion coefficient of the species.

From the slope of the linear relationship observed between E_p and $\log \nu$, the value of α (the cathodic transfer coefficient) at gold electrode was calculated and found to be 0.21 ± 0.02 according to (1), where $T = 298 \text{ K}$ and $n_a = 1$. The deviation from origin of i_p vs $\nu^{1/2}$ dependence shows that the electrode reaction is not under pure diffusion control (Bard and Faulkner 1986).

Values of the symmetry coefficient (α) were also determined from the difference of peak and half-peak cathodic potentials by means of (Bard and Faulkner 1986)

$$E_p - E_{p/2} = 1.857(RT/\alpha n_a F), \quad (3)$$

and were found to be less than 0.5 when $n_a = 1$ (table 2), confirming the irreversible nature of the reduction process. The obtained data revealed that the peak width ($E_p - E_{p/2}$) grows larger with increasing sweep rate which indicates the slow nature of charge transfer process.

Diffusion coefficient (D) of the investigated Co(II) ion in lyotropic liquid crystal was determined via (2) from the slope of the i_p vs $\sqrt{\nu}$ plot and was found to be $2.3 \times 10^{-6} \text{ cm}^2/\text{s}$. The heterogeneous rate constant (k_s) of the electrode reaction can be calculated from cyclic voltammetric data using the following equation (Klingler and Koshi 1981):

$$k_s = 2.18 (D\alpha nF\nu/RT) \cdot \exp[\alpha^2 nF/RT(E_p^a - E_p^c)]. \quad (4)$$

The values of k_s calculated from (4) is cited in table 2.

Table 1. Peak characteristics of the cyclic voltammograms as a function of potential scan rate for the system $\text{Au}/0.2 \text{ M CoAc} + 0.2 \text{ M boric acid} + 0.5 \text{ M sodium acetate} + p\text{-xylene} + \text{P}_{84}$.

ν (V/s)	E_p (V/SCE)	ΔE_p (V/SCE)	$E_p - E_{p/2}$ (V/SCE)
0.050	0.932	0.664	0.100
0.100	0.977	0.702	0.135
0.200	1.003	0.851	0.185
0.500	1.091	0.960	0.230
1.000	1.114	1.005	0.289

The value of E^0 determined from the average value of E_p^c and E_p^a was found to be $0.65 \pm 2 \text{ mV}$.

The cobalt films deposited in pluronic lyotropic liquid crystal on gold electrode were analysed electrochemically by cycling in 1 M aqueous sodium hydroxide between -1.22 V and -0.65 V vs SCE at a scan rate of 0.05 V/s .

Figure 2A shows a typical example of a cyclic voltammogram for an $\text{H}_1\text{-e}$ Co film, deposited in lyotropic liquid crystal at -0.85 V vs SCE. For comparison, a cyclic voltammogram of the deposited film from aqueous media is shown in figure 2B. The different amplitudes of the current in these two voltammograms are clearly noticeable. The increased charge in the case of pluronic liquid crystal is interpreted as a confirmation that the surface area available during sweep is enhanced due to the large internal area of the pores. The observation of a large charge density is due to the mesoporosity of the deposited film (Elliott *et al* 1991; Pletcher 1991; Trasatti and Petri 1992; Nelson *et al* 2002).

As is known, the extent of diffusion layer thickness is time dependent. Thus the diffusion coefficient, D , was

Figure 2. (A) Cyclic voltammetry of deposited cobalt film in pluronic lyotropic liquid crystal and (B) 1 M sodium hydroxide, $\nu = 0.05 \text{ V/s}$ and $T = 298 \text{ K}$.

Table 2. Values of electrochemical parameters of electrodeposited cobalt film via cyclic voltammetry and chronoamperometry techniques.

Technique	Electrochemical parameters			
	E° (V)	$k_s \times 10^5$ (cm/s)	α	$D \times 10^6$ (cm ² /s)
Cyclic voltammetry	0.659	3.1	0.23	2.30
Chronoamperometry	–	3.5	0.21	2.45
Convoluting current	–	–	–	2.60

Table 3. Variation in film thickness with charge.

Pluronic surfactant	Deposition potential	Charge (mC)	Thickness (nm) ± 5 nm (SEM)
P ₈₄	–0.85 V/SCE	75	91
		125	152
		170	207
		255	311
		430	524

Figure 3. (A) Chronoamperogram of cobalt ion in pluronic lyotropic liquid crystal at $E_f = -0.9$ V vs SCE and (B) Cottrell plot (current vs reciprocal square root of time).

evaluated by performing chronoamperometry experiments. The current is given by the Cottrell equation (Schwarz and Shain 1965)

$$i = (nFACD^{1/2}/\sqrt{\pi t}). \quad (5)$$

Figure 3A shows an $i-t$ transient during the reduction of Co^{2+} ion on lyotropic liquid crystal template at $E_f = -0.9$ V vs SCE. By selecting the data points from the experimental data detected in figure (3A), a Cottrell plot is obtained as current vs the reciprocal square root of time and presented in figure 3B. The values obtained from chronoamperometric experiment for the diffusion coefficient were in good agreement with the results obtained from cyclic voltammetry (table 2). Here, the deviation of the plot i vs $1/\sqrt{t}$ from the origin indicates that the kinetic of the electrode process is not under pure diffusion control.

A series of chronoamperograms was captured in which the step potential, E_f , was made successively closer to E° value of the system. For each current–time curve a plot of i vs $t^{-1/2}$ was made which upon extrapolation to $t = 0$ yielded i_o , the cathodic exchange current, which is defined in (6) (Thlyathem and Geiger 1985)

$$i_o = nFk_s C^\circ \exp[\alpha nF(E - E^\circ)/RT]. \quad (6)$$

Plotting of $\ln i_o$ against $(E - E^\circ)$ gave a straight line, and from the intercept (equal to $\ln nFk_s C^\circ$) a k_s value of 3.5×10^{-5} cm/s was calculated at 298 K. Value of the transfer coefficient (α) was determined from the slope of the plot and was found to be 0.21 ± 0.02 . These values are in good agreement with the values of k_s and α calculated from cyclic voltammetry measurements at a gold electrode and verify the slow nature of the electrode reaction. The obtained results are summarized in table 2.

The convoluted current (I_1) for a simple electron transfer is obtained from (7), where t is the total elapsed time (Grenness and Oldhan 1972)

$$I_1 = I^* \frac{1}{\sqrt{\pi t}} = \frac{1}{\sqrt{\pi}} \int_0^t \frac{i(u)}{\sqrt{(t-u)}} du. \quad (7)$$

The diffusion coefficient, $D = 2.6 \times 10^{-6} \text{ cm}^2/\text{s}$ was determined from deduced limiting convoluted current using the following relationship (El-Hallag and Ghoneim 1996, 2000)

$$I_{\text{lim}} = ip_{\text{irr}}/3.099 \sqrt{(\alpha n_a \nu)}, \quad (8)$$

$$I_{\text{lim}} = nFAC^0\sqrt{D}, \quad (9)$$

where I_{lim} is the limiting convoluted current for I_1 at the potential driven past the wave. Other terms have their usual meanings.

Based on the above discussion and the interpretation of the electrochemical behaviour, the electroreduction of Co(II) ion can proceed as

The overall rate of conversion of Co(II) to Co metal is determined by the kinetics of the $\text{Co(II)}/\text{Co(I)}$ couple involving the transfer of a single electron, assuming that reaction (11) is the rapid step.

Figure 4. Scanning electron microscopy of an $\text{H}_1\text{-e}$ Co film deposited on evaporated gold electrode. The film was deposited from a mixture of 53.13 wt% aq. Co, 44.64 wt% P_{84} , 2.23 wt% p -xylene: (A) surface image and (B) cross-section image.

The cobalt films deposited from the hexagonal template mixture on large area $\sim 1 \text{ cm}^2$ electrodes and the thickness of the resulting film was measured using SEM. The deposited films were silvery metallic and adhered well to the evaporated gold electrodes used from deposition.

Figure 4A shows an SEM image of an $\text{H}_1\text{-e}$ Co film electrodeposited at -0.85 V vs SCE, at a temperature of 25°C . As shown the film is smooth, relatively flat, dense and featureless surface morphology observed in SEM. Figure 4B shows a cross-section of the cobalt deposit; the actual film thickness was estimated to be 175 nm. Further SEM analysis of films deposited showed that the film thickness varied linearly with the charge density as shown in table 3. Figure 5 indicates the variation of charge density with the film thickness.

Cobalt films electrodeposited from aqueous acetate solution have larger feature sizes, typically $> 1.5 \mu\text{m}$ (Fan

Figure 5. Plot of charge density vs film thickness.

Figure 6. SEM of $\text{H}_1\text{-e}$ Co of macroporous cobalt film electrodeposited from aqueous solution.

et al 1993). This result was confirmed by the study of cobalt films grown at -0.8 V from acetate solution in the absence of surfactant (Bartlett *et al* 2003). Figure 6 shows a large scale SEM image for a mesoporous cobalt film electrodeposited at -0.95 V vs SCE from a plating solution containing 0.1 M cobalt sulfate and 0.1 M boric acid, using 750 nm template spheres. As is shown the micrograph shows that 750 nm template spheres scanning electron microscopy confirms the presence of a highly regular macroporous structure. The spherical pores left in the cobalt films after removal of the polystyrene latex spheres are arranged in a well ordered three dimensional hexagonal close packed structure (Bartlett *et al* 2000, 2003).

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