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*S. Minu Xavier Sebastini, P. Daniel Nixon, C. Joseph Kennady***ELECTRODEPOSITION OF NICKEL HYDROXIDE FOR SUPERCAPACITOR APPLICATIONS USING SURFACTANT-CONTAINING ELECTROLYTE****Karunya Institute of Technology and Sciences, Coimbatore, India**

Nickel hydroxide is a promising material for supercapacitor application due to its relatively low cost, well-defined electrochemical redox nature and easy to prepare with different structural morphologies. In the present study, nickel hydroxide was cathodically deposited on a stainless steel surface from an electrolyte containing $\text{Ni}(\text{NO}_3)_2$ as a result of local increase in pH at the cathode. A nonionic surfactant (Pluronic P 123, $\text{HO}(\text{CH}_2\text{CH}_2\text{O})_{20}(\text{CH}_2\text{CH}(\text{CH}_3)\text{O})_{70}(\text{CH}_2\text{CH}_2\text{O})_{20}\text{H}$) was added to the solution in order to get enhanced nanocrystalline nickel hydroxide film. The film was characterized using scanning electron microscopy, energy dispersive X-ray analysis, X-ray diffraction method and Fourier transform infrared spectroscopy to investigate its surface and morphological characteristics. The grain size of the as prepared nickel hydroxide was about 11 nm and this was achieved because of the presence of nonionic surfactant, which influences the microstructure of the deposit. Cyclic voltammetry was used to study the reduction and oxidation processes in the electrodeposited nickel hydroxide electrode, characterize the specific capacitance and evaluate the suitability of the synthesized films for supercapacitor application. The charge-discharge dependences were recorded to study the capacitive property of the material. The results showed that the prepared nickel hydroxide electrodes have specific capacitance of about 494 F/g.

Keywords: super capacitor, oxide electrode, surfactant, electrodeposition, surface characterization, cyclic voltammetry, charge-discharge curve.

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Introduction

An interest in development of supercapacitors has increased recently because of the high demand for energy production and storage resulting from rapid population growth and high-energy consumption in the industrial sector [1]. Various electrode materials can be used in supercapacitors [2,3]. Metal oxide-based supercapacitors as storage devices are gaining momentum in recent years due to their fast power energy delivery, extended life cycle and high power and reasonably high energy density. Among different oxides, RuO_2 and amorphous hydrous ruthenium oxide are the most capable material for supercapacitors because of their elevated specific capacitance, excellent reversibility and long cycle-life [4,5]. However, this material's high cost and potential to harm the environment have limited its commercial application in supercapacitors. Several alternative electrode materials have been studied, including carbonaceous materials, conducting

polymers, metal hydroxides and metal oxides [6–9]. Base metal oxides, such as MnO_2 , NiO , Fe_3O_4 and Mn-Ni oxide, have been proposed as promising electrode materials because of their environmental compatibility, low cost, abundant availability, environmental compatibility and wide potential windows [10–12].

Different electrode materials that have low cost, comparable capacitive behavior as compared with ruthenium oxide were studied. NiO found to be a potential alternative to RuO_2 as electrode material. NiO films exhibit high specific capacitance value [13] and many authors studied this material in varying aspects. Some examples are as follows: nanocrystalline NiO [14], nanoporous electrodeposited nickel oxide films [15], nickel oxide/hydroxide nanoplatelets [16], and nickel oxide films on different substrates [17].

In the present study, $\text{Ni}(\text{OH})_2$ films were electrodeposited on stainless steel at room

temperature from an electrolyte containing a nonionic surfactant in order to get more refined nanostructure. The deposited nickel hydroxide electrodes were annealed at 300°C. The surface and morphological characterization of the prepared nickel oxide films was performed by using X-ray diffraction method, energy dispersive X-ray analysis and scanning electron microscopy. The deposited nickel hydroxide electrodes were also subjected to FT-IR study to ascertain the bonding and stretching between nickel and hydroxide. Cyclic voltammetry and galvanostatic charge-discharge studies were carried out using the structurally and morphologically optimized nickel oxide electrode to study the redox behavior and calculate the specific capacitance value.

Materials and methods

Stainless steel (grade 304) samples with the dimensions of 1.0×3.0×0.1 cm were used as a substrate for electrodepositing nickel hydroxide. The substrate was fine polished with emery paper and washed with distilled water. To get a uniform etching of the surface, the substrate was immersed in a solution containing 0.5 ml/L of concentrated sulfuric and hydrochloric acid each. Time of dipping was 20–30 minutes. Ni(OH)₂ was electrodeposited from a solution containing 0.1 M of nickel nitrate. 0.1 g/L of Pluronic P123 surfactant was added to this solution. Nickel nitrate was a source for Ni(OH)₂ and the surfactant acted as a structure directing agent which does not participate in electrochemical reactions.

The surfactant was a symmetric triblock copolymer comprising polyethylene oxide (PEO) and polypropylene oxide (PPO) in an alternating linear fashion, PEO–PPO–PEO. It's chemical formula is HO(CH₂CH₂O)₂₀(CH₂CH(CH₃)O)₇₀(CH₂CH₂O)₂₀H. This surfactant was chosen due to its high molecular weight and alternate arrangement of PEO and PPO. The pH of the solution was 5.1. All experiments were carried out at 30°C.

Nickel hydroxide film was electrodeposited using an Electrochemical Workstation-CHI770d. The electrochemical cell consisted of three electrodes, i.e. pre-treated stainless steel acted as a working electrode, platinum wire was a counter electrode and Ag/AgCl electrode served as a reference electrode. The electrolysis was carried out under the potentiostatic conditions by applying electrode potentials of –0.7, –0.9 and –1.1 V. The duration of electrodeposition was fixed as 60 minutes. After electrodeposition, the working electrode was taken out, rinsed with distilled water and annealed at 300°C for 60 minutes.

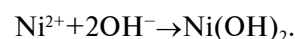
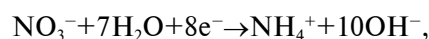
The prepared nickel oxide electrodes were

subjected to structural and morphological study using X-ray diffraction method (XRD) and scanning electron microscopy (SEM). Elements present in the electrode were analyzed by means of energy dispersive X-ray analysis (EDAX). Cyclic voltammetry (CV) experiments were carried out with the prepared nickel oxide electrode using CHI 770d instrument. For cyclic voltammetric experiments, the electrode surface was masked and an area of 0.196 cm² was exposed to the electrolyte. The constant current charge-discharge behavior of the nickel oxide electrode was investigated galvanostatically at a current of 5 mA.

Results and discussion

Electrodeposition

The deposition of well adherent and uniform dark green colored nickel oxide was performed by applying a constant potential of –0.9 V vs. Ag/AgCl for a deposition time of 60 min. It is demonstrated that the electrodeposition process of the Ni(OH)₂ films could include an electrochemical reaction followed by a precipitation reaction expressed as follows:



When electric current passes through the electrolyte containing Ni(NO₃)₂, nitrate ions are reduced on the cathodic surface to produce hydroxide ions. The generation of OH[–] ions at the cathode raises the local pH, resulting in the precipitation of Ni(OH)₂ at the electrode surface. The deposited electrode was annealed at 300°C for 2 hours.

Structural and morphological studies

Figure 1 represents the results of X-ray diffraction analysis which was used to determine the crystalline phase, orientation and grain size of the prepared materials. The experimental data were compared with the crystal structures available in PCPDF WIN crystal structure database. The different peaks with various intensities were marked and the d-values were calculated from these peaks. The grain size was calculated using Scherrer formula:

$$\text{Grain size } (X_s) = k\lambda / \beta \cos\theta$$

where X_s is the size of crystalline, λ is X-ray wavelength, β is full width at half maximum of the diffraction peak, θ is diffraction angle and k is Scherrer constant.

The grain size of the prepared nickel hydroxide was about 11 nm and this was achieved because of the application of a nonionic surfactant, which

enhanced the orientation of atom building in the deposit.

The morphological nature of the deposited $\text{Ni}(\text{OH})_2$ was examined using scanning electron microscopy. SEM micrograph (Fig. 2) reveals that the deposited $\text{Ni}(\text{OH})_2$ is uniform and shows minor cracks in its surface. Porous space observed in between may enhance the redox behavior of the oxide. In this structure, fine-grained nanostructure is also visible which is due to the presence of surfactant in the electrolyte.

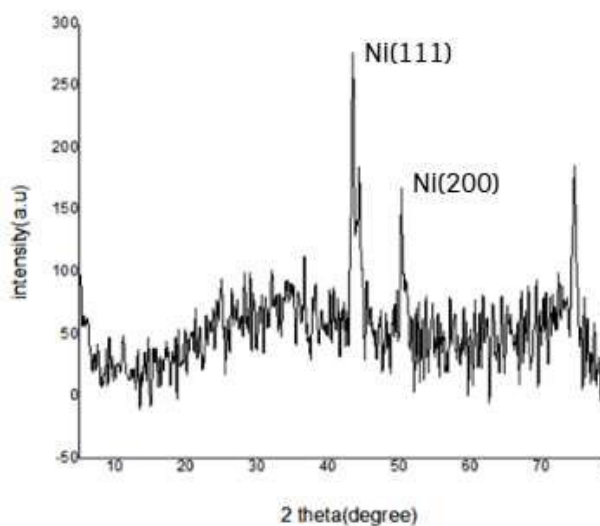


Fig. 1. XRD pattern of the electrodeposited $\text{Ni}(\text{OH})_2$ film

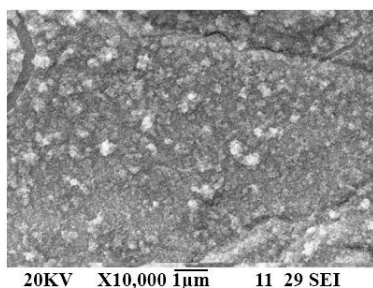


Fig. 2. SEM image of the electrodeposited $\text{Ni}(\text{OH})_2$

The result of EDAX study is presented in Fig. 3. EDAX confirms the presence of nickel. Also, iron and chromium were detected; they were in the substrate, stainless steel, which was used for the electrodeposition. This result indicates that there are no other impurities in the obtained film.

FTIR study

Figure 4 shows the FTIR spectrum of the prepared $\text{Ni}(\text{OH})_2$ which can reveal the presence of some organic and inorganic functional groups in $\text{Ni}(\text{OH})_2$. The peak at 619 cm^{-1} arises from the in-

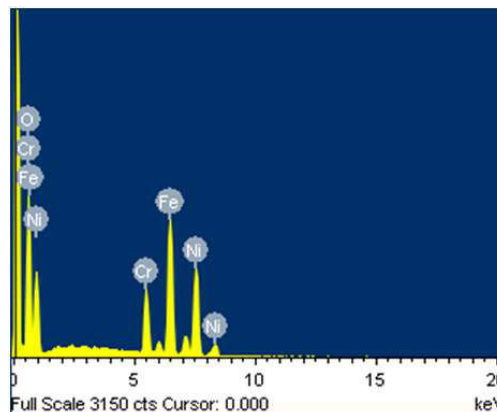


Fig. 3. EDAX graph of the electrodeposited $\text{Ni}(\text{OH})_2$

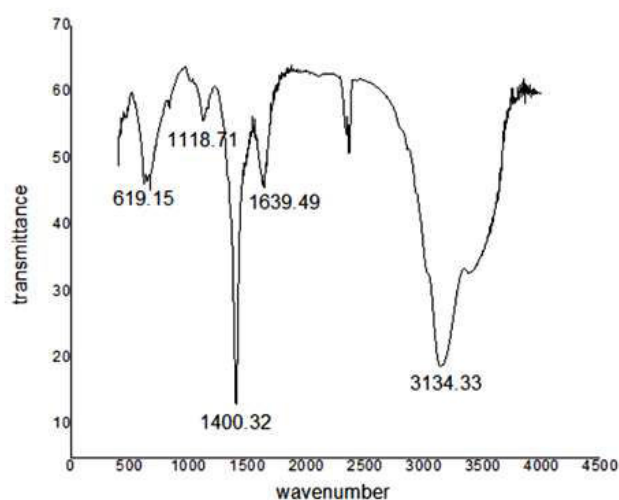


Fig. 4. FTIR spectrum of electrodeposited $\text{Ni}(\text{OH})_2$

plane $\text{Ni}-\text{OH}$ bending vibration of the $\text{Ni}(\text{OH})_2$ lattice. The broad peak at 1400 cm^{-1} was attributed to $\text{O}-\text{H}$ bending of lattice OH . The absorption band at 3134 cm^{-1} is associated with hydrogen-bonded OH stretching.

Cyclic voltammetry study

Cyclic voltammetric experiments were carried out in 2 M KOH electrolyte. The CV curve for $\text{Ni}(\text{OH})_2$ deposited on stainless steel sheet at different scan rate with a potential window -0.5 V to 0.5 V are presented in Fig. 5. There is a peak in the reverse sweep in all the cyclic voltammograms; it represents the reduction of Ni^{4+} to Ni^{2+} . This Ni^{2+} ions in the forward sweep is oxidized forming Ni^{4+} which was not noticed by a prominent peak, since the potentials of the hydrogen evolution reaction and the nickel oxidation overlap each other.

Charge-discharge study

The constant current charge-discharge behavior of the nickel oxide electrode was investigated

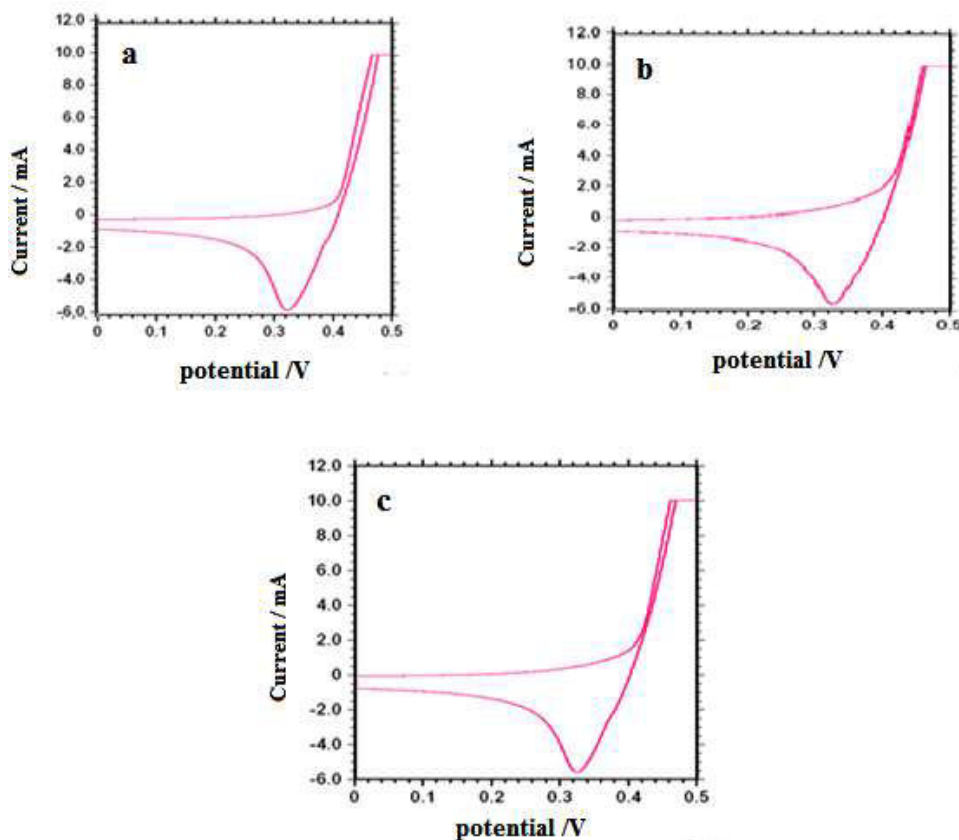


Fig. 5. Cyclic voltammograms of nickel hydroxide in 2.0 M KOH at a scan rate of (a) 20, (b) 50 and (c) 100 mV/s

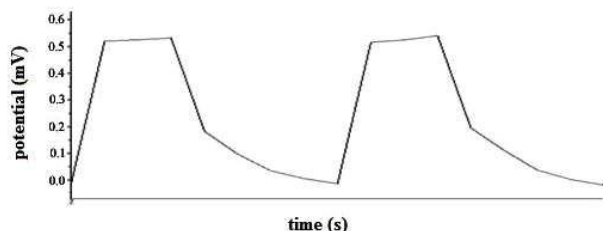


Fig. 6. Charge-discharge curve of the electrodeposited Ni(OH)₂ electrode in 2.0 M KOH

galvanostatically at a current of 5 mA. The resultant plot is illustrated in Fig. 6. It is seen from the plot that electrodeposited Ni(OH)₂ can hold the charge for longer duration and thereby it can be used as an electrode material for supercapacitors. The result suggests that the Ni(OH)₂ electrode has a good rate capability, which is very important for the electrode materials of a supercapacitor to provide high power density. Based on the charge-discharge plot obtained, specific capacitance was calculated and found to be 494 F/g.

Conclusions

The electrodeposition of Ni(OH)₂ electrode from an electrolyte containing nickel nitrate and a

nonionic surfactant yields a uniform smooth nanosized electrode material. The SEM micrograph reveals that the deposited Ni(OH)₂ is uniform in its surface morphology and exhibit minor cracks on the surface. Porous space observed in between enhances the redox behavior of the oxide. Fine-grained nanostructure is also visible. XRD result reveals that the grain size of the electrodeposited nickel hydroxide is about 11 nm. This was achieved because of the nonionic surfactant, which enhances the orientation of atom building in the deposit. EDAX confirms the presence of nickel and also iron and chromium, which are in the substrate, stainless steel, used for the electrodeposition. In FTIR spectrum, the peak at 619 cm⁻¹ arises from the in-plane Ni-OH bending vibration of the α -Ni(OH)₂ lattice.

There is a peak in the reverse sweep of the cyclic voltammogram, it represents the reduction of Ni⁴⁺ to Ni²⁺. This Ni²⁺ in the forward sweep oxidizes forming Ni⁴⁺ that is not noticed by a prominent peak, which may be due to overlapping the potentials of hydrogen evolution nickel (II) oxidation. The charge-discharge plot shows that the electrodeposited Ni(OH)₂ film can hold the charge for longer duration and thereby it can be used as an electrode material

for supercapacitors. Based on the charge-discharge plot obtained, specific capacitance was calculated and found to be 494 F/g. The smaller particle size with effective electroactive surface area of the electrode is responsible for the improved charge transfer performance of the oxide electrode. This is possible because of the nanosized structure of the nickel oxide electrode, which was achieved by the presence of the surfactant. The nonionic surfactant enhances the orientation of atom building in the deposit.

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ЕЛЕКТРООСАДЖЕННЯ НІКЕЛЬ ГІДРОКСИДУ ДЛЯ ВИКОРИСТАННЯ У СУПЕРКОНДЕНСАТОРАХ З ВИКОРИСТАННЯМ ЕЛЕКТРОЛІТУ, ЩО МІСТИТЬ ПОВЕРХНЕВО-АКТИВНУ РЕЧОВИНУ

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Нікель(II) гідроксид є перспективним матеріалом для використання в суперконденсаторах через його відносно низьку вартість, однозначну електрохімічну редокс-поведінку і простоту синтезу зразків з різноманітною структурною морфологією. В даній роботі нікель(II) гідроксид був катодно осаджений на поверхні нержавіючої сталі з електроліту, що містить Ni(NO₃)₂, в результаті локального підвищення рН біля катода. Неіоногенна поверхнево-активна речовина (Pluronic P 123, HO(CH₂CH₂O)₂₀(CH₂CH(CH₃)O)₇(CH₂CH₂O)₂₀H) додавалася до розчину з метою отримати покращений нанокристалічних шар нікель(II) гідроксиду. Отримані шари були характеризовані методами сканівної електронної мікроскопії, енергорозсіювального рентгенівського аналізу, рентгеноструктурного методу та інфрачервоної спектроскопії з Фур'є-перетворенням для вивчення поверхневих та морфологічних характеристик. Розмір кристалітів виготовленого нікель(II) гідроксиду дорівнював приблизно 11 нм, що досягнуто за рахунок наявності неіоногенної поверхнево-активної речовини, що впливає на мікроструктуру осаду. Циклічна вольтамперометрія була використана для дослідження процесів окислення і відновлення в електроосадженому гідроксидно-нікелевому електроді, а також для визначення питомої ємності і оцінювання придатності синтезованих шарів для використання в суперконденсаторах. Зарядно-розрядні залежності були використані для вивчення ємнісних властивостей одержаного матеріалу. Результати

тати дослідження показали, що виготовлені гідроксидно-нікелеві електроди мають питому ємність близько 494 Ф/г.

Ключові слова: суперконденсатор; оксидний електрод; поверхнево-активна речовина; електроосадження; характеристики поверхні; циклічна вольтамперометрія; зарядно-розрядна крива.

ELECTRODEPOSITION OF NICKEL HYDROXIDE FOR SUPERCAPACITOR APPLICATIONS USING SURFACTANT-CONTAINING ELECTROLYTE

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Nickel hydroxide is a promising material for supercapacitor application due to its relatively low cost, well-defined electrochemical redox nature and easy to prepare with different structural morphologies. In the present study, nickel hydroxide was cathodically deposited on a stainless steel surface from an electrolyte containing $\text{Ni}(\text{NO}_3)_2$ as a result of local increase in pH at the cathode. A nonionic surfactant (Pluronic P 123, $\text{HO}(\text{CH}_2\text{CH}_2\text{O})_2(\text{CH}_2\text{CH}(\text{CH}_3)\text{O})_7(\text{CH}_2\text{CH}_2\text{O})_{30}\text{H}$) was added to the solution in order to get enhanced nanocrystalline nickel hydroxide film. The film was characterized using scanning electron microscopy, energy dispersive X-ray analysis, X-ray diffraction method and Fourier transform infrared spectroscopy to investigate its surface and morphological characteristics. The grain size of the as prepared nickel hydroxide was about 11 nm and this was achieved because of the presence of nonionic surfactant, which influences the microstructure of the deposit. Cyclic voltammetry was used to study the reduction and oxidation processes in the electrodeposited nickel hydroxide electrode, characterize the specific capacitance and evaluate the suitability of the synthesized films for supercapacitor application. The charge-discharge dependences were recorded to study the capacitive property of the material. The results showed that the prepared nickel hydroxide electrodes have specific capacitance of about 494 F/g.

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