

ELECTRODEPOSITION OF NICKEL POWDER FROM NICKEL SULPHATE SOLUTION IN PRESENCE OF GLYCEROL AND SULPHURIC ACID

S.G. Viswanath*¹ and Manish M.Jachak

*Department of Chemistry, Laxminarayan Institute of Technology,
R.T.M Nagpur University, Nagpur-440033, India.*

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Abstract

Nickel powder was obtained by electrodeposition of nickel from boric acid, glycerol and sulphuric acid. The morphology and particle size of these powders were studied. Spongy, irregular, flaky, fibrous and aggregate particles were obtained. Size of more than 85% particles was smaller than 384 μ m. From XRD graphs, it was found that the smaller particles are in the range of 106 and 373 nm. The apparent density of nickel powder decreased with increase in concentration of glycerol. The stability of the powder and current efficiency were also studied. In absence of nickel sulphate there was some nickel deposition on the cathode. The effect was discussed in present work. New definition for electrodeposition was suggested.

Keywords: Electrodeposition, Nickel, Stability, SEM, XRD, Particle size, Electrocatalytic and auto electrodeposition

Introduction

Copson et al. [1] and Kuroda et al. [2] patented their work on electrolytic nickel powder preparation. Preparation of finely dispersed nickel as powder was presented by Loshkarev [3]. Kerfoot et al. [4] produced nickel powder by the reduction of nickel oxide with hydrogen gas. Rambla et al. [5] performed nickel electrowinning using platinum catalyzed hydrogen diffusion anode and stainless steel cathode. Jana et al. [6] reported results on the direct electrowinning of valuable metals from sea nodules using aqueous chloride bath and the effect of addition of sodium sulphide on electrowinning process. Holm and O' Keefe [7] examined the effect of electrolytic parameters on the electrowinning of nickel. Brillas et al. [8] studied the nickel electrowinning using platinum catalyzed hydrogen diffusion anode and the effect of chloride and sulphate ions. Lupi and Pasquali [9] studied the electrolytic nickel recovery from lithium ion

* Corresponding author: S.G. Viswanath, gortiviswanath@yahoo.com

batteries. Borikar et al prepared copper [10], nickel [11], cadmium [12] and zinc [13] powders by electrowinning process, in acetone and sulphuric acid medium. Viswanath and George reported preparation of electrolytic nickel powder [14] by electrowinning process from glycerol and ammonical medium.

Alieltoum et al. [15] studied the electrodeposition of Nickel in gluconate bath. Abdolahi et al. [16] reported high speed electroplating of nickel. Violeta et al. [17] examined the influence of polyvinyl pyrrolidone additive on the hardness of nickel electrodeposit obtained from watt baths. Genardo et al. [18] studied electrodeposition of nickel by current pulse reduction technique. Kumar et al. [19] observed deformations in nano crystalline nickel electrodeposits. Abott et al. [20] studied electrodeposition of nickel using solution of nickel chloride with urea, ethylene glycol and choline chloride.

Recently Viswanath and Jachak studied electrodeposition of copper [21] and cadmium [22] in glycerol and sulphuric acid medium. They concluded that electrodeposition is a combination of electro dissolution of anode by electrocatalytic effect and electrowinning processes. They also reported that copper ion concentration decreased and cadmium ion concentration increases during electrodeposition process.

In the present investigation, an attempt has been made to study the morphology and particle size of electrodeposited nickel powder from glycerol and sulphuric acid where the glycerol percentage and current were varied. Apparent densities of nickel powders were determined. These densities may help to assess the nature and size of particles of the powder. The stability of electrodeposited nickel powder was also studied for its susceptibility to oxidation.

Material and Method

Instruments

The bath solution (NiSO_4 , glycerol, sulphuric acid saturated with boric acid) was placed into a single compartment of two-electrode cell. The electrodeposition experiments were performed using nickel plate ($10 \times 2.5 \times 0.3 \text{ cm}$) as cathode and anode. Current was supplied by a DC power supplier 34 B DCPS (Tektronix). All the experiments were carried out at $25 \pm 1^\circ \text{C}$. The temperature of the bath remained almost constant during the experiment. A current of 0.5, 1, 1.5 and 2A was applied to the electrolytic cell. The current variation was $\pm 0.01 \text{ A}$. The particle size analysis was performed on Saturn Digitizer II 5205 V1.01, at Jawaharlal Nehru Aluminum Research Centre, Nagpur, India. X-ray diffraction (XRD) analysis was performed on Bruker AXSD8 Advance and morphological analysis was performed on scanning electron microscope (SEM) JEOL Model JSM - 6390LV operated at 1 pA to 1mA at Sophisticated Test and Instrumentation Center, Kochi, India.

Method of nickel estimation

The bath solution contains 60 g hydrated nickel sulphate and 0.05N sulphuric acid and varying concentration of glycerol. The volume percent of glycerol was varied from 10 to 30. The total volume of the electrolytic bath solution was made up to 200 ml with distilled water. These solutions were saturated with the boric acid. The chemically clean solutions were used. Concentration of nickel sulphate in the solution, before and after the experiment, was estimated by titrating the solution with 0.01N sodium salt of Ethylenediaminetetraacetic acid (EDTA), using Ammonium Perpurate (Murexide)

indicator. Volume of solution was measured after experiment. The current was switched on for four hours to get sufficient quantity of powder for different types of analysis. The current was varied from 0.5 to 2A. The deposit from the cathode was removed into the distilled water by simple scratching with glass rod. After washing with plenty of distilled water, the deposit was ground for about 30 min by adding 10 ml of distilled water. The nickel powder was separated by decantation and filtration. The powder was dried in a hot air oven at about 90-100°C and stored in air tight bottle.

Symbols abbreviation used in the text

A: Current in amperes

C_a: Mass of anode dissolved in g

C_c: Mass of metal powder deposited on cathode in g (yield) or electrowinning process

C_g: Percent glycerol

C_i: initial concentration of nickel in g

C_f: Final concentration of nickel in g

Δc: C_i - C_f

d_a: Apparent density g ml⁻¹

d_w: Density of water at experimental temperature

E_f: Electrocatalytic effect efficiency

f: Number of faradays = A×t / F

F: Faraday = 96500 coulombs

Os: Oxidative stability of nickel powder

t: Time in sec

w: Equivalent mass of nickel

PF_D: Percent of faraday required for deposition

PF_E: Percent of faraday required for electrolysis of water

PF_W: Percent of faraday required for electrowinning

Physical Properties

Determination of apparent density of nickel powder

The apparent density, d_a is given by the equation as:

$$d_a = d_w(W_3 - W_1) / (W_2 - W_1 + W_4 - W_3) \quad (1)$$

where: W₁ - the mass of dry empty density bottle, W₂ - the mass of bottle and distilled water; W₃ - the mass of dry empty density bottle and nickel powder (approximately from 1 to 1.5 g); W₄ - the mass of bottle with nickel powder and distilled water; d_w - the density of water at that temperature.

The apparent density of nickel powder, obtained at different current levels and percent of glycerol is presented in Table 1. The apparent density may be expressed by the following equation:

$$d_a = (-0.356A^2 + 0.7092A - 0.72) \ln(C_g) - 1.5312A + 6.038 \quad (2)$$

Table 1. Apparent density of nickel powder obtained at different current and percent of glycerol

A	C _g and d _a (g/ml)		
	10%	20%	30%
0.5	4.2	3.9	3.7
1.0	3.8	3.5	3.4
1.5	2.5	2.2	2.0
2.0	1.8	1.4	1.2

Determination of oxidative stability of nickel powder

Nickel powder is stored for around fifty days in an air tight sealed bottle then it is studied for its stability. Accurately weighed (0.7 ± 0.3) gram of nickel powder was taken in 100 ml 0.5 N H₂SO₄. The solution is stirred with a magnetic stirrer for one hour. The solution is filtered and the dissolved nickel in the filtrate was estimated by titrating the filtrate against standard EDTA (0.01 N) using Ammonium Perpurate (Murexide) indicator. Nickel powder is susceptible to oxidation and forms nickel oxide (NiO). This oxide reacts with sulphuric acid and forms nickel sulphate. However, nickel does not react with sulfuric acid. The oxidative stability (OS) of nickel was estimated using the expression:

$$\frac{\text{Weight of metal powder undissolved}}{\text{Weight metal powder taken}} \times 100 \quad (3)$$

The oxidative stability data of nickel are presented in Table 2. The oxidative stability may be expressed by the following equation:

$$O_s = -A^2(0.005C_g^2 + 0.05)C_g + A(0.0135C_g^2 - 0.385C_g + 2.4) - 0.0062C_g^2 + 0.2375C_g + 88 \quad (4)$$

Table 2. Oxidative stability of nickel powder obtained from different currents and percent of glycerol

A	Percent of glycerol an oxidative stability of nickel		
	10%	20%	30%
0.5	90	90	90
1.0	89	88	87
1.5	88	84	81
2.0	86	79	72

Electrochemical studies

Oxidation of glycerol

The glycerol is oxidized by the oxygen liberated at anode and gives organic acids like glycerol acid, tartaric acid and mesoxalic acid [14, 15]. The oxidation of glycerol is

also due to the oxygen liberated during electrowinning process. This would be explained later in the mechanism of electrodeposition studies.

Electrocatalytic(polarization) effect and electrodisolution study of nickel

0.5A current was passed through 0.5N sulphuric acid solution keeping two nickel plates as anode and cathode. The anode lost some mass. The solution became green. But there was no metal deposit found on the cathode. A black shade loose powder deposit was found on the anode. This deposit could be removed by simple scratching. If the anode was left alone for some time either in the solution or outside of it, this deposit became hard and could not be removed by simple scratching. The chemical analysis indicated that the black powder was nickel and the green color of the solution was due to formation of nickel sulphate. In 0.05N sulphuric acid or 0.1N ammonium hydroxide, a large amount of green precipitate was observed in the solution that settled at the bottom of the cell and the solution became colorless. On the anode black powder along with some green particles were found. The green particles were nickel hydroxide, Ni(OH)₂. In presence of glycerol, nickel hydroxide formation was not observed because nickel hydroxide reacted with the organic acids and formed corresponding organic acid metal salts. This solution was green.

The current was applied to the electrolytic cell containing saturated boric acid solution. The current did not rise more than 0.03A. In this situation, there was some little deposit on the cathode and solution became pale green. At the same time, very small quantity of black loose deposit was formed on the anode having similar properties as described earlier. Boric acid is a very weak electrolyte and on the other hand the solution is saturated with boric acid. The conducting power of this solution is very low. When 0.05N sulphuric acid solution saturated with boric acid was used, the current could be raised to any value because the conducting power of the solution increased. Then large amount of nickel was deposited on the cathode. The solution became green. Same black loose powder was observed on the anode. This is due to electrocatalytic effect. When current is applied to the cell containing acid, metal anode is charged positively. The positively charged anode is attacked by the hydroxyl ions of water and forms corresponding hydroxide of the metal. This hydroxide reacts with acid and forms corresponding metal salt. This nickel deposition on the cathode in sulphuric acid and boric acid is termed as auto electrodeposition.

Threshold current for electrodisolution of anode

It appears that a minimum current must be applied to electrolytic cell to initiate the electrodisolution of anode. The minimum current, threshold current, to be applied to the electrolytic cell for electrodisolution of nickel anode is 0.03A (0.48-0.47V) and 0.02A (0.35-0.34V) when the sulphuric acid concentrations are 0.5 and 1N, respectively. For 0.05N sulphuric acid solution saturated with boric acid, 0.03A current is required to initiate the electrodisolution of nickel anode.

Percent of Faraday distribution for various processes

When the current is passed through solution, electrowinning of metal, electrolysis of water and warming of the solution (increase of entropy) occur. The current required for warming of solution is very small and so it may be ignored. The percent of Faraday used for electrodisolution (PFD) is calculated from the number of grams of anode dissolved:

$$\text{PFD} = (C_a/wf) \times 100 \quad (5)$$

The percent of Faraday used for electrowinning (PFW) of the metal is calculated from the number of grams of metal deposited on cathode:

$$\text{PFW} = (C_c/wf) \times 100 \quad (6)$$

The percent of Faraday required for electrolysis of water (PFE) is:

$$\text{PFE} = 100 - \text{PFW} \quad (7)$$

The data of percent Faraday distribution for nickel deposition at different current and percent of glycerol were presented in Table 3. The first law of Faraday states that the amount of chemical decomposition produced by a current is proportional to the quantity of the electricity passing through the electrolytic solution. Here, if the metal salt is considered as decomposing substance, then electrodisolution does not require much current. Also, amount of current used for electrodisolution is small as evident from the studies of threshold current for electrodisolution of anode. The glycerol oxidation is explained in earlier part of this paper. So this may be neglected. Therefore current is required only for electrowinning (PFW) and electrolysis of water (PFE). The PFD, PFW and PFE data for auto electrodeposition studies were presented in the same table in bold lettering.

Table 3. Percent faraday distribution for various processes of electrodeposition of nickel at different current and percent of glycerol

C _g	A	PFD	PFW	PFE	C _g	A	PFD	PFW	PFE
10	0.5	32.1	63.1	36.9	10	1	21.1	41.4	58.6
20	0.5	44.0	37.8	62.2	20	1	38.5	42.8	57.2
30	0.5	44.4	17.9	82.1	30	1	33.8	42.8	57.2
10	1.5	28.5	37.1	62.9	10	2	29.6	28.9	71.1
20	1.5	36.8	37.4	62.6	20	2	27.6	30.0	70.0
30	1.5	26.3	24.3	75.7	30	2	26.6	30.4	69.6
0.0	0.5	43.4	7.7	92.3	10	0.5	40.6	17.2	82.9
10	0.5	39.1	15.4	85.6	30	0.5	39.1	0.1	99.1

Reaction mechanism of electrodeposition of nickel

In boric acid medium

The electrochemical dissolution of anode is as follows:

Boric acid does not dissociate in aqueous solution as a Brønsted acid, but is a Lewis acid which interacts with water molecules to form the tetrahydroxyborate ion, as confirmed by Raman spectroscopy. The dissociation constant of the boric acid is 5.8×10^{-10} mol/l (pKa = 9.24). Therefore, the dissociation of boric acid may be written as:

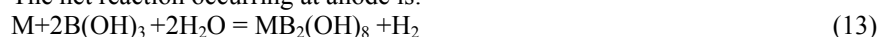


The electrochemical dissolution of anode is as follows:

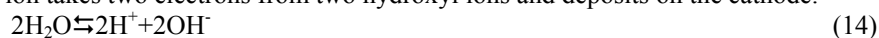




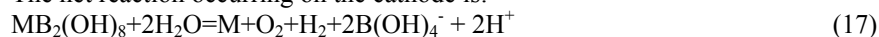
The net reaction occurring at anode is:



Electrowinning occurs at cathode. The metal borate solution dissociates. Each metal ion takes two electrons from two hydroxyl ions and deposits on the cathode.



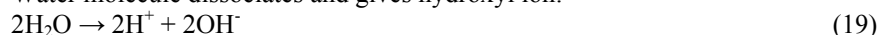
The net reaction occurring on the cathode is:



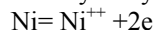
When one g atom of metal is dissolved, two g moles of water are lost from the solution, eq.9. One g mole of hydrogen is also lost, eq.12. When one g atom of metal is deposited, two g moles of water are lost, eq. 14 or 17. Four g moles of water are lost from solution during the electrodeposition process. This suggested mechanism is based on the fact that approximate calculation for total water loss is four moles. This water loss is neither due to electrolysis of water nor accountable to Faraday laws. These reactions occur even though metal sulphate is not present, but boric acid must be essential. This is the reason that this process is called as auto electrodeposition. It is noticed that there is metal deposition on the cathode in absence of sulphuric acid. However, this reaction is slow due to low ionic environment, since the boric acid is a weak electrolyte.

Reaction mechanism of electrodisolution in sulphuric acid

Water molecule dissociates and gives hydroxyl ion:



This hydroxyl ion reacts with nickel anode and forms nickel hydroxide:



The formed nickel hydroxide reacts with sulphuric acid and nickel sulphate is obtained:



The net reaction at anode:



The dissolution of nickel in the sulphuric acid is due to applied current to the electrolytic cell. If no current is applied to the cell, nickel ion does not dissolve. This dissolution of nickel is the result of electrocatalytic effect.

Change in concentration of metal ion

The nickel ion concentration decreased during the electrodeposition process. The plot of percent glycerol against Δc , change in the concentration, gives a straight line for all current values. Δc may be expressed by the following equation as:

$$\Delta c = C_i - C_f = (0.1797A^3 - 0.3206A^2 - 0.0526A - 0.0555)C_g - 5.4116A^3 + 9.6834A^2 + 1.5202A + 4.1681 \quad (23)$$

The electrodisolution of anode, in g, may be given by the following equation:

$$C_a = (-0.0038C_g^2 + 0.1347 C_g + 0.2781)C + 0.0006 C_g^{2.0275} \quad (24)$$

The electrodeposition on the cathode in g, may be expressed by the following equation:

$$C_c = (-0.0062 C_g^2 + 0.2723 C_g - 1.3482)C - 1.196 \ln(C_g) + 3.7495 \quad (25)$$

Particle size analysis

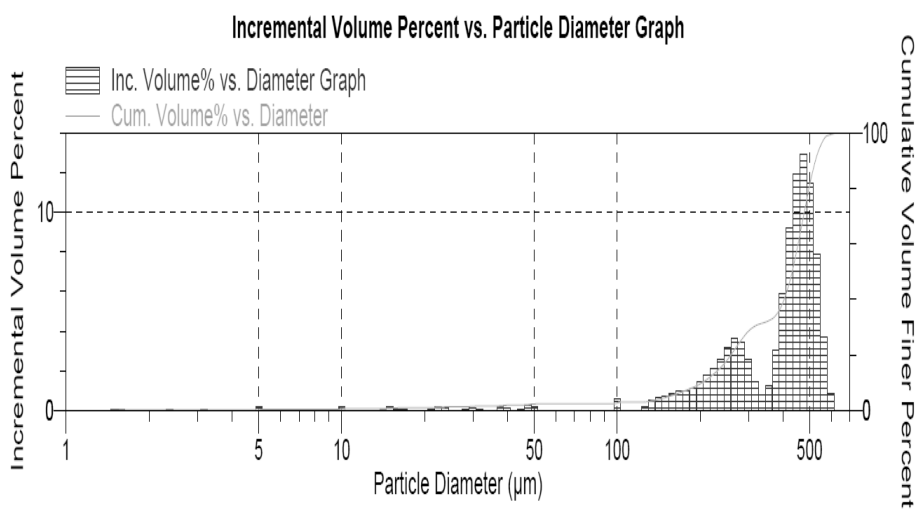
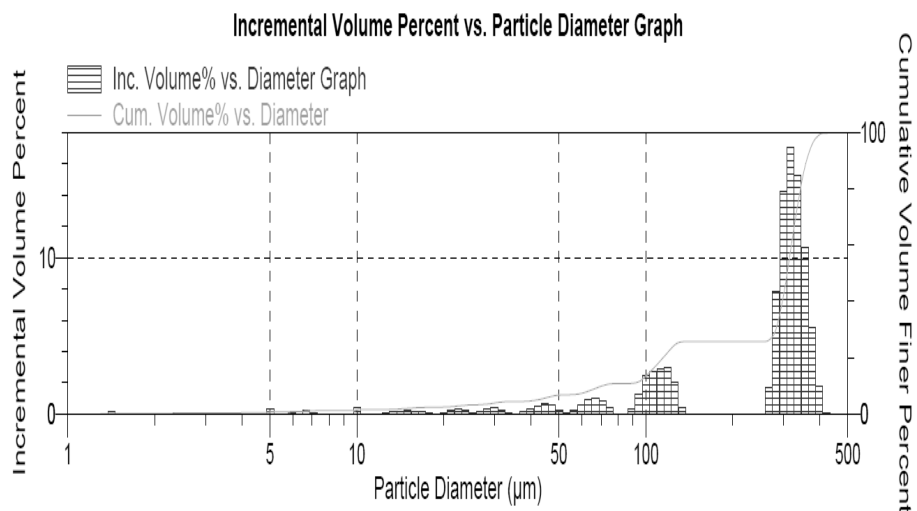
The particle size of nickel powder was analyzed by two methods. One is particle size distribution curve method which gives particles in μm . Other one is XRD method. Debye Sharer formula is used for calculating particle size in nm.

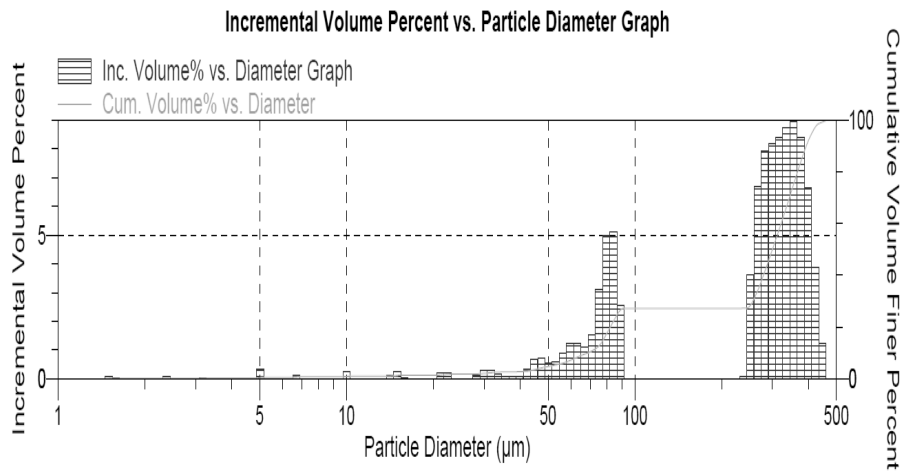
Particle size distribution method

The distribution of nickel particle size is shown in Fig.1 and the data of distribution is given in Table 4. In 20% glycerol medium with 1.5A current, more than 75% particles were below 358 μm . Under similar condition, the size of nano -particles lies between 106-120nm. This is also evident from SEM and XRD studies.

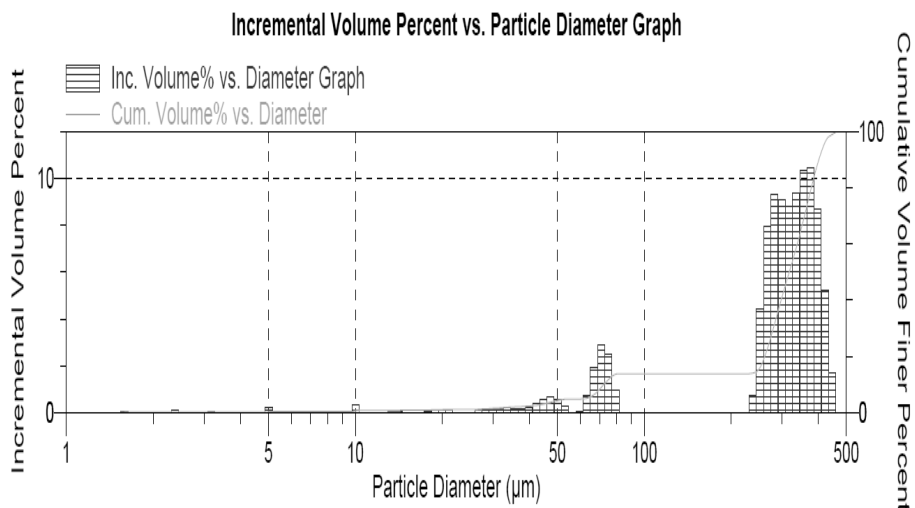
Table 4. Particle size of nickel powder obtained from different Current densities and percent of glycerol

A & C _g	Percent of particles						
	1-15	15-30	30-45	45-60	60-75	75-85	85-99
Size of particles in μm							
2 & 10	6.78	13.47	281.71	302.55	318.64	335.98	349.89
	13.47	281.71	302.55	318.64	335.98	349.89	395.06
2 & 20	22.04	235.20	311.93	419.14	453.62	485.18	509.42
	235.20	311.93	419.14	453.62	485.18	509.42	575.97
1.5&20	31.31	80.42	239.76	278.45	316.07	358.23	384.90
	80.422	239.77	278.45	316.07	358.23	384.90	444.51
1.5& 30	14.295	77.62	256.52	289.39	321.32	354.55	378.64
	77.619	256.52	289.39	321.32	354.55	378.64	437.32





(c)



(d)

Fig. 1. Particle size distribution a) 10% glycerol & 2A (b) 20% glycerol & 2A., (c) 20% glycerol & 1.5 A and (d) 30% glycerol & 1.5 A

XRD studies of particle size

The particle size is calculated from XRD data of peaks from graph and by using Debye-Sharer formula:

$$D = k \lambda / \beta \cos \theta \tag{26}$$

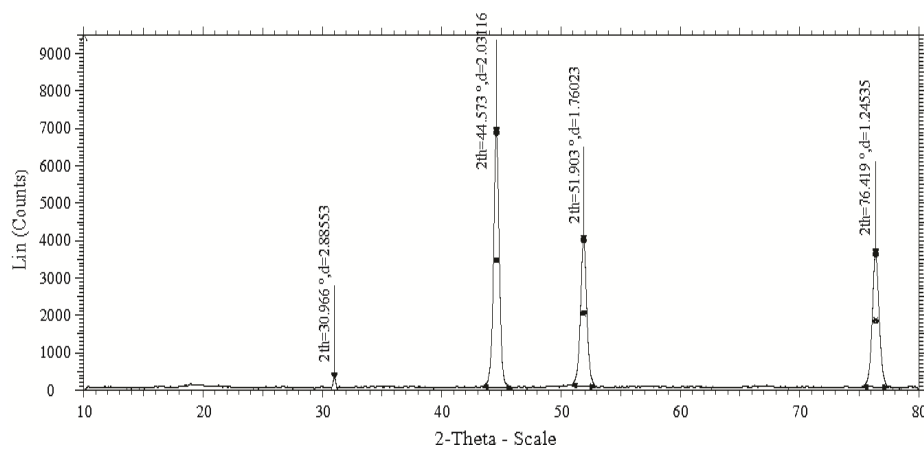
where: k - crystalline shape factor and λ - wave length in angstrom (Å)

$$\beta \text{ (radian)} = \text{FWHM} \times \pi / 180 \tag{27}$$

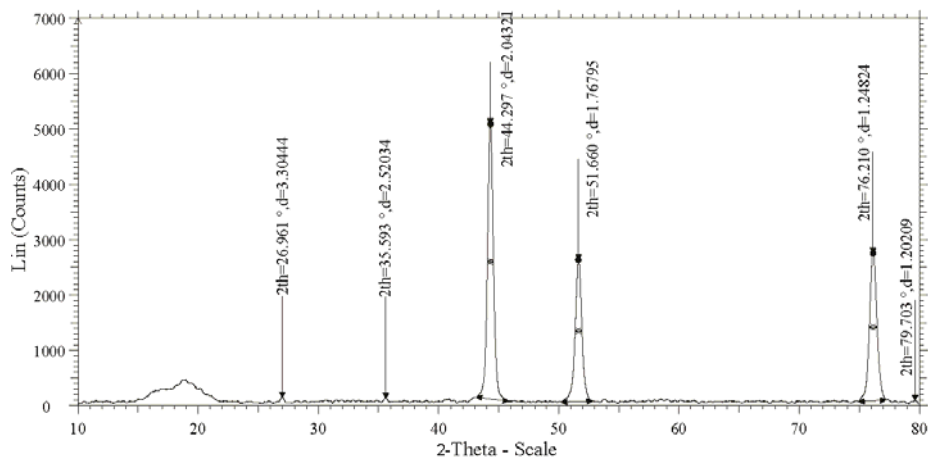
where: Full-Width Half-Maximum (FWHM) - from instrument data, π is 22.7 and θ is angle. Particle size is shown in Table 5. XRD pattern of nickel powder particles of some samples are shown in Fig.2. A peak shows 2θ values and is related to the grain size of the particle in nm. The height of the peak indicates intensity of diffraction or may be related to number of particles.

Table 5. particle size of Nickel powder obtained at different current and percent of glycerol

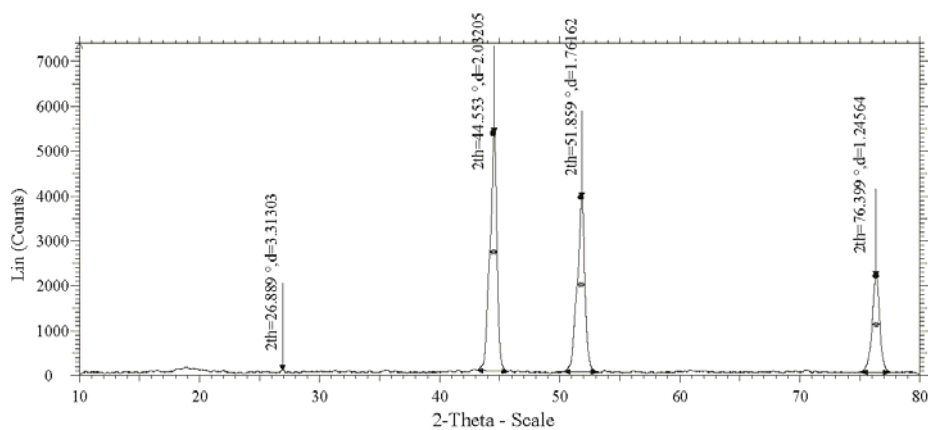
Current & Percent of glycerol	Particle size in nm
2 A & 10%	127.3, 130.3, 131.6, 266.5
2 A & 20%	118.5, 120.1, 129, 292.2,
1.5 A & 20%	106.4, 108, 119.9
1.5 A & 30%	119.6, 131, 156.5, 373.9



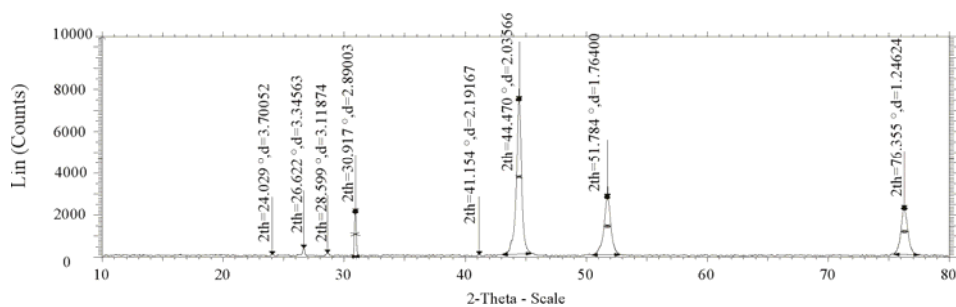
a)



b)



c)

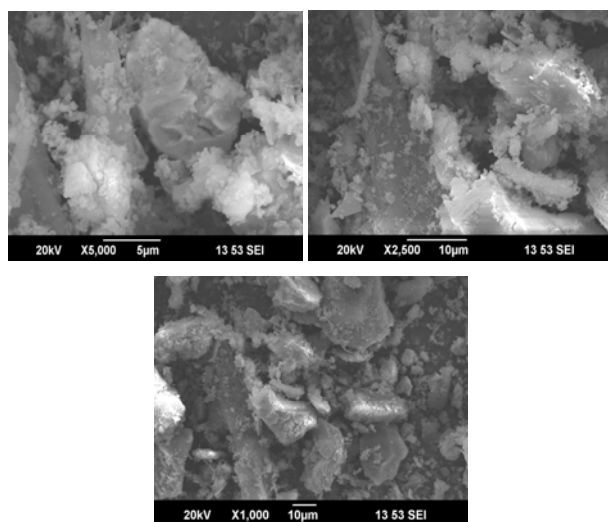


d)

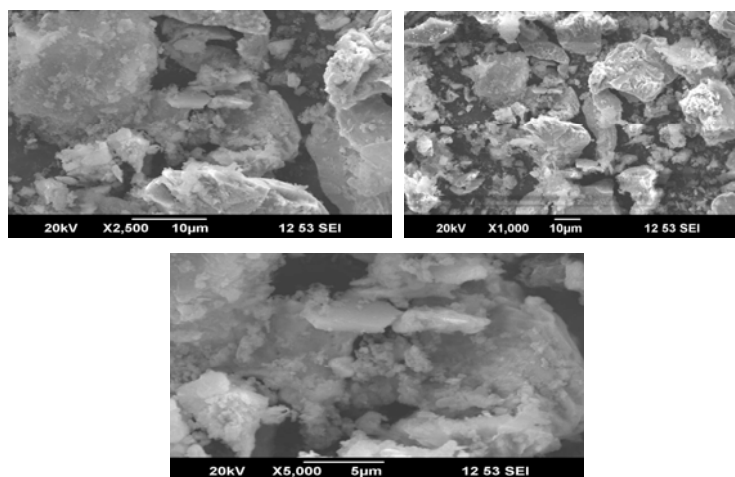
Fig. 2. XRD graphs (a) 10% glycerol & 2A (b) 20% glycerol & 2A., (c) 20% glycerol & 1.5A and (d) 30% glycerol & 1.5A

Morphological studies

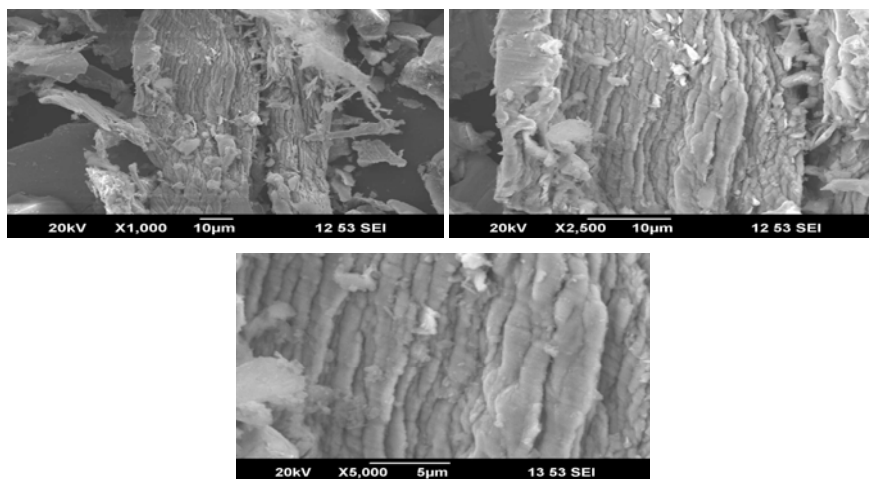
SEM microphotographs of nickel powder are shown in Fig. 3. The relevant physical data of respective powders are presented in Table 6. These results indicate that with decrease of the apparent density the smaller particle size of electrodeposited powder will be obtained.



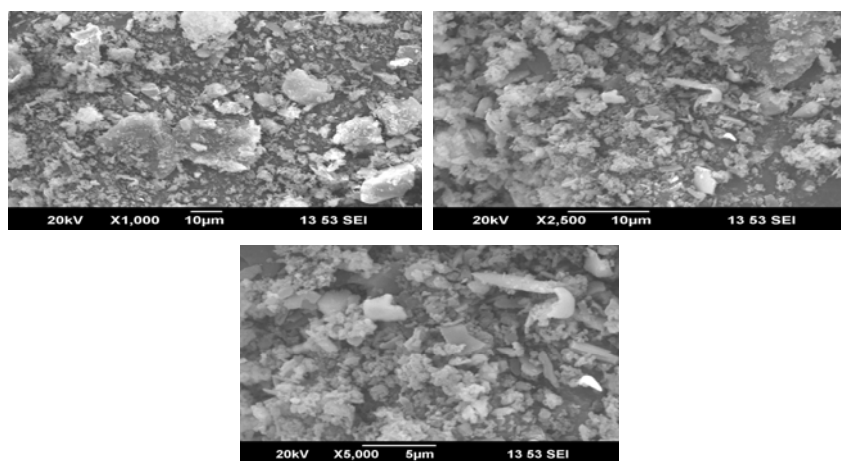
(a)



(b)



(c)



(d)

Fig.3-SEM microphotographs a) 10% glycerol & 2A (b)20%glycerol & 2A.,
(c)20 % glycerol & 1.5 A and (d)30% glycerol & 1.5 A

Table 6. Morphology of nickel powders and related data

A & C _g	d _a	Os	Morphology of the powder, and % of particles below ,100 µm	
2 A & 10 %	1.4	86	Angular, flaky, spongy, irregular	30
2 A & 20 %	1.2	79	Spongy, irregular	15
1.5 A & 20 %	3.4	82	Irregular, spongy flaky	30
1.5 A & 30 %	2.0	83	Spongy, irregular, fibrous, aggregate.	30

Discussion

The apparent density of the powder decreases with increasing percent of glycerol and current. Therefore, the decrease in apparent density may be considered as a measure of decrease of dendrites. The percent of glycerol between 20 and 30% and current from 1.5 to 2A produce powders which contain more of spongy, irregular, flaky, fibrous and aggregate particles and weakly bonded dendrites particles.

In most the particle size analysis shows that 85% of particles are smaller than 384 μm , whereas 75% of particles are smaller than 358 μm . Increase in the applied current and percent of glycerol increase the size of particles, but decrease the oxidative stability of powder. Xrd studies indicate that 1.5 to 2A current and 20-30% glycerol gives 106-374nm size particles. Powders prepared in 0-5 percent glycerol are metal flaks with metallic sheen.

When the electrodeposition process was completed the acid concentration was increased. This increase of the acid concentration is due to the formation of sulphuric acid from sulphate ions and different carboxylic acids formed by the electrolytic oxidation of glycerol as well as oxygen molecules liberated during electrodeposition process, eq.16, and elimination of water molecules from the solution by electrowinning process.

During electrodeposition process nickel ion concentration is decreased. Even in the case of copper electrodeposition, copper ion concentration decreased. The electrodisolution process is slower than electrowinning process. If the metal is attracted by acids, there is an increase in concentration of the metal ion. The electrowinning is slower than electrodeposition. This is observed in cadmium electrodeposition process [22]. The conditions of electrowinning and electrodeposition are the same. Replacement of the anode makes difference between the two processes. If inactive metal like platinum is used as anode, this becomes electrowinning process. However, any metal or even graphite cannot be used as the cathode. It is very important to note that only platinum should be used as anode. In the electrodeposition process, inactive anode is replaced with corresponding metal anode. The hydroxyl ions play an important role in electrodeposition and electrowinning processes. The electrocatalytic dissolution of anode is a spontaneous reaction which is generally zero order.

The nickel sulphate is moderately strong electrolyte. Perhaps, its dissociation is not even 75%. Under these conditions, some current is unlisted for dissociation of nickel sulphate and boric acid. The PFE values not only include percent of Faraday required for electrolysis of water, but also include percent of Faraday required for dissociation of electrolytes. Glycerol percent is also high and σ conducting power of solution decreases with increasing glycerol concentration. The percent of Faraday utilized can be calculated, using second law of thermodynamics, if heat of dissociation is known.

Conclusions

It may be concluded that 20 % glycerol and 1.5 A current produce powder with lower particle size and high oxidative stability. Under these conditions, the size of 85% particles is smaller than 384 μm and powders are free from dendrites and stability is around 83%. This electrocatalytic and auto deposition studies indicate that electrodeposition is a very complex process. This electrocatalytic effect may be helpful

in preparation of salts, particularly metal salts, of organic acids. A new definition is given to electrodeposition process.

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