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The deposition of mesoporous Ni/Co alloy using cetyltrimethylammonium bromide as the surfactant in the lyotropic liquid crystalline phase bath

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ABSTRACT

The procedure for the electrodeposition of a mesoporous nickel/cobalt layer from a liquid crystalline plating bath based on the cheap, commercial surfactant, cetyltrimethylammonium bromide and an aqueous solution containing 0.84 M $NiCl_2$ and 0.20 M $CoCl_2$, has been investigated. The phase diagram for these mixtures is reported and it is shown that the H_1 liquid crystalline phase has a high conductivity. The conditions for deposition have been established using cyclic voltammetry and potential step and deposits are characterised using scanning electron microscopy (SEM), electron diffraction analysis (EDX) and helium ion microscopy (HIM). Uniform thickness deposits with a Ni/Co ratio ~4/1 can be prepared and they have a high surface area; in 1 M NaOH Ni/Co alloy layers with a thickness of ~2 μm can store ~1 C cm^{-2} in the $Ni(OH)_2$/NiOOH couple. This charge may be cycled >20 times.

1. Introduction

The need for energy storage devices with much enhanced performance has focused attention on the development of new materials. One class of material finding application in batteries and supercapacitors is the nanoporous layers produced by template electrodeposition. The layers are electrodeposited directly from a lyotropic liquid crystalline medium and have an ordered array of pores on a scale of a few nanometres giving a high surface area. Since the initial studies of the deposition of nanoporous platinum [1,2], a wide range of metals and some alloys with this novel architecture have been electrodeposited [3–5]. Particularly relevant to the work are the papers on the deposition of nanoporous nickel [6–9], cobalt [10], NiCo alloy [11,12] and nickel oxides [13]. In general, however, the lyotropic liquid crystalline medium employs a rather expensive surfactant, usually octaethyleneglycolmonohexadecyl ether ($C_{16}EO_8$) or the related commercial surfactant Brij® 56.

In a recent patent [14], the company Nanotecture has described the fabrication of such nanoporous materials using the much cheaper surfactant, cetyltrimethylammonium bromide. We now wish to report a study of the electrodeposition of mesoporous nickel/cobalt alloy from the H_1 phase of a cetyltrimethylammonium bromide/aqueous solution. The speciation of the Ni(II) and Co(II) in this phase will be different from that reported for H_1 phases prepared with neutral surfactants [15]. The Ni(II) and Co(II) probably exist as anionic halocomplexes and it is these, rather than Ni^{2+} and Co^{2+}, that interact with the cationic surfactant.

2. Experimental

The surfactant, cetyltrimethylammonium bromide (CTAB) (98% purity) was purchased from Fluka, nickel chloride hexahydrate (99.9% purity) from Alfa Aesar, and cobalt chloride hexahydrate and ruthenium hexaamine (99% purity) from Aldrich. The compounds were used as received. All aqueous solutions were prepared with deionised water from a Whatman Still and RO 50 water purification system (18 MΩ cm). The argon gas used was of high purity grade (BOC gases, 99.9% purity).

Electrochemical deposition and cyclic voltammetry were carried out using an EG&G model 263A potentiostat/galvanostat and a three electrode cell. The three electrode system consisted of the working electrode, a large area platinum gauze, counter electrode and either a homemade saturated calomel reference electrode (SCE) or a homemade saturated mercurous sulphate reference electrode (SMSE). Platinum, stainless steel and nickel disc microelectrodes were used as working electrodes in most experiments; they were fabricated by sealing microwires of appropriate diameters in glass. The microdisc electrodes were polished using silicon carbide paper (CC 1200, English Abrasive) and water/alumina slurries (Buehler) with particle sizes of 1 μm and 0.3 μm to obtain a mirror finish. Depositions were carried out onto both stainless steel and copper plates. Some depositions were carried out in a commercial, 267 cm^3 Hull Cell supplied by Kocour Inc., type TCACG-267, fitted with a heater. The working electrode was a steel

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or copper plate 10 cm wide × 5 cm high and the counter electrode was a Pt/Ti mesh plate, 6 cm wide × 5 cm high. The insulating walls were 12.7 cm and 4.8 cm. The local current densities across the working electrode were calculated using software written in Southampton.

The plating mixtures were made of the surfactant (CTAB) and an aqueous solution of the metal salts. For voltammetry and electrodepositions, the constituents were heated in a sealed vial to 40 °C for 30 min then stirred in order to produce a homogeneous mixture. The vial was again sealed (to avoid the evaporation of water) and placed in the oven at 40 °C for a further 30 min. The template mixtures have different compositions. In order to make the phase diagram, the percentage by weight of CTAB was changed from 30 to 70 wt.% mixed with the appropriate weight of a solution 0.84 M $NiCl_2$ and 0.20 M $CoCl_2$.The different lyotropic liquid crystalline phases were confirmed by using an Olympus BH-2 polarized light microscope equipped with a Linkam TMS90 heating/cooling stage and control unit. The experiment consisted of preparing a thin film of the mixture between a cover slip and a glass slide. Most voltammetry and depositions of mesoporous Ni and Co films were from template mixtures containing 50 wt.% CTAB + 50 wt.% 0.84 M $NiCl_2$ and 0.20 M $CoCl_2$ at 317 K since this composition fell at the centre of the H_1 phase. Experiments with microdisc electrodes were carried out by spreading a layer of the liquid crystal mixture across the Pt gauze counter electrode and then pushing the working and reference electodes into this layer.

The determinations of conductivity used electrochemical impedance spectroscopy carried out with a Bio-Logic VMP II instrument; the frequency range was between 200 kHz and 0.1 Hz and the amplitude was 10 mV peak-to-peak. The gap between two Pt plates (5 mm × 5 mm) spaced by 5 mm was filled with the mixture of 50 wt.% CTAB + 50 wt.% 0.84 M $NiCl_2$ and 0.20 M $CoCl_2$. The temperature was increased in steps from 298 to 353 K and a Nyquist plot obtained at each temperature. The conductivities were calculated from the high frequency intercept on the real axis.

SEM images were recorded with a Phillips XL30 ESEM microscope fitted with an EDX elemental analysis unit. The He ion microscopy employed a Zeiss Microscope, Model Orion®. The image was processed using the software ImageJ. A Fast Fourier Transfer and the 'Sharpen' command were used to remove the noise.

3. Results and discussion

3.1. The phase diagram

Before investigating the electrodeposition of mesoporous NiCo films, the phase diagram for mixtures of cetyltrimethylammonium bromide (CTAB) with aqueous solutions of nickel and cobalt chloride was established. Mixtures were prepared at room temperature and then allowed to stand overnight in a closed vial in order to equilibrate. The optical textures were followed using the polarised optical microscope; the temperature(s) for phase changes were noted. Samples were first heated at 10 K/min to estimate the temperature for phase transitions and later samples were heated at 1 K/min and 0.1 K/min in order to obtain better definition of the temperature for the phase transition. Fig. 1 shows the phase transition data obtained for the system, CTAB and an aqueous solution containing 0.84 M $NiCl_2$ and 0.20 M $CoCl_2$. The lines are drawn from our experience of such phase diagrams but should be taken only as a guide. Since our interest was in the deposition of the mesoporous nanostructure found with plating baths with the H_1 liquid crystalline phase, all later experiments focused on the 50/50 mixture and a temperature 317 K. It was noted, however, that in these conditions the medium did age; initially, the phase has a greenish tinge but after about 30 min it changed to a darker blue, presumably due to a change in the speciation of the transition metal ions in this medium with a very high halide ion content.

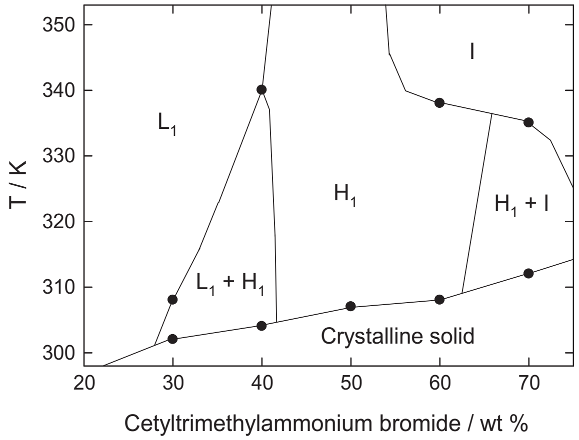

Fig. 1. Pseudobinary phase diagram of cetyltrimethylammonium bromide (CTAB) and an aqueous solution containing 0.84 M $NiCl_2$ and 0.20 M $CoCl_2$. The solid lines showing the phase boundaries are drawn as a guide.

3.2. Medium conductivity

Having determined the medium for the electrodepositions, 50 wt.% CTAB + 50 wt.% of an aqueous solution containing 0.84 M $NiCl_2$ and 0.20 M $CoCl_2$, its conductivity was determined as a function of temperature using an impedance technique. Fig. 2 shows the data over the temperature range 283–353 K as an Arrhenius plot. Initially, at 283 K the mixture is present as a crystalline solid and the conductivity is low. The conductivity increases quite rapidly with heating until 307 K when the H_1 phase is formed and the Arrhenius plot then becomes linear. There is little hysteresis between heating and cooling above 307 K but below this temperature, super-cooling occurs and the H_1 is retained until the crystalline solid is reformed; at the same temperature the conductivity of the H_1 phase is substantially higher than the solid.

At 317 K, the conductivity of the H_1 phase is 0.15 S cm^{-1}, very similar to that for aqueous 1 M KCl at this temperature [16]. It is also a factor of ~6 higher than a similar lyotropic liquid crystalline mixture based on the neutral surfactant, Brij® 56 [17]. The high

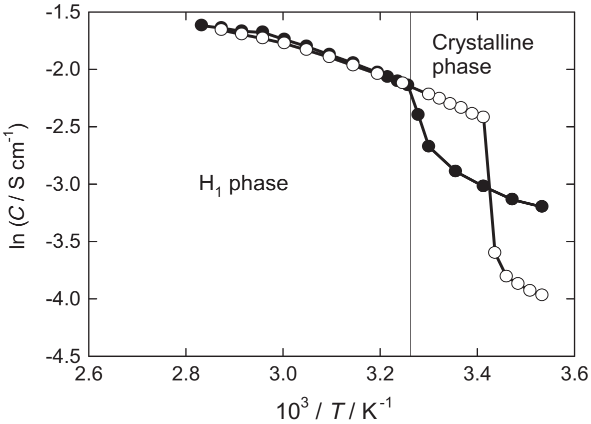

Fig. 2. Variation of the conductivity with temperature of a mixture containing 50 wt.% CTAB and 50 wt.% of an aqueous solution containing 0.84 M $NiCl_2$ and 0.20 M $CoCl_2$. (●) Data recorded while the temperature was being increased and (○) data were recorded when the temperature was being decreased.