PRELIMINARY STUDY ON AUTO-ELECTRODEPOSITION OF COPPER, CADMIUM, NICKEL, AND COBALT IN ACID AND GLYCEROL MEDIUM

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Abstract

Electrodeposition can be carried out even without corresponding metal ions in the solution, but the respective metal electrode acts as anode. This process is called auto-electrodeposition. It occurs under similar conditions applied for electrowinning or electrodeposition. The electrochemical mechanism of electrowinning and auto-electrodeposition is suggested. Hydroxyl ions play very important role in this process. In this process, a black loss deposit is formed on the anode metal. The auto-electrodeposition is combination of electrodissolution process and electrowinning process.

Keywords: auto-electrodeposition, electrowinning, copper, cadmium, nickel, cobalt

Introduction

The auto-electrodeposition of metals has not been reported in the literature till now to best our knowledge. A very little attempt has been made about this process by Viswanath and Jachak in the study of electrodeposition of copper [1], cadmium [2], nickel [3] and cobalt [4] in sulphuric acid and glycerol medium to get electrolytic powder of these metals. Generally, the elecrtowinning and electrodeposition conditions are always the same. The term electrocatalytic effect is suggested in place of polarization effect since a negligible amount of current is consumed for electrodissolution of anode metal. These auto-electrodeposition experiments of copper, cadmium, nickel and cobalt have been divided into two types of studies: quantitative and qualitative**.** In the quantitative study mass of anode dissolved, mass of metal (as powder) deposited, metal ion concentration and volume change of the electrolytic solution are determined. The color and state of the powder deposit formed on both anode and cathode are observed. In the qualitative study, however, the experiment

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consists of observance whether dissolution and deposition of metal and volume change of electrolytic solution will occur or not. The color and state of the powder deposit formed on both anode and cathode are also observed. In this paper, the theory of auto-electrodeposition is presented. This theory is applicable for electrodeposition process too.

Experimental

Instruments

For the preparation of metal powder a two-electrode single compartment cell was used. The cell consisted of two electrodes, i.e. anode and cathode, of the same metal. The electrodepositions were conducted by using copper (13x2.3x0.2cm), cadmium (15x2.3x0.2 cm), nickel (10x2.5x0.3cm) and cobalt (8x2x0.1cm) metal plate as cathode and anode. The electrodes were connected to the Regulated DC supplier model 34 B DCPS (Testronix) for stable current supply. The applied current was varied from 0.5 to 2A for all experiments and the variation was $\pm$ 0.01A. All the experiments were carried out at 25 ± 1^oC.The temperature of the bath remained almost constant during the experiments.

Method of preparation of solutions for different auto-electrodeposition studies

200 ml of bath solution was used for all experimental runs. For copper and cadmium auto-electrodeposition studies, solutions containing 0.5N sulphuric acid and glycerol with different volume percent were prepared. The percent of glycerol was varied from 0 to 20%.

Similarly, for nickel and cobalt auto electrodeposition studies, solutions containing 0.05N sulphuric acid and glycerol with different volume percent were prepared. The percent of glycerol varied from 0 to 30%. These solutions were saturated with boric acid.

The electrodeposition experiments were performed using metal plates. 0.5A and 1.0A current was passed through the electrolytic cell for three hour, for copper and cadmium studies. 0.5A current was passed through the cell for four hours, for nickel and cobalt studies. The mass loss of anode and the volume loss of solution were determined and also the metal ion formed due to electrodissolution of anode was estimated by EDTA titrations at the end of the experiment. The difference of mass loss of anode and the concentration of metal ions formed in the solution gives amount of metal deposited on the cathode.

Copper and cadmium auto-electrodeposition studies were conducted in 0.5M ammonium hydroxide and ammonium sulphate medium. Similarly, a nickel and cobalt auto electrodeposition study was conducted in 0.5M ammonium hydroxide solution saturated with boric acid. These studies were carried out to develop the mechanism of electrodeposition in different media. These studies were purely qualitative in nature.

Role of glycerol

Glycerol was used, in the original experiments of electrodeposition studies, to obtain metal powders. Just to compare these electrodeposition studies with auto electrodeposition experiments, glycerol was also used here. Glycerol is oxidized by the oxygen liberated at anode forms organic acids like glycerol, tartonic and mesoxalic acids. The oxidation of glycerol is also due to the oxygen liberated during

electrowinning process. The increase of acid concentration was observed in electrowinning studies of copper in the presence of sulphuric acid and glycerol. This type of increase in acid concentration is also observed in electrodeposition studies of copper and cadmium in sulphuric acid glycerol medium.

Electrocatalytic (polarization) effect and electrodissolution study of metal

The electrocatalytic effect may be regarded as the polarization of electrode [5]. This is polarization of anode occurs during electrodissolution process and causes metal passivity. The passivity of metals will be briefly discussed.

Electrochemical passivity

Metals like iron, cobalt, nickel etc dissolve quantitatively in accordance with the requirement of Faraday's laws of electrolysis. Passivity of metal occurs not immediately, but after passing current for a period of time. Perhaps, the surface of the metal which is in nano particle state reacts with atomic oxygen liberated at anode instead of OH ions produced from water. This oxide does not react with sulphuric acid to form metal sulphate. Then metal shows electrochemical passivity. The chemical passivity also depends on current density, medium (acid and alkaline) etc. Metals like molybdenum, tungsten and lead show passivity in acid medium.

In number of cases, the sum of percent of faraday required for deposition (PDF)

Percent of faraday required for electrowinning (PFW) exceeds 100%. Mostly current is consumed for electrowinning, electrolysis of water, dissociation of boric acid. Amount of current utilized for electrodissolution of anode is very small as evident from the threshold current studies. In practiced, large amount of current is required for electrowinning process.

Characteristics of Auto Electrodeposition

Theory of Electrodissolution of metals

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 form**s** corresponding hydroxide of the metal. This hydroxide reacts with acid and forms corresponding metal salt.

In ammonium hydroxide solution also the positively charged anode reacts with hydroxyl ions and form**s** metal hydroxide. If sufficient anions, in present case the anions are sulphate and borate, are present then this hydroxide reacts with ammonium salts and forms soluble ammonia complex salt. Otherwise the metal hydroxide precipitates and settles at the bottom of the cell.

Auto-electrodeposition study of copper

It was observed that in 0.5N sulphuric acid medium, anode lost some mass. There was some 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, this deposit became hard and could not be removed by simple scratching. This type of black shade loose powder was not found in experiments where copper sulphate was present. The chemical analysis indicated that this black powder is copper metal. When similar experiment was carried in 0.05N sulphuric acid or 0.1N ammonium hydroxide, after some time a large amount

of blue precipitate was observed in solution that settled at the bottom of the cell and the solution became colorless. At the same time, on the anode black-colored powder along with some blue particles were found. The blue particles were found to be copper hydroxide, $Cu(OH)_2$. If sufficient acid is not present, but glycerol was present in the solution, no precipitate was found. The copper hydroxide might have reacted with glyceric acid, tartonic acid and mesoxalic acid forming copper salts. The color of solution was blue. The blacker layer formation may be found in sulphuric acid medium than less in sulphuric acid and glycerol medium. This copper sulphate, formed due to electrodissolution metal, acts as medium for electrowinning. Plots of mass of anode dissolved against percent of glycerol in absence of copper sulphate (Abs) as well as in presence of 0.2N copper sulphate (Prs) are presented in Figure 1. Plot of mass of metal deposited on cathode against glycerol percent is shown in Figure 2.
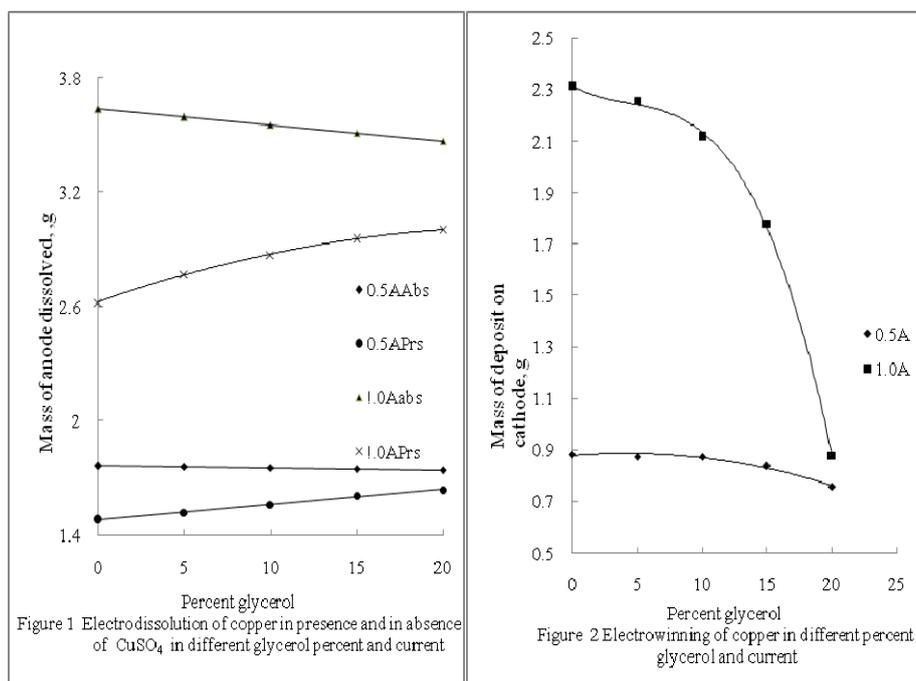
Figure 1 Electrodissolution of copper in presence and in absence of $CuSO_4$ in different glycerol percent and current

Figure 2 Electrowinning of copper in different percent glycerol and current

When current was passed through 0.5N ammonium hydroxide and ammonium sulphate medium, the solution became deep blue due to the formation of copper ammonia complex ion, $Cu(NH_3)_6^{++}$. There was some metal deposited on the cathode. At the same time, black hue loose powder deposit was found on the anode. In ammonia boric acid medium, black loose powder deposit was found on the cathode and brownish yellow deposit was found on the anode. In 0.05N sulphuric acid solution saturated with boric acid, black hue deposit found on the both electrodes.

Auto-electrodeposition study of cadmium

Similar studies were performed for cadmium. Here, black hue loose powder deposit was found on the anode. This powder was identified as cadmium. The other results were the same as observed for copper. $Cd(OH)_2$ is a white precipitate. The

cadmium organic acids salts are formed in the solution. This solution is colorless. The plots of mass of anode dissolved against percent of glycerol in presence of 0.2M cadmium sulphate and in absence of cadmium sulphate solution are presented in Figure 3. Plot of mass of metal deposited on cathode against glycerol percent is presented in Figure 4. All these solutions contained 0.5N sulphuric acid.
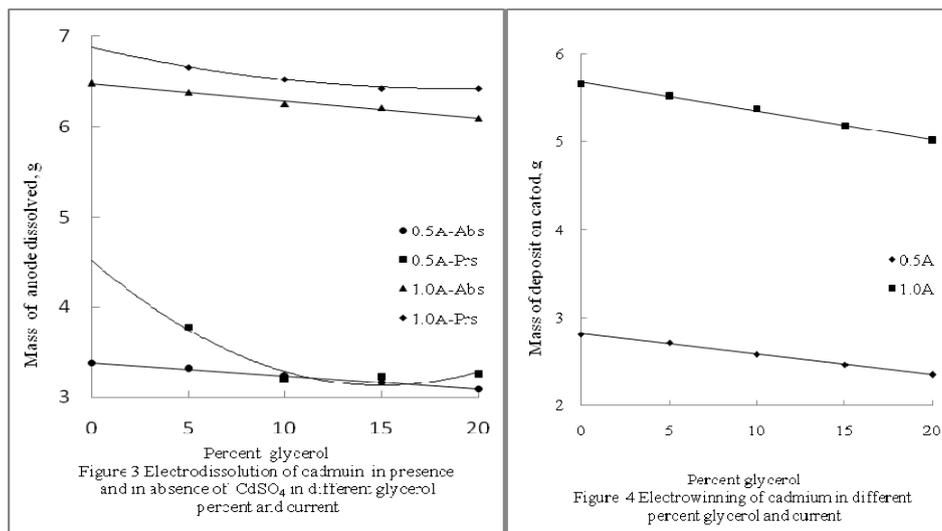
Figure 3 Electrodissolution of cadmuin in presence and in absence of CdSO$_4$ in different glycerol percent and current

Figure 4 Electrowinning of cadmium in different percent glycerol and current

Similar experiment was conducted in 0.5N ammonium hydroxide and ammonium sulphate medium. Ammonia cadmium complex ion, $Cd(NH_3)_4^{++}$, was formed and the solution was colorless. There was some metal deposited on the cathode. Similar black color loose powder deposit was found on the anode. In ammonia boric acid medium, black loose powder deposit was found on the cathode and white deposit was found on anode. In 0.05N sulphuric acid solution saturated with boric acid, black hue deposit found on the both electrodes.

Auto-electrodeposition study of nickel

In 0.5N sulphuric acid medium black color loose powder was formed on the anode. The black loose powder had the similar properties that were discussed in the auto deposition study of copper. This powder was found to be nickel metal. However, no metal deposit was found on the cathode. In 0.05N sulphuric acid or 0.1N ammonium hydroxide a large amount of green precipitate was observed in solution that settled at the bottom of the cell after some time and the solution became colorless. At the same time, 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.

Figure 5 Electrodissolution of nickel in presence and in absence of $NiSO_4$ in boric acid and different glycerol percent

Figure 6 Electrowinning of nickel in different percent of lycerol
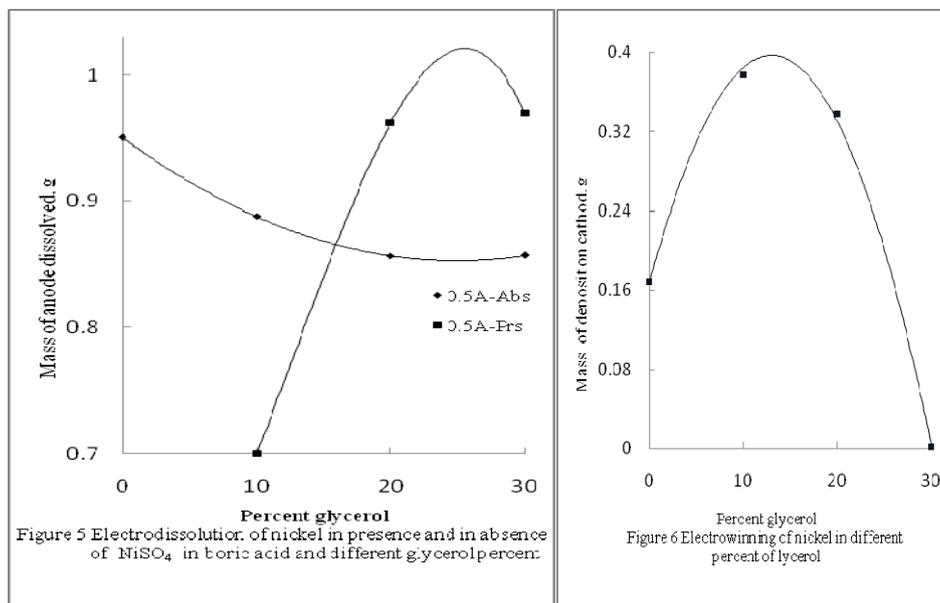
With saturated boric acid solution, the applied current to the electrolytic cell did not rise more than 0.03A. But there was some small amount of deposit on the cathode and solution became pale green. At the same time very small quantity of black loose deposit was formed on anode having similar properties as described earlier. 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. Plots of mass of anode dissolved against percent of glycerol in presence of 1.2M nickel sulphate and in absence of nickel sulphate solution are illustrated in Figure 5. Plot of mass of metal deposited on cathode against glycerol percent is presented in Figure 6.

Similar experiment was conducted in 0.5N ammonium hydroxide and ammonium sulphate medium. The solution became deep blue due to the formation of nickel ammonia complex ion, $Ni(NH_3)_6^{++}$. There was some metal deposited on the cathode. Similar black color loose powder deposit was found on the anode.

Experiment was also conducted in 1.0N ammonium hydroxide saturated with boric acid. The solution became deep blue due to the formation of nickel ammonia complex ion, $Ni(NH_3)_6^{++}$. There was some metal deposited on the cathode. Similar black color loose powder deposit was found on the anode. It was observed in these experiments, that the black color loose powder formation was significantly less in presence of glycerol.

Auto-electrodeposition study of cobalt

All observations concerning for the auto-electrodeposition studies of nickel were similar as previously described except the color of compounds that were formed during the process. Black loose powder deposit was observed on the anode. The cobalt sulphate solution is pink in color. The cobalt hydroxide precipitate, $Co(OH)_2$, is pink. The cobalt

ammonia complex, $Co(NH_3)_6^{++}$, formed in ammonium hydroxide and ammonium sulphate medium is in dark rose-red color.

Figure 7 Electrodissolution of cobalt in presence and in absence of $CoSO_4$ in boric acid and different glycerol percent

Figure 8 Electrowinning of cobolt in different percent of glycerol
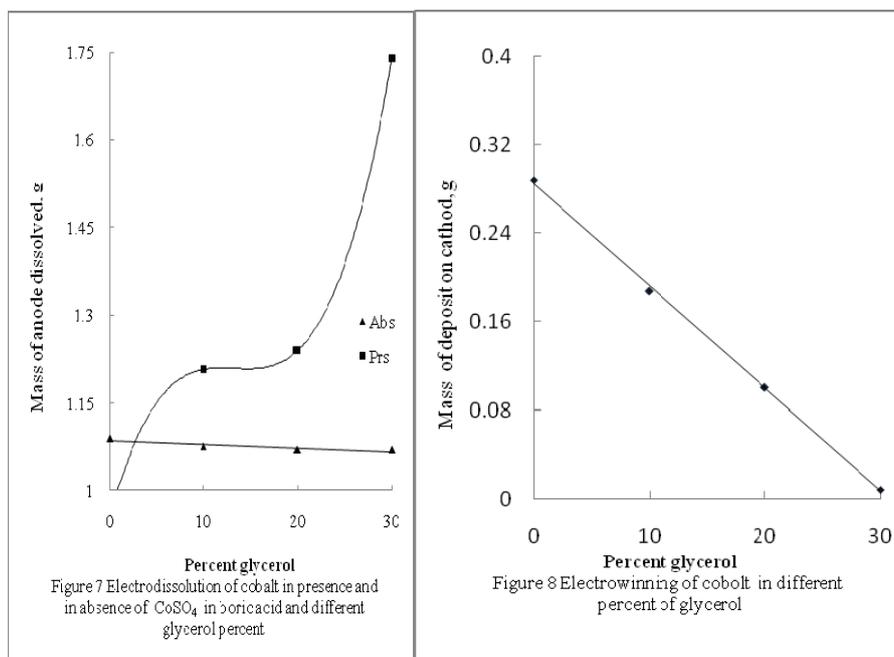
    Plots of mass of anode dissolved against percent of glycerol in presence of 1.2M cobalt sulphate and in absence of cobalt sulphate solution are shown in Figure 7. Plot of mass of metal deposited on cathode against glycerol percent is presented in Figure 8.

Mechanism of electrodissolution and electrowinning processes

Sulphuric acid medium
    When current is applied to the cell, 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 sulphuric acid and forms corresponding metal sulphate. M stands for copper or cadmium.
    The electrochemical dissolution of anode:

$$2H_2O \leftrightarrows 2H^+ + 2OH^- \tag{1}$$

$$M+2OH^-=M(OH)_2+2e \tag{2}$$

$$2H^++2e=H_2 \tag{3}$$

$$M(OH)_2+ H_2SO_4 = MSO_4 + 2H_2O \tag{4}$$

The net reaction occurring at anode is:
$$M+H_2SO_4=MSO_4+H_2 \tag{5}$$

The dissolution of anode is due to electrocatalytic effect.

Electrowinning occurs at cathode. The metal sulphate solution dissociates. Each metal ion takes two electrons from two hydroxyl ions and deposit on the cathode as:

$$2H_2O \leftrightarrows 2H+ + 2OH^- \tag{6}$$

$$MSO_4 = M^{++} + SO_4^{--} \tag{7}$$

$$M^{++} + 2OH-- = M + 2OH \tag{8}$$

$$2OH= O_2 + H_2 \tag{9}$$

$$2H+ + SO_4^{--} = H_2SO_4 \tag{10}$$
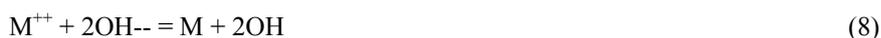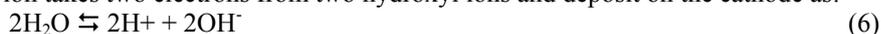
The net reaction taking place at cathode is:

$$MSO_4 + 2H_2O = M + H_2SO_4 + O_2 + H_2 \tag{11}$$

One hydrogen molecule is removed from acid according to eq. 3. This may be considered nearly equivalent to one water molecule. Two water molecules are removed according to eq. 9. Thus, effectively three molecules of water are lost during the electrodeposition. This suggested mechanism is based on the calculation of total water loss which is three molecules. 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 sulphuric acid is required. This is the reason that this process is called as auto-electrodeposition.

It is observed that nickel and cobalt dissolve in sulphuric acid and corresponding metal salts form. However, there is no metal deposition on the cathode.

Boric acid medium

0.05N sulphuric acid and glycerol solution is prepared. This solution is saturated with boric acid and clear solution is placed in the electrolytic cell. M stands for nickel or cobalt.

The electrochemical dissolution of anode occurs as follows:

Boric acid does not dissociate in aqueous solution as a Brønsted acid, but it is a Lewis acid which interacts with water molecules to form the tetrahydroxyborate ion, as confirmed by Raman spectroscopy. The dissociation constant of boric acid is $5.8x10^{-10}$ mol/l (pKa = 9.24). Therefore**,** the dissociation of boric acid may be written as:

$$B(OH)_3 + H_2O \leftrightarrows 2B(OH)_4^- + H^+ \tag{12}$$

The electrochemical dissolution of anode is as follows:

$$2B(OH)_3 + 2H_2O \leftrightarrows 2B(OH)_4^- + 2H^+ \tag{13}$$

$$M = M^{++} + 2e \tag{14}$$

$$M^{++} + 2B(OH)_4^- = MB_2(OH)_8 \tag{15}$$

$$H^+ + 2e = H_2 \tag{16}$$

The net reaction occurring at anode is:

$$M + 2B(OH)_3 + 2H_2O = MB_2(OH)_8 + H_2 \tag{17}$$
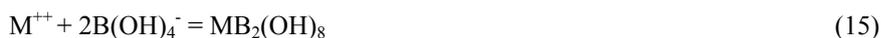
Electrowinning occurs at cathode. The metal borate solution dissociates. Each metal ion takes two electrons from two hydroxyl ions and deposit**s** on the cathode.

$$2H_2O \leftrightarrows 2H^+ + 2OH^- \tag{18}$$

$$MB_2(OH)_8 = M^{++} + 2B(OH)_4^- \tag{19}$$

$$M^{++} + 2OH^- = M + O_2 + H_2 \tag{20}$$

The net reaction occurring at cathode is:
$$MB_2(OH)_8 + 2H_2O = M + O_2 + H_2 + 2B(OH)_4^- + 2H^+ \tag{21}$$
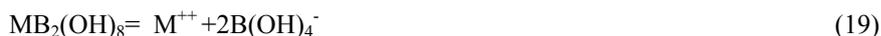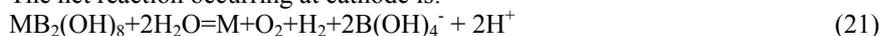
When one gram atom of metal is dissolved, two gram moles of water are lost from the solution, eq. 13. One gram mole of hydrogen is also lost, eq. 16. When one gram atom of metal is deposited, two gram moles of water are lost from the solution**,** eq. 18. Nearly, five g moles of water are lost from solution during the electrodeposition process. This mechanism is suggested according to the fact that approximate calculation for total water loss is five moles. This water loss is neither due to electrolysis of water nor is 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 boric acid is a weak electrolyte.

Ammonium hydroxide medium

1.0M ammonia and 0.5M ammonium sulphate solution is placed in electrolyte cell for copper and cadmium auto electrodeposition studies. In case of nickel and cobalt studies, 1.0M ammonia solution saturated with boric acid is used. The corresponding electrode is placed in the solution and 0.5A current is applied to the cell. M stands for copper or cadmium or nickel or cobalt and n is coordination number of the metal. The following reactions occur in ammonium hydroxide and ammonium sulphate solution.

The electrochemical dissolution of anode is as follows:
$$M = M^{++} + 2e \tag{22}$$
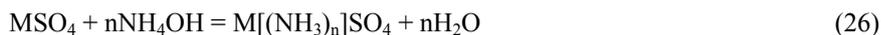
$$2NH_4OH + M^{++} = M(OH)_2 + 2NH_4^+ \tag{23}$$

$$2NH_4^+ + 2H_2O + 2e = 2NH_4OH + H_2 \tag{24}$$

$$(NH_4)_2SO_4 + M(OH)_2 = MSO_4 + 2NH_4OH \tag{25}$$

$$MSO_4 + nNH_4OH = M[(NH_3)_n]SO_4 + nH_2O \tag{26}$$

The complex molecule dissociates as:
$$M[(NH_3)_n]SO_4 = M[(NH_3)_n]^{++} + SO_4^{--} \tag{27}$$

The net reaction occurring at anode is:

$$M + (NH_4)_2SO_4 + nNH_4OH = M[(NH_3)_n]^{++} + SO_4^{--} + (n-2)H_2O \tag{28}$$

Electrowinning occurs at cathode:

$$2NH_4OH + M[(NH_3)_n]^{++} = M + 2NH_4^+ + nNH_3 + O_2 + H_2 \tag{29}$$

$$2NH_4^+ + SO_4^{--} = (NH_4)_2SO_4 \tag{30}$$

$$nNH_3 + nH_2O = nNH_4OH \tag{31}$$

The net reaction occurring at cathode is:

$$M[(NH_3)_n]^{++} + SO_4^{--} + nH_2O = M + (NH_4)_2SO_4 + (n-2)NH_4OH + O_2 + H_2 \tag{32}$$
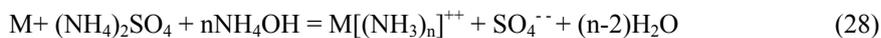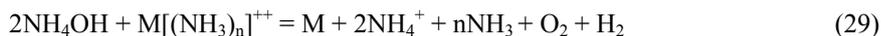
In ammonium hydroxide and ammonium borate medium only electrodeposition of nickel and cobalt is studied.

The electrochemical dissolution of anode is as follows:
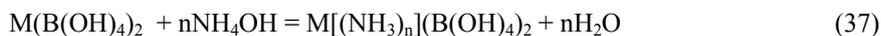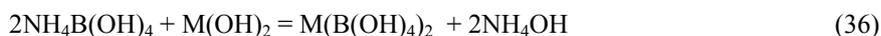
$$M = M^{++} + 2e \tag{33}$$

$$2NH_4OH + M^{++} = M(OH)_2 + 2NH_4^+ \tag{34}$$

$$2NH_4^+ + 2H_2O + 2e = 2NH_4OH + H_2 \tag{35}$$

$$2NH_4B(OH)_4 + M(OH)_2 = M(B(OH)_4)_2 + 2NH_4OH \tag{36}$$

$$M(B(OH)_4)_2 + nNH_4OH = M[(NH_3)_n](B(OH)_4)_2 + nH_2O \tag{37}$$

The complex molecule dissociates as:

$$M[(NH_3)_n](B(OH)_4)_2 = M[(NH_3)_n]^{++} + B(OH)_4^- \tag{38}$$

The net reaction occurring at anode is:

$$M + 2NH_4B(OH)_4 + nNH_4OH = M[(NH_3)_n]^{++} + 2B(OH)_4^- + (n-2)H_2O \tag{39}$$

Electrowinning occurs at cathode.

$$2NH_4OH + M[(NH_3)_n]^{++} = M + 2NH_4^+ + nNH_3 + O_2 + H_2 \tag{40}$$

$$2NH_4^+ + 2B(OH)_4^- = 2NH_4B(OH)_4 \tag{41}$$

$$nNH_3 + nH_2O = nNH_4OH \tag{42}$$

The net reaction taking place at anode:

$$M[(NH_3)_n]^{++} + 2B(OH)_4^- + nH_2O = M + 2NH_4B(OH)_4 + (n-2)NH_4OH + O_2 + H_2$$

$$\tag{43}$$
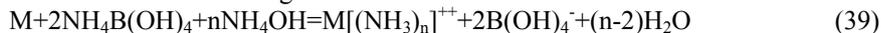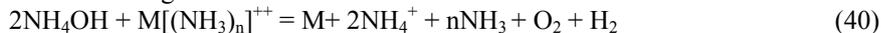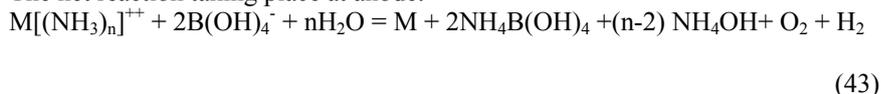
If sufficient ammonia is not present, the metal ions precipitate as metal hydroxide. If the solution temperature is decreased to the temperature at which solution is saturated with boric acid then boric acid precipitates out.

Threshold current for electrodissolution of anode

It appears that a minimum current must be applied to electrolytic cell to initiate the electrodissolution of anode. In case of copper, 0.02A (0.81-0.82V) and 0.01A (0.72-0.74V) current must be applied to initiate electrodissolution processes of anode, when the sulphuric acid concentration is 0.5N and 1N, respectively. Cadmium reacts slowly with acid. The applied current enhances the electrodissolution of anode. Therefore, the maximum current is utilized for electrowinning process. When the acid concentration is 0.5N, 0.005A (0.1V) current accelerates this process. Threshold current required for electrodissolution of anode of nickel is 0.03A (0.48-0.47V) and 0.02A (0.35-0.34V) when the sulphuric acid concentration is 0.5 and 1N, respectively. For 0.05N sulphuric acid solution saturated with boric acid, 0.03A current is required to initiate the electrodissolution of nickel anode. The similar conditions are applicable for electrodissolution of cobalt anode. Minimum current required for electrodissolution of cobalt anode is 0.01A (0.33-0.34) and 0.005A (0.22-.23) when the sulphuric acid concentration is 0.5N and 1N, respectively.

Percent of faraday distribution for the 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 it may be ignored. The percent of Faraday used for electrodissolution (PFD) is calculated from the number of grams of anode dissolved:

$$PFD = (It/wf) \times 100$$

where I, t, and w are amount of current passing through the solution in amperes, time of current passed through the solution in seconds and equivalent mass of the metal, respectively. The percent of Faraday used for electrowinning (PFW) of the metal is calculated from the number of grams of metal deposited on cathode:

$$PFW = (It/wf) \times 100$$

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

$$PFE = 100 - PFW$$

The data of percent on Faraday distribution for copper and cadmium deposition at different current and percent of glycerol were presented in Table 1 and nickel and cobalt in Table 2. 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 electrodissolution does not require much current. Also amount of current used for electrodissolution is small as evident from the studies of threshold current for electrodissolution of anode. The glycerol oxidation is explained in the previous part of this chapter and it may be neglected. Therefore, current is required only for electrowinning (PFW) and electrolysis of water (PFE).

Table 1. Percent Faraday distribution for copper and cadmium for various processes at different current and percent of glycerol.

C_g	Current	Copper			Cadmium		
	(A)	PFD	PFW	PFE	PFD	PFW	PFE
0	0.5	99.1	49.7	50.3	107.7	89.1	10.9
5	0.5	98.9	49.2	50.8	105.4	85.9	14.1
10	0.5	98.8	49.1	50.9	102.8	88.4	11.6
15	0.5	98.6	47.0	53.0	100.7	78.3	21.3
20	0.5	98.0	42.7	57.3	98.3	74.5	25.5
0	1.0	101.6	65.0	35.0	103.0	90.0	10.0
5	1.0	101.2	63.9	37.1	101.4	87.6	12.4
10	1.0	100.2	59.5	41.5	99.4	85.5	14.5
15	1.0	95.6	50.0	50.0	98.4	82.4	17.6
20	1.0	97.5	49.4	51.6	97.0	96.6	20.4

Table 2. Percent Faraday distribution for nickel and cobalt for various processes at different current and percent of glycerol.

C_g	Current	Nickel			Cobalt		
	(A)	PFD	PFW	PFE	PFD	PFW	PFE
0	0.5	43.4	7.7	92.3	62.8	12.9	87.1
10	0.5	40.6	17.2	82.9	57.5	8.5	91.5
20	0.5	39.1	15.4	85.1	55.6	4.5	95.5
30	0.5	39.1	0.1	99.9	49	0.01	99.9

Results and Discussion

The electrodissolution of anode metal by electrocatalytic effect is very common phenomena. First author observed this effect in several incidents In the electrowinning of copper sulphate solution in sulphuric acid and 1,4-dioxane medium [6], iron plate was used as anode. After completion of the experiment, the electrolytic solution was contaminated with iron salts. Similarly, gold plate was used as anode in the electrowinning of copper sulphate solution in sulphuric acid and glycerol medium. It was observed that the gold plate not only lost some mass, but also there was reddish-brown coating on the plate. Acidified water was electrolyzed between two plates of aluminum. A black loose coating was noticed on anode. Prolonged use of inert metal like platinum also looses a very little mass and surface becomes coarse.

Similar black loose powder was observed in case of iron and aluminum during electrodissolution in 0.5N sulphuric acid medium. When graphite was used as anode, the graphite was corroded and black particles were settled at the bottom of the cell.

In 1875, Kohlrasuch [8] coated the platinum electrodes with a layer finely divided platinum black by electroplating technique and these are called platinized platinum electrodes which are used in the conductance measurements. The large surface area of the finely divided platinum appears to catalyze the reunion of hydrogen and oxygen which tend to be liberated by the successive pulses of the alternative current. The black loose coating observed on these plates may be finely divided-

adherent metal. These are very minute particles with free valences. Within a short time they form strong metallic bond with parent metal and become part of the metal. As the size of metal powder decreases, its color also changes. Most of metal powders become black as they reach nano state.

The electrodissolution of metal is due to electrocatalytic effect. The electrodissolution requires very small quantity of current as evident from the threshold current studies. This is a spontaneous process and is very similar to corrosion of metals. Thus, it may be also called as electrolytic corrosion. This type of black powder was not observed when the solution contained metal ions. The electrolytic cell was filled with 2N sulphuric acid and copper electrodes were placed and two amperes of current was passed for ten minutes. The anode was removed and examined. There was black coating on it. This black coating on anode was removed and cleaned. The plate was placed in the same solution and current was passed for twenty minutes. There was no black deposit observed on the plate. When the passage of current was continued for more than forty five minutes, without removing and cleaning the anode, black coating on the anode breaks and falls in the solution. Therefore, it appears that some metal ions are needed to avoid the formation of black coating. These metal ions catalyze the faster formation of the metal hydroxide, without allowing metal to settle back on the anode. This fact may be realized from the plots showing that in the number of cases the electrodissolution of anode in presence of metal ions is faster than in absence of metal ions.

The present electrolytic cell may be considered as thermodynamically reversible concentration cell. In a concentration cell the electrical energy arises due to the transferee of material from one concentration to the other. The chemical reaction occurring in the cell is exactly reversible when electromotive force (EMF) is applied to the cell. Here, metal ion dissolve at anode and deposit on cathode. The OH ions consumed at anode are released at cathode. A large volume of water is lost during electrodissolution and electrowinning process. This volume loss is not due to electrolysis of water. As per the calculations, the number of Faradays required for electrolysis of water lies in between 0.6 to 1.0. The number of Faradays passed through solution in three hours is 0.056. The formation of metal hydroxide in acid and ammonia medium is very important observation. To form metal ions, some anion should be present. In present case sulphate ions and borate ions are the anions. During the elecrtowinning and electrodeposition studies, there is large amount of increase in the acid concentration. Keeping all these facts in mind, the above electrochemical mechanisms are presented for deferent media.

The conditions for auto-electrodeposition and electrowinning are always the same. The electrowinning occurs only when metal ions take electrons from hydroxyl ions to form metal atoms which deposit on the cathode. Due to the presence of glycerol in solution, ionic environment in the solution decreases. Hence, the rate of electrodissolution and electrowinning processes decreases. Alternatively, the organic acids formed due to oxidation of glycerol react with the metal hydroxide and form corresponding organic metal salts. This salt may also slowly undergo electrowinning process.

The formation of black deposit on the anode decreases as concentration of metal ion formation increases in the solution. If the metal ion is present initially in the solution no black deposit is found on the anode. This may be due to catalytic action of metal ion

which increases the rate of reaction between positively charged metal anode with OH ion.

Conclusions

Hydroxyl ions play a major role in electrodissolution and electrowinning of metals. The black powder is found on all metal anodes. This powder may be nano in nature. The present study indicates that without metal ions the electrodeposition can be carried out.

References

[1] S.G.Viswanath ,Manish.M.Jachak, Metall. Mater. Eng. 19 (2013) 119-135.
[2] S.G.Viswanath ,Manish.M.Jachak, ibid., 19 (2013)137-153.
[3] S.G.Viswanath ,Manish.M.Jachak, ibid., 19(3) (2013) 233-238.
[4] S.G.Viswanath ,Manish.M.Jachak, J.Metall. Mater.Sci. 55(3) (2013).
[5] Samuel Glasstone, "An Introduction to Electro Chemistry", Tenth Print, An East-West Edition. Affiliated East-West Press Private Limited, New Delhi and Madras, p. 491-93.
[6] C.N Wadasker, Dissertation submitted for Ph.D., RTM Nagpur University, Nagpur ,India , Oct 2008, "Preparation, study and its characterization of some metal powders by electrolytic method in aqueous medium in presence of organic additive 1,4-dioxane". (Supervised by S.G.Viswanath)
[7] Samuel Glasstone, "An Introduction to Electro Chemistry", Tenth Print, An East-West Edition. Affiliated East-West Press Private Limited, New Delhi and Madras, p. 35.