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ELECTROWINNING OF NICKEL POWDER FROM GLYCEROL AND AMMONICAL MEDIUM -STUDY OF MORPHOLOGY AND NANO-NATURE OF THE POWDER

S.G. Viswanath[*], Sajimol George

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 electrowinning nickel from different concentrations of ammonium hydroxide and percent of glycerol. The current efficiency, morphology, stability and particle size of the deposited nickel powder as well as the kinetics of electro deposition were studied. The current efficiency and stability of the powder increased up to 10% glycerol then decreased with the increase in concentration of glycerol for all concentrations of ammonium hydroxide. The stability of electrowon nickel powder is in the range of 86 to 94 %. The metal powder was dendrite, cubical, spherical and polygonal. The average size of deposited powder was found to be decreasing as the concentration of glycerol increased in the medium. Keeping the concentration of ammonium hydroxide within the range 0.5 M to 1 M, and glycerol in 5 to 20 % range, the average size of the particles are in the range of 3.5 to 21.4 microns. The apparent density of nickel powder may be correlated with the particle size. A mathematical relation between apparent density, current efficiency and stability as a function of glycerol percent and ammonium hydroxide concentration were presented.

Keywords: Electrowinning, Nickel, Stability, SEM, Particle size, Avrami-Erofeev kinetics

Introduction

The best known for its use in coinage, nickel (Ni) has become much more important for its many industrial applications due to a unique combination of properties. Nickel has a relatively high melting point of 1,453°C (2,647°F) and a face-centered cubic crystal structure, which gives the metal good ductility. Nickel alloys exhibit a high resistance to corrosion in a wide variety of media and have the ability to withstand a range of high and low temperatures. In stainless steels, nickel improves the stability of

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[*] Corresponding author. Gorti Viswanath, gortiviswanath@yahoo.com

the protective oxide film that provides corrosion resistance. Its major contribution is in conjunction with chromium in austenitic stainless steels, in which nickel enables the austenitic structure to be retained at room temperature. Modern technology is heavily dependent on these materials, which form a vital part of the chemical, petrochemical, power, and related industries.

Nickel powder has important applications in the field of fabrication and in industry. Copson et al. [1] and Kuroda et al. [2] patented their works on electrolytic nickel powder preparation. Cathodic preparation of finely dispersed nickel 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. et al. [6] studied the direct electrowinning of valuable metals from sea nodules using aqueous chloride bath and the effect of addition of sodium sulphide to the ground nodules on the dissolution behavior ofvarious metals. Holm and O' Keefe [7] studied the effect of electrolytic parameters on the electrowinning of nickel. Brillas et al. [8] studied the nickel electrowinning using platinum catalysed hydrogen diffusion anode and the effect of chloride and sulphate ions. Lupi and Pasquali [9] studied the electrolytic nickel recovery from lithium ion batteries. Borikar, Umare and Viswanath studied the effect of acetone on the electrowinning process for preparing copper [10], nickel [11], cadmium [12] and zinc [13] powders. Recently, Viswanath and George reported preparation of cadmium [14] and copper [15] powders in sulphuric acid and glycerol medium.

In the present work an attempt has been made to study the influence of glycerol on the electro winning of nickel from ammonia bath and on the morphology and particle size of electro deposited nickel powder and its correlation with kinetic parameters. The apparent density of nickel powder may be correlated with the particle size. An attempt was made to study Avrami–Erofeev kinetics and the value of Avrami kinetics is correlated to the shape of the particles.

Experimental

Instruments

The bath solution ($NiSO_4$, NH_4Cl and NH_4OH) was taken in a single compartment of electrode cell. The electro winning experiments were performed using nickel plate.(6cm×1.5cm ×1mm) as cathode and gold plate as anode. Current was supplied by a regulated DC power supplier model L3202 (Aplab). Current and voltage were indicated digitally by the instrument itself. All the experiments were carried out at room temperature. The temperature of the bath remained constant during the experiment.

A current of 0.5 amps was applied to the bath. The current variation was ± 0.01 amp. The applied current strength should not exceed 0.5 amps. The large current densities warm the solution and the bath temperature rises which increases the rate of deposition of the powder which is not desirable.

The bath solution contains 0.04M hydrated nickel sulphate and 0.2M ammonium chloride, varing concentration of ammonium hydroxide from 0.5 t 0 2.0M and glycerol from 0 to 20% by volume percent. Electrowinning of high concentration of nickel sulphate produes flaky product, not powder. This is due to the fact that one nickel ion reqires six molecules of ammonia for complex formation. Therefore, large concentration of ammonium hydroxide is required. The amonium chloride and ammonia hydroxide form buffer solution which gives a pH from 8 to 9.2 ml of solution is taken at ten minutes intervals and analyzed for nickel to study the kinetics of nickel deposition by titration the solution against 0.01M EDTA (sodium salt of ethylene diamine tetra acetic acid) solution using ammonium perpurate as indicator. The electrolytic deposition is continued for two hours. The nickel powder was removed from the electrode, washed several times with water then with acetone or methanol and dried at 80^{o} C in an air oven. The product is preserved in an air tight container.

Determination of apparent density

The apparent density, da is given by the formula as:

$$da = dw(W3 - W1)/(W2 - W1 + W4 - W3) \qquad (1)$$

W1 - the mass of dry empty dry density bottle,
W2 - mass of density bottle with distilled water,
W3 - mass dry empty density bottle and nickel powder (about 1 to 1.5g),
W4 - mass of density bottle with nickel powder and distilled water,
dw - the density of water at that temperature.

The apparent density of nickel powder, obtained at different concentrations of ammonium hydroxide and percent of glycerol is presented in Table 1.

Table 1. Apparent density of nickel powder obtained from different concentration of ammonium hydroxide and percent of glycerol

NH_4OH Concentration	Percent of glycerol and apparent density of nickel (g/ ml)				
(M)	0%	5%	10%	15%	20%
0.5	7.3	6.0	4.9	4.1	3.4
1.0	7.2	5.5	4.2	3.2	2.5
1.5	7.1	5.1	3.9	2.8	2.7
2.0	6.8	4.9	3.7	2.7	2.1

The apparent density, data can be expressed as an exponential function of concentration of ammonium hydroxide, ca and percent of glycerol, cg as:

$$da = \exp(cg(0.0116ca2 - 0.0432ca - 0.0207) + (-0.0116ca2 - 0.0113ca + 2.0)] \qquad (2)$$

Cathodic current efficiency (C.E.)

Study of C.E. was performed by measuring the nickel content in the bath solution. The metallic nickel deposited was actually estimated by titrating the bath solution against standard EDTA using ammonium perpurate indicator. Based on the current used for the particular period of electrolysis, the theoretically expected weight of nickel deposition was calculated using Faraday's Law:

$$W = Z\,I\,t \tag{3}$$

where: W, Z and t are theoretically expected mass of nickel deposit, electrochemical equivalent of nickel, and t time in seconds, respectively.

The C.E. was calculated using the relation:

$$C.E = (w/W) \times 100 \tag{4}$$

where: w is the mass of nickel deposited in the actual practice. The data of current efficiency are presented in Table 2. The current efficiency, CE, can be expressed as a function of concentration of ammonium hydroxide, c_a and percent of glycerol, c_g in two different equations:

$$CE= (c_g + 223c_a^3 - 900.66c_a^2 + 1093\,c_a - 159.3)/(2.9c_a^3 - 11.2c_a^2 + 13.1c_a - 1.9) \tag{5}$$

Table 2. Cathodic current efficiency of nickel winning process at different concentrations of ammonium hydroxide and percent of glycerol

NH_4OH Concentration	Percent of glycerol and cathodic current efficiency				
(M)	0%	5%	10%	15%	20%
0.5	86.3	89.9	90.9	84.5	77.2
1.0	88.1	89.5	91.5	85.4	80.4
1.5	85.4	87.8	89.5	86.3	79.8
2.0	71.2	73.4	74.5	68.3	61.2

This above equation is valid when the percent of glycerol is in the range 0 to 10%.

However, the following equation is valid when the percent of glycerol is in the range 10 to 20%:

$$CE= (c_g + 51.8\,c_a^3 - 143.7c_a^2 + 94.16c_a - 94.4)/(0.453\,c_a^3 - 1.26\,c_a^2 + 0.757c_a - 0.85) \tag{6}$$

Determination of Stability

Nickel powder was kept for 45 days and in an air tight sealed bottle then the study of its stability was performed. About one gram of nickel powder, which was weighed accurately (± 1000th of a gram) was taken in 100 ml 0.05M sulphuric acid. The solution was stirred with a magnetic stirrer for one hour. The solution was filtered and the dissolved nickel in the filtrate was estimated by titrating against standard EDTA (0.01M) using Ammonium Perpurate as indicator. Nickel powder is susceptible to oxidation and forms NiO and Ni_2O_3.The oxidative stability of nickel was estimated using the formula:

$$\text{Oxidative Stability} = \frac{\text{Weight of the metal powder undissolved}}{\text{Weight of the metal powder taken}} \times 100 \qquad (7)$$

The data are presented in the Table 3. The oxidative stability, OS, can be expressed as a function of concentration of ammonium hydroxide, c_a and percent of glycerol, c_g in two different equations:

$$OS= (c_g+1926c_a^3 -6709.8c_a^2+6742.6\, c_a -1797.1)/(-3.259c_a^3+12.274c_a^2-12.35x+5.121) \qquad (8)$$

Table 3. Oxidative stability of nickel powder obtained from different concentrations of ammonium hydroxide and percent of glycerol

NH_4OH Concentration	Percent of glycerol and oxidative stability of the powder				
(M)	0%	5%	10%	15%	20%
0.5	86.3	88.0	92.0	82.0	78.0
1.0	90.0	84.0	95.0	86.4	84.0
1.5	87.0	89.0	90.0	78.0	74.0
2.0	74.5	76.0	77.4	72.1	69.0

This above equation is valid when the percent of glycerol is in the range 0 to 10%.

When the percent of glycerol is in the range 10 to 20% the next equation is valid:

$$OS= (c_g-142.5c_a^3+512.4c_a^2 - 551.6\, c_a+94)/(-1.635c_a^3+ 5.692c_a^2 -5.975c_a+1.096) \qquad (9)$$

Results

Electrode reactions

The important chemical and electrode reactions during the electro winning process are given below.

$$2H_2O \rightarrow 2H^+ +2OH^- \qquad (10)$$

$$NiSO_4 \rightarrow Ni^{2+} + SO_4^{2+} \qquad (11)$$

Nickel forms complex with ammonia:

$$Ni^{2+} + 4NH_4OH \rightarrow [Ni(NH_3)_4]^{2+} + 4H_2O \qquad (12)$$

The reactions at cathode are:

$$[Ni\,(NH_3)_4]^{2+} +4H_2O + 2e \rightarrow Ni + 4NH_4OH \qquad (13)$$

$$2H^+ + 2e^- \rightarrow H_2$$

The net reaction at cathode is:

$[Ni\ (NH_3)_4]^{2+} + 2H^+ + 4H_2O + 4e \rightarrow Ni + H_2 + 4NH_4OH$ (14)

The reactions at anode are:

$4OH^- \rightarrow 2H_2O + 2O + 4e^-$ (15)

$2O \rightarrow O_2$ (16)

The net reaction at anode is:

$4OH^- \rightarrow 2H_2O + 2O + 4e^-$ (17)

The overall cell reaction is:

$[Ni(NH_3)_4]^{2+} + 2H^+ + 4HO^- + 4H_2O \rightarrow Ni + H_2 + O_2 + 4NH_4OH$ (18)

$H_2SO_4 + 2NH_4OH \rightarrow (NH_4)_2SO_4 + 2H_2O$ (19)

Oxidation of glycerol

These reactions are discussed by Viswanath and George [14.15]. While liberated oxygen at anode reacts with glycerol and forms several products, the two primary alchoholic groups in glycerol are capable of being oxidized to aldehyde and then to the carboxyl group.

$CH_2OH\text{-}\ CHOH\text{-}\ CH_2OH \rightarrow CHO.\ CHOH\text{-}\ CH_2OH \rightarrow COOH.\ CHOH\text{-}\ CH_2OH \longrightarrow$

(glycerol) (glyceraldehyde) (glyceric acid)

$COOH\text{-}CHOH\text{-}COOH \longrightarrow COOH\text{-}\ CO - COOH$ (20)

(tartonic acid) (mesoxalic acid)

While the secondary alchoholic group is oxidized to carbonyl group.

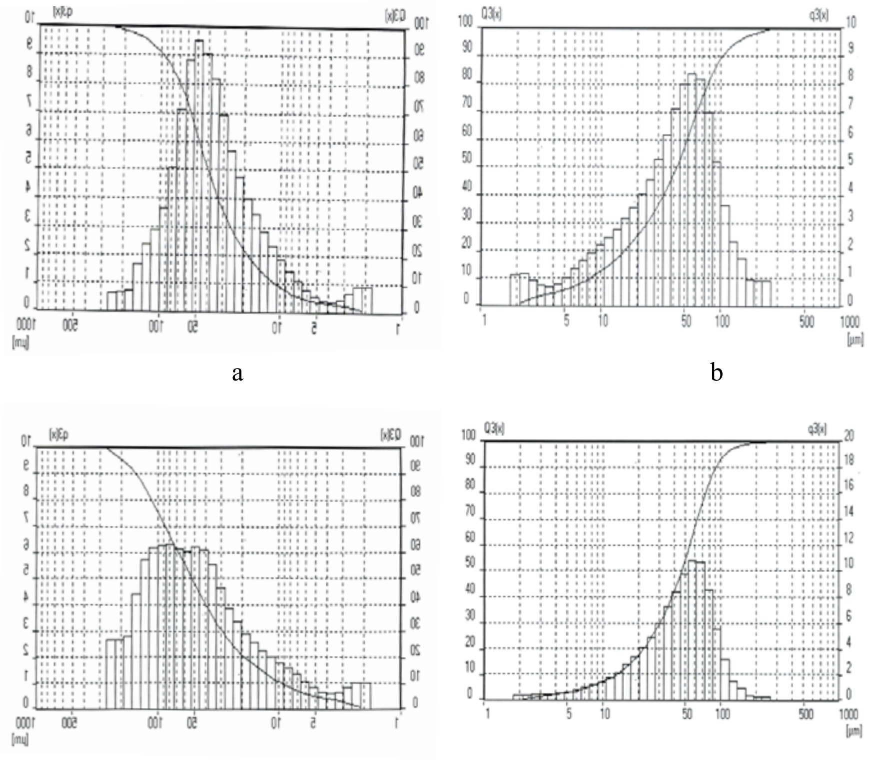
$CH_2OH\text{-}\ CHOH\text{-}\ CH_2OH \longrightarrow CH_2OH\text{-}\ CO\text{-}\ CH_2OH \longrightarrow COOH.\ CO - COOH$ (21)

(glycerol) (dihydroxy acetone) (mesoxalic acid)

In the electrolysis, all positive ions are aligned and migrate towards cathode while negative ions migrate towards anode. The metal ion is discharged at the cathode. The solid metal atoms so deposited on the cathode should have a strong metallic bond. However, the electrolyte solution containing organic solvents, which is covalent in nature, disturbs this ion environment particularly at cathode causing lose bonding between metal-metal atoms. Also, the large amount of hydrogen gas at cathode makes deposit very porous that results in the formation metallic powder.

Particle size analysis

The distribution of nickel particle size is shown in Fig. 1(a-d). The data of distribution is given in Table 4. With 5% glycerol in the bath solution, the cumulative frequency of particle size decreases by about 3.5%. It is also observed that with 10% glycerol in the bath solution the particle size decreases by 17% while with 20% glycerol in the bath the decrease in the particle size increased to 21.4%. It may be concluded that, keeping the concentration of ammonium hydroxide within the range 0.5 M to 1 M, and glycerol in 5 to 20 % range, the average size of the particles are in the range of 3.5 to 21.4 microns.



a b

c d

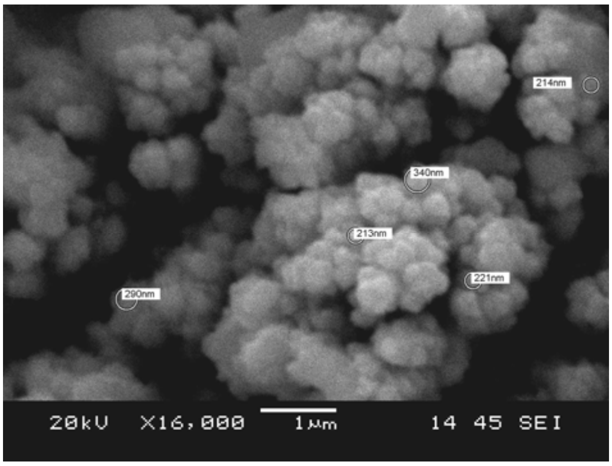
Figure.1.Distribution of particle size of cadmium powder obtained from different media a) 0.5N NH4OH +0% glycerol (b) 0.5N NH4OH + 5% glycerol (c) 1N NH4OH + 10% glycerol and (d) 1N NH4OH + 20% glycerol.

Table 4. Particle size of nickel in different concentrations of NH4OH and % glycerol

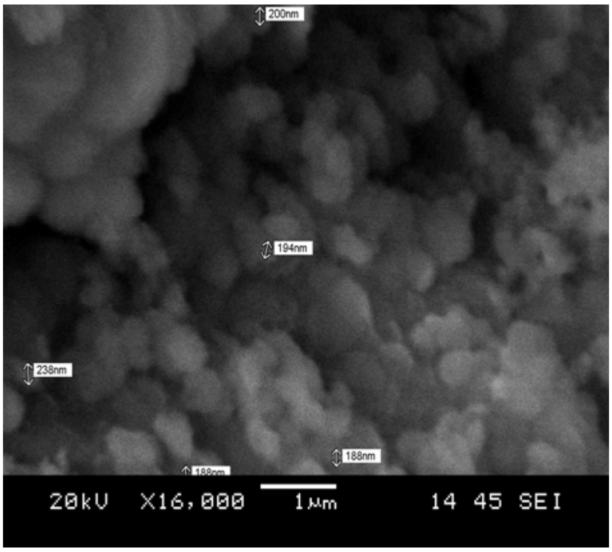
NH_4OH concentration (M)+%glycerol	% of particles in different range of μm			
	1.77-20.25 (1)	20.25-53.03 (2)	53.03-100.75 (3)	100.75-263.81 (4)
0.5+0	22.13	44.18	24.67	9.02
0.5+5	25.48	35.23	28.74	10.55
1.0+10	21.04	29.72	24.8	24.44
1.0+20	17.84	40, 22	35.52	6.42

Morphological Studies

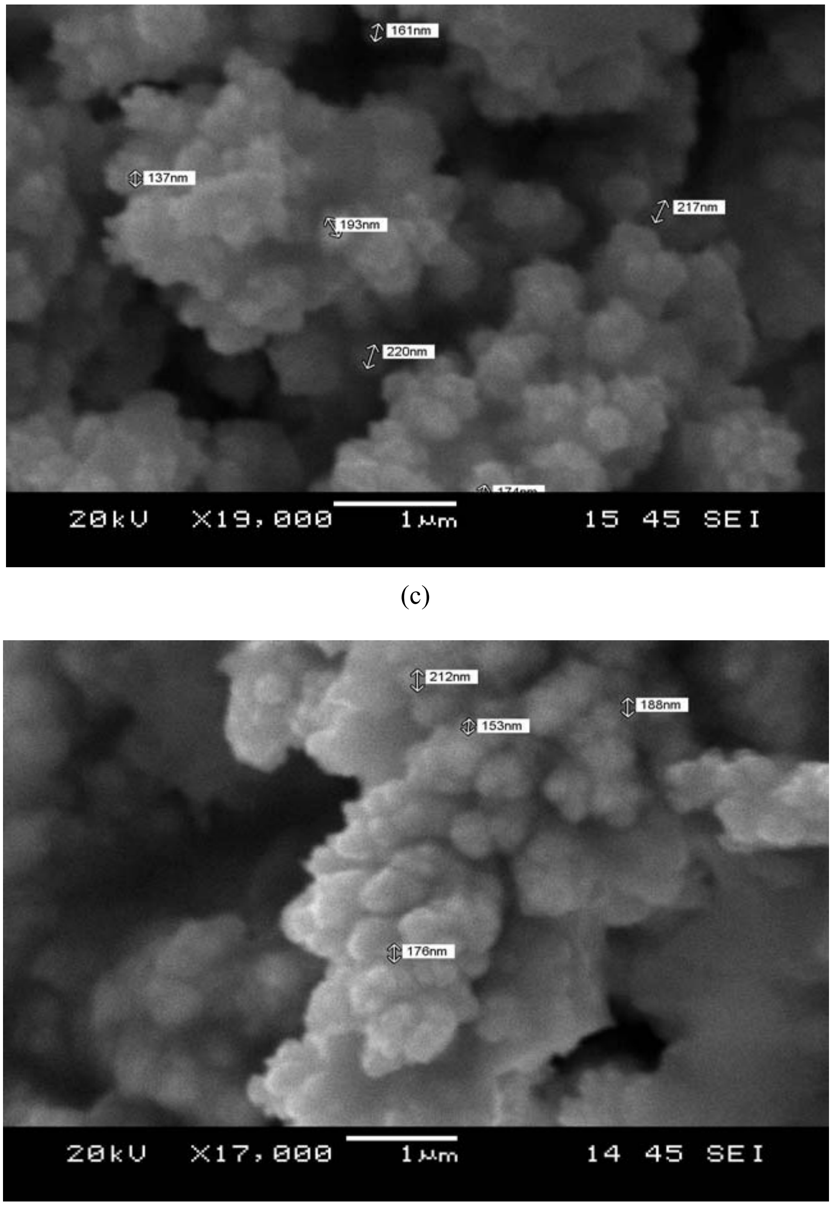
SEM micrographs of nickel powders were investigated and photographs are presented in Fig 2(a-d). Relevant physical data of respective powders are presented in Table 5. This shows some sort of relationship between these properties and morphology of electrodeposited powders. The arrows in the SEM picture indicate size of the particles. The smallest size of nano particle found is 137 and 153 nm for the powders obtained from 1.0M NH4OH and 10% glycerol and 1.0M NH4OH and 20% glycerol, respectively.



(a)



(b)



(c)

(d)

Figure 2 SEM photo graphs of nickel powder obtained from different media (a) 0.5N NH4Cl +0% glycerol (b) 0.5N NH4Cl + 5% glycerol (c) 1N NH4Cl + 10% glycerol and (d) 1N NH4Cl + 20% glycerol

Table 5. Morphology of nickel powders and related data.

NH_4OH concentration (M)+%glycerol	Apparent density	Stability	Morphology of the powder, nano particle size (nm) and % particles below 101µm
5+0	7.3	86.0	Sponge and dendrite, 167-525and 90.98
0.5+5	4.5	92.0	Dendrite, polygonal, 188-418 and 89.45
1.0+10	2.8	86.0	Polygonal, cubical, spherical 137-377, and 75.56
1.0+20	2.5	84.0	Polygonal, Cubical, spherical 140-310 and 93.58

Kinetics of deposition of nickel

Chemical kinetics

The kinetics of electrodeposition of nickel in the presence of different volume percents of glycerol, and different concentrations of ammonium hydroxide was studied, α the fraction of nickel present in the solution, is defined as:

$$\alpha = C_t / C_i \quad (22)$$

where: C_i and $C_{t'}$ are initial concentration and concentration of Ni^{2+} at any time t respectively. (1-α) is the fraction of nickel metal deposited. The rate of change of concentration with respective time is written as:

$$d\alpha/dt = k(1 - \alpha)^n \quad (23)$$

where: n and k are order of reaction and reaction rate constant, respectively. For zero order reaction the integrated form of the above equation is written as:

$$\alpha = kt \quad (24)$$

Plot of α against time, t gives a linear plot passing through the origin with the slope equal to k. Fig. 3(a-c) show the zero order plots for the electrodeposition of nickel in different concentration of ammonium hydroxide and volume percent of glycerol, whereas in Table 5 the k values are given. The kinetics was followed from 20 to 60 min. Later part of the reaction data is in good agreement with zero order reaction. This indicates that the rate of deposition is purely independent of nickel ion concentration.

The reaction rate constants as function of percent of glycerol and ammonia can be written as:

$$k = -0{,}002c_g + 0.104c_a^{-0.08} \quad (26)$$

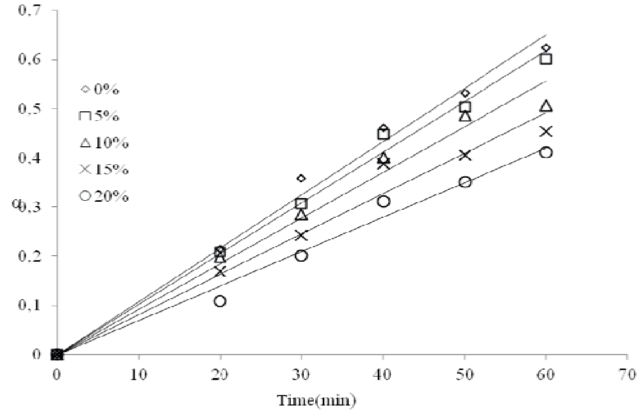


Fig 3a. Plot of α against time in 0.5N NH_4OH In different percent of glycerol

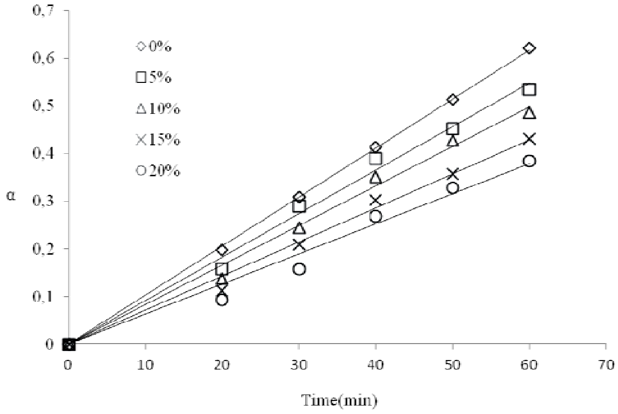


Fig 3b. Plot of α against time in 1.0N NH_4OH In different percent of glycerol

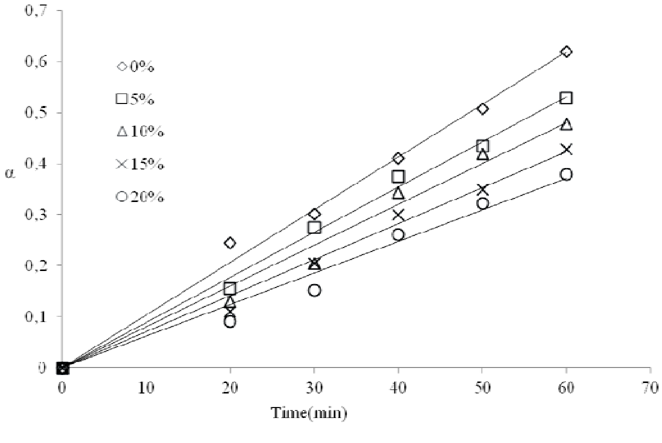


Fig 3c. Plot of α against time in 1.5N NH_4OH In different percent of glycerol

Table 6 Reaction rate constants of the electrodeposition kinetics

NH_4OH Concentration	Percent of glycerol and reaction rate constant				
(M)	0%	5%	10%	15%	20%
0.5	0.0108	0.0103	0.0092	0.0082	0.0070
1.0	0.0103	0.0091	0.0083	0.0072	0.0063
1.5	0.0103	0.0083	0.0080	0.0071	0.0062

Avrami-Erofeev kinetics

The chemical kinetics of electrodeposition of nickel is tried to correlate with Avrami-Erofeev kinetics. Avrami-Erofeev kinetics gives some clue about the morphology and size of the particle. The equation is given below:

$$(1-\alpha) = \exp(-kt^n) \tag{27}$$

and the logarithmic form of equation is written as:

$$\ln\{-\ln(1-\alpha)\} = n \ln(t) - \ln(k) \tag{28}$$

where: n and k are order of reaction and rate constant of the reaction, respectively. Plot of ln{-ln(1-α)} against ln(t) gives a straight line with slope equals to n, while and intercept equals to ln(k). The plots are shown in Fig. 4(a-c) of nickel in different concentration of ammonium hydroxide and volume percent of glycerol. In Table 6 n and ln(k) values are given.

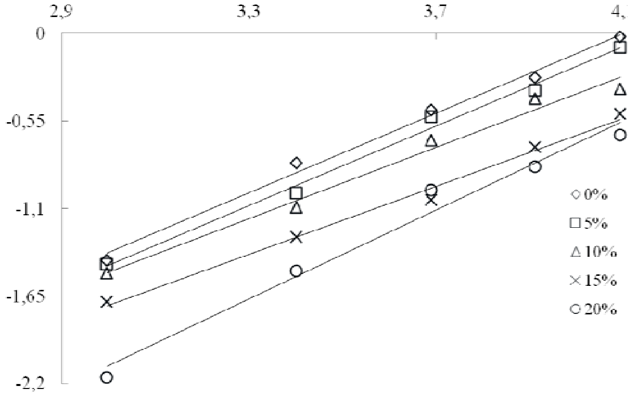


Fig 4a. Plot of (1-ln(1-α)) against ln(time) in 0.5N NH4OH In different percent of glycerol

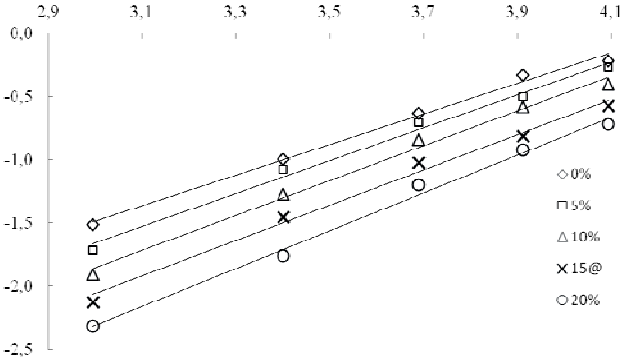


Fig 4b. Plot of (1-ln(1-α)) against ln(time) in 1.0N NH_4OH In different percent of glycerol

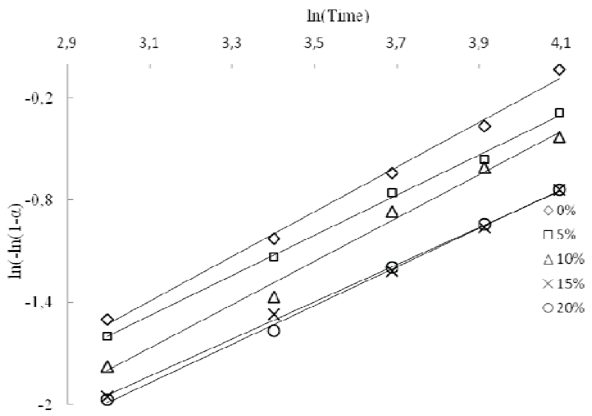


Fig 4c. Plot of (1-ln(1-α)) against ln(time) in 1.5N NH4OH In different percent of glycerol

Table 7 Avrami-Erofeev kinetic constant

% glycerol	ammonium mydroxide concentration (M)					
	0.5		1.0		1.5	
	(n)	ln(k)	(n)	ln(k)	(n)	ln(k)
0	1.247	-5.117	1.212	-5.123	1.312	-5.462
5	1.248	-5.200	1.302	-5.567	1.178	-5.132
10	1.12	-4.856	1.383	-6.007	1.272	-5.612
15	1.069	-4.915	1.400	-6.262	1.088	-5.204
20	1.396	-6.274	1.497	-6.010	1.135	-5.391

Discussion

From the equation 2 necessary conditions can be determined for the preparation of nickel powder of desired density. The apparent density decreases with increasing percent of glycerol as well as ammonium hydroxide concentration. Also, the percent of dendrites in the powder decreases with increase of concentration of glycerol and ammonium hydroxide. Therefore, the decrease in the apparent density may be correlated to decrease of dendrites in the powder. The Avrami-Erofeev n value is almost 1, and does not vary with percent of glycerol and ammonium hydroxide concentration. This is an indication that particles are two dimensional.

When the concentration of ammonium hydroxide in the bath is 0.5 M and 5% glycerol the produced powders are in the form of sponge or agglomerates. When the rate of deposition is comparatively higher these types of particles are produced. Particle size studies revealed that 50% particles have the average size of 42.2 μm. Increase in the rate constant as well as Avrami-Erofeev kinetics may be the result of comparatively higher ion environment, or ion strength, due to the lower glycerol present in the medium.

When the percent of glycerol is 5 to 10 and ammonium hydroxide concentration is about 1 M, about 50% particles are in 52.2 μm size and above 70% particles are in 79.5 μm size. The powder contains more of cubical and spherical particles and the size of particles lies between 9.45 to 152.6 μm. This powder contains less percentage of agglomerated particles. Generally, spherical particles have smaller size because of the strong inter atomic forces firmly holding the particles together. Agglomerated particles and dendrites will have the large surface area hence the particle size is above 75 μm.

It is found that increase in the percentage of glycerol from 5 to 10% and ammonium hydroxide concentration to 1 M the oxidative stability increases up to 88 %. If the powder has small surface area, the oxidative stability is higher. In the present case, the oxidative stability of the powder may be due to the small particle size with small surface area.

SEM micrographs show that, when the concentration of glycerol is 10 to 15% and ammonium hydroxide up to 1.5 M the morphology of the particles is spherical, cubical and a low percentage of weakly bonded dendrites is also detected. SEM micrographs also show the presence of nano particles for the sample having high percentage of glycerol and the apparent density is low. Decrease in the apparent density, indicates the increase in the fraction of nano particles in the sample as well as decrease in the size of the nano particles.

For all concentrations of ammonium hydroxide when the percent of glycerol is 10%, the current efficiency and the oxidative stability reached a maximum value then decreased. The highest current efficacy and stability is found for those powders prepared in 1 N ammonium hydroxide for all glycerol percents.

During electrolysis all positive ions align and migrate towards cathode, while negative ions migrate towards anode. The metal ion is discharged at the cathode. The solid metal atoms so deposited on the cathode should have a strong metallic bond. A large amount of hydrogen liberated at cathode makes the deposit porous. The solution containing organic solvent which is covalent in nature disturbs this ion environment particularly at cathode. These factors cause lose bonding between metal-metal atoms that result in the formation of metallic powder

Conclusions

It may be concluded that 10 to 15 % glycerol and 0.5 M to 1M ammonium hydroxide produce powders having good properties. The large current densities (more than 0.5 amp) warm the solution and the bath temperature rises which increases the rate of deposition of the powder which is not desirable.The slower rate of deposition of powder is an important factor that gives powders having good properties.

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