International Journal of ELECTROCHEMICAL SCIENCE www.electrochemsci.org

Fabrication and Characterization of Nanostructured Mesoporous Ni(OH)₂ Electrode Using Pluronic P84 PEO/PPO/PEO Triblock CopolymerTemplate

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Received: 31 March 2021 / Accepted: 22 May 2021 / Published: 30 June 2021

Block, copolymer of polyethylene oxide/ polypropylene oxide/ polyethylene oxide (PEO/PPE/PEO) (Pluronic P84) are utilized as template for constructing electrode with high surface area. This electrode is of much interest for many applications including electrochemical detectors, batteries, and fuel cells. Pluronic P84 are example of a triblock copolymer to template the electrodeposition of a mesoporous nickel film. This method is found to give a high increase in surface area. TEM and XRD of Pluronic P84 templated nickel on gold surfaces shows a peak consistent with a pore to pore spacing of 9.5 nm. Electrochemical inspection of the deposited film using cyclic voltammetric exhibits that the nanostructured have high surface area and a pore structure that allows extremely fast diffusion of species to active sites within the structure.

Keywords: mesoporous; nanostructured; pluronic P84; x-ray diffraction.

1. INTRODUCTION

The synthesis of nanostructured porous electrode using self-assembling surfactants and polymers as templates producing high surface area with good characteristics. This idea pioneered by Beck et al. [1] to make up mesoporous silica containing arranged arrays of pores with internal radius of 1–2.5 nm and configuration of a narrow pore size. Attard et al, indicated that the utilize of such a method for fabrication of a porous platinum layer on planar electrodes [2]. This method was extended to other metals such as Sn [3, 4], Co [5], and Ni [6]. Here, we are intended to conducting such methods to fabricate arranged nanostructured porous electrode with high surface area. The structure of the nanostructured mesoporous metal films has been concerned to cylindrical pores ordered as hexagonal arrays. Triblock copolymers of the Pluronic family exhibit a very large range of framework depending upon temperature,

and constituents. Further, the phase diagrams have been extensively investigated [7, 8], and so can give a starting point for determining the constituents and temperature which might produce a particular nanostructured. Such copolymers have been reported previously for working well in the templating of porous silica [9].

To the best of our knowledge, there is no work reported for fabricate nanostructured mesoporous Ni film using block, copolymers of polyethylene oxide/ polypropylene oxide/ polyethylene oxide (PEO/PPE/PEO) (pluronic P84). In this article, a simple method for electrodeposition of ordered mesopore hexagonal electrodeposited Ni(OH)₂ "H1-e Ni (OH)₂" films from the hexagonal template of pluronic 84 was described. The properties of capacitive of the H1-e Ni(OH)₂ hydroxide thin films were examined via cyclic voltammetry method. The influence of potential sweep rates on the capacitance properties of H1–e Ni (OH)₂ films were analyzed for performing optimum conditions for deposited H1– e Ni (OH)₂ film with the best capacitive characteristics.

2. EXPERIMENTAL

2.1 Materials and solutions

All chemicals were very pure and used as supplied. Nickel acetate (NiAc2.4H2O 99.5%), potassium acetate (KAc 99%) and P-xylene (99%) were supplied from Fluka. Plouronic 84 is a polyethylene oxide/ polypropylene oxide/ polyethylene oxide (PEO/PPE/PEO) copolymer. Pluronic P84 non –ionic surfactant [(EO)19(PO)43(EO)], aqueous solution of NiAc₂.4H2O, KAc and p-xylene are utilized as a mixture for plating process. The fabricated hexagonal phase (Hl) of plating bath consists of 53.13 wt% aqueous Ni acetate & K acetate, 44.6% weight of pluronic P84 and 2.23% weight of p-xylene which remain stable at room temperature for more than a four weeks.

2.2 Instrumentation

The apparatus used for electrochemical deposition and cyclic voltammetry (CV) measurements are Potentiostat EG & G 283 and a three electrode cell (15 cm³ volume space).

2.3 Electrodeposition process

The H1-e Ni(OH)2 films were electrodeposited in a three-electrode cell at ambient temperature. The radius of gold electrode was a 0.5 mm, while for the morphology investigation of, the working electrode was flat gold substrate with geometrical surface area 100 mm². Platinum gauze with area 100 mm² was used as auxiliary electrode and saturated calomel electrode (SCE) as the standard electrode. The cleaning process of gold disk electrode was carried out by polishing paper with grade 1200 followed by alumina powder of two grades: 1.0 and 0.3 μ m then rinsed with very pure water. The plating mixture described previously was used as electrolyte, at constant potential equal -0.91 V vs. SCE for achievement the electrochemical experiments for deposition process. The deposition of Ni(OH)₂ film was performed

by passing the charge for definite time in the electrochemical cell. After deposition, the electrodes were cleaned with too much amounts of very pure water to get rid of the surfactant.

2.4 Cyclic voltammetry characterization

The Ni(OH)₂ film was electrodeposited on disk gold electrode and characterized via cyclic voltammetry at various scan rates (v) and at ambient temperature.

2.5 X-ray diffraction characterization

Bruker D8 x-ray diffractometer using Cu K α radiation ($\lambda = 0.154$ nm) was used XRD with Cu K α radiation to confirm the formation of a nanostructured mesoporous film and for the measurement the diameter of electrodeposited Hl-e Ni(OH)2 films.

2.6 TEM measurements

The ordered and homogeneity of the mesoporous structure was achieved using JEOL 2000FX transmission electron microscope (TEM) operating at an accelerating voltage of 200 KV.

2.7 SEM characterization

The scanning electron microscope (SEM) (JEOL 6400) was applied to look at the morphology and thickness of the electrodeposited nickel hydroxide films.

2.8. Convolutive voltammetry

Convolution-deconvolution voltammetry were achieved using EG & G condecon software program. It was used to examine the nature of electrode reaction and determining the some electrochemical and chemical parameters such as diffusion coefficient (D), standard redox potential (E^{o}) and homogeneous chemical rate constant (k_{c}).

2.9 Digital simulation

Condesim EG & G package was used for performing the simulation process. Simulation method aim to confirm the electrochemical and chemical parameters calculated from experimental cyclic voltammograms.

3. RESULTS AND DISCUSSION

Here in this work, pluronic 84 (P84) has been employed as the surfactant. When mixed with the aqueous solution of the metal salt, the hydrophobic blocks cluster together and the hydrophilic blocks

dissolve in the water, producing the lyotropic liquid crystal phases. The most attractive phase of this article is the hexagonal phase (HI) where the surfactant molecules aggregate into parallel cylindrical rods arranged in a hexagonal pattern (Figure 1). The central of the surfactant rod is hydrophobic while the aqueous species exist in the inter-distance between singleton rods [10]. The deposited H1-e Ni(OH)₂ films were investigated utilizing cyclic voltammetry, scanning electron microscopy (SEM), transmission electron microscopy (TEM), x-ray diffraction (XRD), convolutive voltammetry and digital simulation.



Figure 1 A. Phase diagram of Pluronic® P84 (PEO/PPO/PEO) in water and *p*-xylene at 25 °C. 11, H1, V1, Lα, V2, H2 and 12 indicate normal micellar cubic, normal hexagonal, normal bicontinuous cubic, lamellar, reverse bicontinuous cubic, reverse hexagonal and reverse micellar phases, consequently.



Figure 1B. The growth stages of the mesoporous hexagonal (H1-e Ni(OH)₂) films electrodeposited in the existence of a hexagonal liquid crystal template

3.1. Cyclic voltammetry characterization



Figure 2. Cyclic voltammograms of deposit H1-e Ni(OH)₂ film from pluronic P84 in 0.1M KOH at different sweep rates.

In this work the H1-e Ni(OH)₂ electrode were used as supercapacitors and their achievement was tested using cyclic sweep voltammetry. Figure 2 indicates that the CV curves of the HI–e Ni(OH)₂ film electrode at different sweep rates. The shape of the CV waves exhibits that the capacitance properties of H1-e Ni(OH)₂ is distinct from that of the electric double-layer capacitance, which would give a CV wave adjoining to an ideal rectangular shape. Also, the shape of the CV waves for the HI – eNi(OH)₂ plate is not quite affected by variation the sweep rates. This can be ascribed to the enhanced mass transportation and electron transfer within the material due to its systematically ordered mesoporous. The voltammetric waves shown in figure 2 indicate that the current peaks are directly proportional to the sweep rate, revealing ideally capacitive nature [11]. It can also be seen that when the scan rate grow, the peak current grows rapidly and the distance between the reductive and oxidative waves becomes wider, which is mostly due to the polarization of the cell under high sweep rate. It is

well established that the anodic and cathodic waves are entitled to the oxidation of Ni(OH)₂ to NiOOH and the reverse process, respectively. The specific capacitance (C) of the deposited films can be determined in accordance with the upcoming equation [12-14]:

 $C = Q / m v \Delta V$

Where Q is the half of the area of the CV waves and the symbols have their usual meaning. The numerical values of specific capacitance calculated from the cyclic voltammetry experiments were listed in Table 1.The effects of potential sweep rates on the capacitive properties of electrodeposited films are indicated in Figure 3. The decrease in the value of capacitance with increasing the sweep rate arises from the presence of inner active sites, which cannot precede the redox transitions completely at higher scan rates of cyclic voltammograms [15].



Figure 3. Specific capacitance of electrodeposited mesoporous nickel hydroxide films at different sweep rates.

Table 1.	Values of specific	capacitance of	f electrodeposite	d mesoporous	nickel hydro	xide films at
di	fferent sweep rates					

Sweep rate (mVs ⁻¹	Specific capacitance			
	(F g⁻¹)			
10	980			
20	870			
50	715			
100	630			
200	513			
500	440			

The specific capacitance obtained at the slowest scan rate is believed to be close to that of full utilization of the electrode material [15]. The lower sweep rates permit greater time for the proton to enter the main mass of the nanostructured materialness. Such large values of capacitance are attributed to the typical morphology and amorphous nature of the film [15].

Figure 4 displays the CV scan of the electrodeposited Ni(OH)₂ films with and without template. The templated film exhibited approximately fourfold increase in surface area over that without template (blank). Accordingly, the electrodeposited film contained some surface roughness inherent to electrodeposition that increased the actual surface area of the nickel electrode surface in case of the absence of template.



Figure 4. Cyclic voltammograms of plan Ni electrode and electrodeposited HI-eNi(OH)₂ film in 0.1M KOH

3.2. X-ray characterization

Figure 5A describe the low – angle XRD patterns of the "pluronic P84" template (curve a) and the deposited H1-e Ni(OH)₂ film (curve b), separately. Both curves indicate peaks at small angles, which clarify the presence of a size – controlled nanoporosity. The hexagonal template displays a clear diffraction peak with d – spacing of 9.2 nm at approximately $2\Theta = 1.12^{\circ}$ (curve a), which can be ordered as the (100) plane.





Figure 5. (A) Low –angle XRD for the H_1 -Ni(OH)₂ from pluronic P84 (a), for electrodeposited H_1 -eNi(OH)₂ film on gold substrate (b) and (B) wide – angle XRD for electrodeposited H_1 -eNi(OH)₂ film on a gold substrate.

The pore to pore distance for this hexagonal arrangement, given by $d100/\cos 30$, is 9.2 nm. The HI – e Ni(OH)₂ film also indicates well defined peak at around $2\Theta = 1.13$ (curve b), which corresponding to a d – spacing of 9.04 nm and a pore to pore distance of 9.25 nm, implying a porous nanostructured extracted from the structure of the template electrolyte. As shown all the peaks are in accordance with the conventions of Ni(OH)₂. The XRD convention consists of the sharp peak at 45°, except the substrate peaks, the XRD result corresponds to the well-known layered of Ni(OH)₂ [16].

From the phase diagram composition we would anticipate to produce arrays of hexagonally ordered pores. The combination of arranged structures indicated by the peaks in the XRD and the surface area increase observed in the CV does not lend itself confirm that electrodeposition into the P84 lyotropic liquid crystal template has given a hexagonal array of pores. The presence of only one peak in the XRD, as has generally been observed in surfactant templated systems, does not indicate hexagonal pore arrangement to be distinguished from cubic or lamellar assembly. Although we consider it greatly likely that the polymer templated coating does consist of arrays of hexagonally arranged pores, it will need TEM to establish this definitively.

3.3. SEM and TEM characterization of HI-e Ni hydroxide films

The scanned images of the HI–e Ni hydroxide films deposited at a potential of - 0.91 V are displayed in Figure 6. Figure 6A indicates that the film is smooth and compact at the deposition potential of -0.91 V. Figure 5B shows a typical TEM of the HI–e Ni (OH)₂ film electrodeposited at -0.91 V. The

Ni(OH)₂ film on gold electrode (Figure 5B) consisting of cylindrical pores of about 9.1 nm in diameter ordered on a hexagonal lattice with distance the adjacent centers of about 9.26 nm.



Figure 6. SEM photographs of the H₁-eNi(OH)₂ film deposited at -0.91 V(A), TEM image of the H₁-eNi(OH)₂ film deposited at potential -0.91 V (B).

It is obvious that all the films have homogeneous and well–ordered mesoprous skeletons. It was notable that the mesostructured of the HI–e–Ni nearly remain unchanged under different depo-sition potentials and after a month long, which is agreeing with the result recorded in literature [17]. This kind of architecture can lead to high surface area and a mesoporous volume, which produce the structural foundation for the high specific capacitance. Such surface morphology with mesoporous structures may feasible for supercapacitor applications. Based on the pore size and wall thickness, a high specific area inside these pores would be anticipated.

3.4. Convolutive Voltammetry

Convolutive voltammetry has been profitably useful to the scrutiny of the strategy of various electrochemical processes [18- 24]. We drove the D value of the studied compound from relationship (1), [19]

$$I_{lim} = nFSD^{1/2}C^{bulk}$$

Where I_{lim} is the limiting current value accomplished for I_1 when the potential is forced to adequately value past the peak, and the other symbols have their normal meanings.

(1)

The I_1 convolutive curve of the examined Ni(OH)₂ film was pictorial in Figure 7 which shows a moderate separation between the forward and backward direction and clearly express the moderate rate of electrode reaction [24]



Figure 7. I₁ convolution of electrodeposited HI-eNi(OH)₂ film from hexagonal pluronic P84 template in 0.1 M KOH at sweep rate 0.1 V.s⁻¹, T = 25 °C.

As shown in Figure 7 the end of the reverse sweep of I_1 curve does not come again to the initial value approve the existence of chemical reaction after the electron transfer [25].

Figure 8 indicates the deconvoluted curve of the electrodeposited HI-eNi(OH)₂ film which reveals the deviation from alignment of the maximum point of the forward peak and the minimum point of the backward one and the average of two points equals to the formal redox potential ($E^{o'}$). Also, the relationship (2)

 $(dI_1/dt)_f = n^2 F^2 SCD^{1/2} v/4RT$ (2)

was used for calculation of the (D) value for moderate fast charge transfer [26, 27], where $(dI_1/dt)_f$ is the distance upward of the forward sweep of the deconvoluted shape, and the other terms have their usual meaning.



Figure 8. Deconvolutive voltammetry of electrodeposited HI-eNi(OH)₂ film from hexagonal pluronic P84 template in 0.1 M KOH at sweep rate 0.1 V.s⁻¹, T = 25 °C.

Hence the relationship (2), gives another accurate route for estimation of the diffusion coefficient (D). Values of (D) determined via different methods (Table 2), indicate a good comparable between the values of D estimated via these methods.

The 'kinetic' convolution I_2 is given by equation (3) [25]. Hence, in the I_2 transforms at t time, each division of i(u) is rated by dividing upon the square root of the time which has passed from t

$$I_{2}(t) = \pi^{-1/2} \int [i(u) \exp(-kc(t-u))]/(t-u)^{1/2} du$$
 (3)

to the fraction u to which the division refers and likewise is scaled by the exponential factor $exp(-k_c(t-u))$. I₂ produce a steady state shape (at zero) on the return of the sweep in cyclic voltammetry and this property allows determination of k_c .

The rate constant of homogeneous chemical reaction (k_c) of HI-e Ni(OH)₂ can be precisely evaluated via "I₂" convolution from by putting trial value of (k_c) into the I₂ vs. E plot until I₂ returned to zero [26]. The true kc value extracted from I₂ convolution is 0.09 s⁻¹ which compare well with the value introduced in virtual cyclic voltammograms. Figure 9 shows the true k_c value of electrodeposited HI-eNi(OH)₂ film.



Figure 9. I₂ transforms of electrodeposited HI-eNi(OH)₂ film from hexagonal pluronic P84 template in 0.1 M KOH at sweep rate 0.1 V. s⁻¹, T = 25 °C.

The values of peak parameters collected in Table 3 confirm that the moderate rate of charge transfer of the system under investigation.

lable	2.	Реак	parameters	10	the	electrodeposited	$HI-eN1(OH)_2$	film	extracted	from	voltammetric
	teo	chniqu	es and digit	al si	mul	ation at 0.1 V.s^{-1} .					

$\Delta Ep/mV$	295	296
Ep-Ep/2 / mV	141 ^(a)	143 ^(c)
ip ^b /ip ^f	0.8 ^(a)	0.81 ^(c)
\mathbf{W}^{p}	195 ^(b)	196 ^(c)
∆ep deconv./ mV	176 ^(b)	175 ^(c)
epf / epb (deconv)	$0.82^{(b)}$	0.83 ^(c)
(a) Values from CV, (b) f	from dI ₁ /dt and (c) from	theoretical CV.

3.5. Digital simulation

In this work, we achieved digital simulation on PC computer via EG & G Condesim package. The simulation process was accomplished using finite difference techniques [27–29]. Algorithms were coded and enforced in the Condesim package supplied via EG & G. A direct examination of the electrode reaction was achieved by creating the theoretical voltammograms of the kind EC mechanism.. Figure 10 compares well between the theoretical and experimental voltammograms of electrodeposited HI-eNi film at 0.1 V.s⁻¹ sweep rate, which validating a moderate fast electron transfer of the electrode reaction which followed by slow rate of chemical reaction (EC mechanism). Table 3 includes the electrochemical parameters calculated experimentally, and that introduced in the simulated voltammogram which confirm the accuracy of the parameters extracted experimentally.



Figure 10. Similarity between the experimental and theoretical voltammograms of electrodeposited HI- $eNi(OH)_2$ film at a sweep rate of 0.1 V.s⁻¹ and T = 25 °C.

Technique	α	Dx10 ⁵	k _s x10 ³	n	E°′	kc
		cm ² .s ⁻¹	cm.s⁻¹		(V)	S ⁻¹
CV	0.34	3.4	2.72		0.64	
Conv.		3.5				0.090
Decon.		3.7			0.65	
Sim.	0.35	3.6	2.51	2.0	0.64	0.091

Table 3. Electrochemical parameters of the of electrodeposited HI-eNi(OH)₂ film via various techniques.

4. CONCLUSION

In the present work, we provide a simple and a novel method for electrodposition of the mesoporous H1-eNi(OH)₂ film on gold electrode from the hexagonal phase of inexpensive nonionic surfactant pluronic P84. The CV, SEM, TEM, XRD, convolutive voltammetry and digital simulation were employed to characterize electrodeposited films. The deposited films displayed the greatest specific capacitance of 980 F.g-1 at a scan rate of 10 mV s⁻¹. The specific capacitance may be attributed to a larger surface area within the mesoporous films. All the results indicate that the experimental conditions have significant effects on the structure and electrochemical capacitance of the prepared HI–e Ni hydroxide films. Also, it was found that a hexagonal pore arrangement has a large, accessible surface area. The electrodeposited nickel films were silver with a mirror-like.

XRD investigation reflect the existence of a hexagonal phase and corresponds to a d-space 9.2 nm which translates into a pore-to-pore distance of 11.2 nm.

ACKNOWLEDGEMENTS

This project was supported by King Saud University, Deanship of Scientific Research, College of Science, Research Center.

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