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Experimental electrolysis under high voltage conditions

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Abstract

The relation V=IR holds good for electrolysis i.e. if voltage is increased current will increase. High current means more charge per unit time and hence results in higher yield. A higher potential difference will supply more energy to bring about electrode reactions. The general potential used for electrolysis is 6V. High voltage in the range of 100V can bring about increase in both current which will increase yield as well the tendency of ions to undergo redox reactions. But the resistance of a strong electrolyte may be as low as .1Ω hence the current may tend to become uncontrollable. This may lead to heavy sparking and also lead to explosions. Domestic supply at 240V-50Hz converted to 230V D.C using a bridge rectifier circuit. This supply has 'high energy'. When suitably controlled and the ripple reduced this can yield useful products because in this case both voltage as well as current is very high. The arrangement is simple, cheap and easy to control. A study of electrolysis of various solutions under high voltage conditions as well as low voltage conditions was carried out and a comparison was drawn based on observations.

Keywords: Electrolysis; Electric field; Anode; Cathode; Oxygen

Introduction

Electrolysis a very useful industrial process depends on both voltage and current. Considering Faraday's first law of electrolysis "*The amount of any substance deposited or liberated at any electrode is directly proportional to the quantity of electricity passed through the electrolytic solution*" a high current is necessary to get a higher yield at a given length of time. This may be expressed as $W \infty Q$. Since $Q=It$, $W \infty I$. So ultimately $W=Zit$. At a fixed value of resistance $I \infty V$. So it is easily concluded that the applied voltage becomes a decisive factor.

For electrolysis the power supply is a dc source at a low voltage. The power required for electro deposition is usually very small between 100-200A at 10-12V and can be obtained from a motor generator set consisting of a standard induction motor driving a heavy current low voltage D.C generator. The generator is preferably separately excited.

Supplies in the range of 6V are used. Wall current is strictly prohibited because of the primary reasons:-

A. Wall current is A.C and not D.C.
B. Even if additional components like rectifiers, the current as well as the voltage may reach dangerously high values which may prove fatal.

On the other hand as voltage is increased anode becomes more positive w.r.t cathode. Owing to the large potential ions which are more difficult to reduce may get reduced at cathode. Also more difficult compounds may get oxidized due to similar reasons. Under high voltage conditions some cumulative processes may occur in the following steps:-

Step 1: Initially high voltage causes high current.

Step 2: The high current causes temperature rise $H=I^2Rt$. The temperature rise is very rapid.

Step 3: Since the resistance of an electrolyte falls with increase in temperature, the current further increases.

Step 4: The increased current cause's further heating and the process goes on.

Hence the products obtained under high voltage conditions *should* vary from those obtained under low voltage conditions. The heat produced can favor some exothermic side reactions.

But the most interesting part is how to tame high voltage (e.g. domestic supply at 230V A.C)? The answer is simple. We need to convert A.C to D.C using a diode bridge rectifier. Then we must feed this voltage to the solution with an inductor and a variable resistance in series. The inductor smoothes the ripple while the resistor controls current.

Various samples were tested using this apparatus (refer to figure). It was seen that in a very short time a large amount of products were obtained. An average time span of about 15 minutes was enough to give satisfactory yield.

The heat generated in the solution depends the resistance offered by it. Strong electrolytes offer very low resistance. Hence maximum voltage drop occurs across the series resistor whereas minimum voltage drop occurs across the solution. Consequently heating and hence temperature rise is minimal. Such a behavior is shown by concentrated NaCl solution, $Ca(NO_3)_2$ solution e.t.c. On the other hand weak electrolytes offer high resistance and cause major portion of voltage drop across them. As a result temperature rises very quickly. Neutral solutions of potassium dichromate, potassium permanganate oxalic acid and acetic acid fall in this category. In case of strong electrolytes as maximum heat is developed across the series resistor, a large ohmic loss occurs. Nevertheless the yield is very fast. Experimentally when voltage across a solution becomes 60V its temperature rises very rapidly. To avoid this the solution must be kept cool by using a water bath.

If it is required to increase the voltage across the solution further, a capacitor should be connected in parallel across the rectifier output. But this is unnecessary under most circumstances.

Apparatus and chemicals required:

a. Apparatus:

1. 240V-50Hz supply lines
2. Copper wire 1.5mm^2
3. Resistance type fan regulator
4. Fluorescent lamp choke
5. Analog voltmeters (Range 0-300V)
6. 625Ω resistance
7. Step down transformer capable of supplying 10±.5V on L.V side
8. 1N407 diodes

b. Chemicals and reagents

1. NaCl
2. KCl
3. NaHSO4.H2O
4. KI
5. Ca(NO3)2.4H2O
6. NiSO4.6-7H2O
7. CuCl2.2H2O
8. KMnO4
9. K2Cr2O7
10. Isopropyl alcohol
11. CH3COOH (40% solution)
12. HCl
13. HNO3(1N solution)
14. SnCl2.2H2O

Experimental diagram

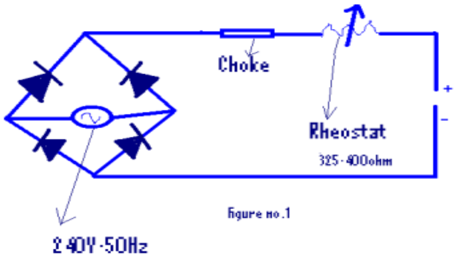

figure no.1

Experimental

Referring to the electroplating of copper, for which a solution is made by dissolving 150-200g $CuSO_4$, 25-37g H_2SO_4 per 1000cc. solution, the concentration of electrolyte in the solution is very high, it is seen that about 17.5g of electrolyte should be dissolved per 100g of solution (we have not considered molar concentration). But as the aim of this experiment is neither electroplating nor ay other related industrial process, the concentration is not so high. Here maximum mass of electrolyte dissolved per 100g solution is only about 5g. So the conductivity is not so high as the one encountered in an industrial process. Instead of referring to standard charts and curves, the resistance of the solutions was directly measured. This was done to determine the practical resistance offered by the solutions under the experimental conditions. For measurement multimeter was not used because the resistance measured by it keeps on varying. Secondly the battery powering the instrument may be harmed.

In this case 2 clean copper electrodes each of area 1.5sq.mm. and length of 1.5cm. were placed 2cm apart in a 100ml. solution. A series resistance of 625Ω was used for current control as well as resistance determination by comparison of voltage drops. Two voltmeters were used, one across the standard resistor and the other across the electrolyte. Here V_1=Voltage drop across the 625Ωresistor, V_2=Voltage drop across the electrolyte, R_1=625Ω and R_2=Resistance of the electrolyte.

Solution	**V_1**	**V_2**	**$R_2=(V_2/V_1)*R_1$**
NaCl+CH3COOH (10drops)	210V	10V	29.76Ω
KI+CH3COOH (10drops)	175V	20V	71.42Ω
K2Cr2O7+KCl+CH3COOH (10drops)	210V	10V	29.76Ω
NiSO4+CH3COOH (10drops)	190V	10V	32.9Ω
NaHSO4+CH3COOH (10drops)	210V	10V	29.76Ω
10drops HNO3+10 drops isopropanol	100V	110V	687.5Ω
SnCl2+10drops dil.HNO3	210V	10V	29.76Ω
Ca(NO3)2	210V	10V	29.76Ω
KMnO4+KCl+H+	210V	10V	29.76Ω
CuCl2+HCl	215V	5V	14.53Ω

After determining the resistances offered by the solutions each one were electrolyzed using copper electrodes using the circuits shown above. From the electrical point of view a transformer has a good regulation so the voltage across the solution in each case was 10.5V and was independent of the resistance offered by the solution. Whereas in figure b the voltage` across the solution was solely dependent on the resistance and voltage varied inversely as the resistance. Also the voltage did not remain constant throughout the process as will be described later.

In order to determine speed with which the anode is corroded a solution was prepared by dissolving 3ml. 35% HCl 20drops HNO3 and 5g NaCl in 100ml.water. The solution offered a resistance ≈20Ω. This solution was electrolyzed using copper electrodes of 1.5sq.mm. Crossectional area and length 2cm kept 1.5cm apart. It was seen that after 11minutes and 20seconds the entire anode corroded.

Observations

The series resistance as shown in figure had a value of 350Ω while the d.c resistance offered by the choke was 60Ω. The combined resistance connected in series with the solution was 410±5Ω which was much higher as compared to the resistance offered by the electrolytes used except for the solution of isopropyl alcohol and nitric acid. Now in a series connection as the same magnitude of current flows through the entire circuit. The voltage drop across any element is given by V=IR where R=Resistance of that element. So maximum voltage dropped across the series resistor while only a small portion was developed across the electrolyte. But this was noticed at the beginning i.e. just after closing the switch. But as the corrosion of the anode occurs its area decreases the resistance offered by the column increases. So the voltage drop across the solution generally increases with time. Finally when the anode totally corrodes the circuit becomes open circuited & under this condition I≈0. So almost the entire voltage drop occurs across the solution. Only a small leakage current in the range of μA flows which need not be taken in to account under practical conditions. The table below records the observations made using the circuit depicted in figure 1 and under influence of high voltage and hence under high electric field:—

Solution used	Observations
NaCl+10drops acetic acid(40%)	At the start solution voltage is 7.5V. As the anode corrodes this value increases. Highest potential of 40V was recorded. When the temperature of the soln. increases by 15-20 ˚C, bubbles are noticed at anode. Insoluble greenish yellow mass is formed which after being allowed to settle for 24 hours, changes to light green ppt. The precipitate dissolves in HCl giving characteristic blue color of Cu^{2+} solution
KI+10drops acetic acid(40%)	At the start soln. voltage is 100V which remains steady for the 1st 4 minutes. The soln. gradually turns yellow. At the 5th minute voltage drops to 80V then 70V & finally 60V was recorded. The solution turned bright yellow and only a small pale blue scummy mass was noticed. Towards the end bubbles were observed at anode. After 1 day the yellow color fades and a bright green ppt. developed which dissolves in HCl.
NiSO4+10drops acetic acid(40%)	At start soln. voltage was 40V which decreased to30V after 4 minutes. Green scummy mass was obtained. At the end voltage across the solution dropped to 20V. The green mass is soluble in HCl.
NaHSO4+10drops acetic acid (40%)	Voltage across the solution did not exceed 10V during the entire duration. A black brown mass was observed at cathode which had sufficient amount of conductivity. The solution remained clear and had a characteristic color of Cu^{2+}.
K2Cr2O7+KCL+10drops acetic acid (40%)	Initially soln. voltage was 8-10V.At the 3rd minute the potential started rising. When it became 20V bubbles were noticed at anode. At t=4minutes the voltage became 40V and remained constant thereafter. The solution became translucent due to formation of insoluble mass which dissolves in HCl.
CuCl2+HCl+10drops acetic acid(40%)	Initially soln. voltage was 7-8V. Right from then voltage started increasing. At t=3minutes potential became 20V and remained constant thereafter. Bubbles were observed at both electrodes during the entire process. A dark brown mass formed at cathode and a strange hissing sound was heard during the entire duration.
Ca(NO3)2+10drops acetic acid (40%)	Initial voltage of 10V was recorded which kept on rising very rapidly. At t=20s it becomes 20V then 30V and within a minute became 100V. Greenish blue mass formed at anode and bubbles were observed at cathode. Red sparks are seen at cathode which resemble flame test of Ca^{2+} ions. Sparking starts as soon as soln. voltage becomes 100V
SnCl2+10drops dil. HNO3	At start potential was 15V and dropped to 10V and remained constant thereafter. A large metallic mass was formed at the cathode
KMnO4+NaCl+H+	Initial voltage of 10V was recorded which remained constant throughout the process. Brown mass floats on top. A slight blue mass was visible at cathode. The brown mass dissolved in HCl.
10drops isopropanol+10drops HNO3	Initial voltage of 20V was recorded at t=0. At t=45s voltage rises to 10V then to 110V. Pale blue floating mass is observed. At t=7minutes voltage drops to 100V. Bubbles were observed at both electrodes.

To compare the characteristics of the products obtained under high voltage conditions to those obtained under low voltage conditions all of the above solutions were electrolyzed separately at low voltage using a step down transformer and a bridge rectifier set. The observations are given under:—

Solution used	Observations
NaCl+10drops acetic acid(40%)	NaCl increases the conductivity of the electrolyte. Almost clear blue solution having characteristic color of Cu2+. After sometime pale blue insoluble mass is formed which resembles freshly prepared $Cu(OH)_2$.
KI+10drops acetic acid(40%)	Yellow substance was observed to form at anode which dissolves instantly turning the solution yellow. Bubbles observed at cathode. A pale blue mass is also visible owing to side reactions. On allowing to remain still for a day or more the yellow color gradually fades.
$NiSO_4$+10drops acetic acid(40%)	Within here minutes pale blue mass starts floating. The solution does not have a very good conductivity. The color of the ppt. is indistinguishable due to green color of the solution itself.
$NaHSO_4$+10drops acetic acid (40%)	A clear blue solution having characteristic color of Cu2+ ions. Large mass of blackish brown substance obtained at cathode. The mass has a good amount of conductivity.
$K_2Cr_2O_7$+KCL+10drops acetic acid (40%)	KCl was added to improve conductivity. A scummy mass was obtained which turned the solution unclear. The color was undistinguishable due to the orange color of the dichromate solution. The scummy mass too appears orange.
$CuCl_2$+HCl+10drops acetic acid(40%)	HCl was added to improve conductivity. Brown and bright blue mass appears at the cathode which later changes to greenish yellow and is insoluble.
$Ca(NO_3)_2$+10drops acetic acid (40%)	Blue colored solution along with bright blue ppt. was obtained. Bubbles appear at cathode. The blue ppt. has a tendency of sticking to cathode.
$SnCl_2$+10drops dil. HNO3	Pale blue-green aoln. Obtained. White ppt. settles to bottom. Bubbles evolved at cathode.
$KMnO_4$+NaCl+H^+	Solution changes colo9r and finally turns colorless. A gas which smells like chlorine. The anode slowly dissolves in the solution.
10drops isopropanol+10drops HNO_3	Pale blue insoluble mass obtained along with bubbles at cathode. No bubble is visible at anode.

The standard electrode potentials have been mentioned under because it will help in the discussions part.

$Cu^{2+} + 2e^- \rightarrow Cu$ .36

$Cu^{2+} + 2e^- \rightarrow Cu^+$ .15

$I_2 + 2e^- \rightarrow 2I^-$ .54

$Ca^{2+} + 2e^- \rightarrow Ca$ -2.87

$K^+ + e^- \rightarrow K$ -2.93

$Na^+ + e^- \rightarrow Na$ -2.93

$Sn^{2+} + 2e^- \rightarrow Sn$ -.16

$Cr_2O_7^{2-} + 4H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$ 1.33

$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$ 1.49

$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$ 1.23

Impression of high voltage on electrolytic solutions produces visible effects. A low steady voltage (as the rectified voltage of a transformer) in the range of 10-12V can be applied continuously for a long time without significant temperature rise. In such a case the products are obtained in accordance with the electrode potentials. For e.g. A solution of NaCl acidified with acetic acid the ionization occurs as

$NaCl \rightarrow Na^+ + Cl^-$

$CH_3COOH \rightarrow H^+ + CH3COO^-$

$H2O \rightarrow H^+ + OH^-$

Both H^+ & Na^+ migrate to cathode but keeping in view the electrode potentials H2 is evolved according to the reaction $2H^+ + 2e^- \rightarrow H_2\uparrow$ which being insoluble escapes in to the air. At anode CH3COO- and OH- migrate but none of them is discharged. Cu ionizes as $Cu\text{-}2e\text{-}\rightarrow Cu^{2+}$ and combines with OH- to give pale blue Cu(OH)2. A small amount of $Cu(OH)_2$ depending on its own concentration, the concentration of acetic acid and the percentage ionization of acetic acid copper acetate is formed which dissolves in the solution imparting a blue color to the solution. After a certain concentration no more $Cu(OH)_2$ can dissolve (because acetic acid is weak acid) and it floats on top as a pale blue scummy mass.

Results and discussions

Impression of high voltage (and hence high gradient) brings about visible differences. A low steady voltage (as the rectified voltage from a transformer) in the range of 10-12V D.C can be applied for a long time. In such a case products are obtained keeping at per with the electrochemical series. A solution of NaCl in acetic acid ionizes as:—

$NaCl \rightarrow Na^+ + Cl^-$

$CH_3COOH \rightarrow CH_3COO^- + H^+$

$H_2O \rightarrow H^+ + OH^-$

Both H^+ and Na^+ migrate to cathode but keeping in view the electrode potentials H2 is evolved as per the reaction $2H^+ + 2e^- \rightarrow H_2\uparrow$. At anode OH- and CH_3COO- migrate but neither is oxidized. Cu being active ionizes to give Cu^{2+}which combines with OH^- to give pale blue $Cu(OH)_2$. A small amount of copper hydroxide depending on the concentration of the solution, the percentage ionization of acetic acid dissolves in the solution copper acetate is formed which dissolves in the solution. The reaction is a simple acid-base neutralization reaction and may be expressed as

$Cu(OH)_2 + 2CH_3COOH \rightarrow Cu(CH_3COO)_2 + 2H_2O$.

After reaching a certain concentration no more copper hydroxide is able to dissolve and hence floats on the surface as a scummy mass. When high voltage is applied due to low resistance of the NaCl solution initial voltage across the solution is very low and maximum voltage drop occurs across the series resistor. As the anode corrodes the resistance between the anode and cathode increases and potential drop increases to about 40V.Due to the more potential the ions get energized and side reactions start to occur. In this condition energy is sufficient to liberate O_2 from OH^-. The reaction may be given as $4OH^- - 4e^- \rightarrow 2H_2O + O_2\uparrow$. A greenish yellow ‘suspension’ is noticed which is the combined effect of these side reactions and the absorption of various wavelengths from the visible spectrum. But its discussion is beyond the scope of this paper.

KI ionizes to give K+ and I- ions. The solution has negative hydroxyl, iodide and acetate ions all of which migrate to anode and look to get oxidized. But only I- releases electrons to form molecular iodine I2. This being soluble in water dissolves readily imparting yellow color to the solution. A small amount of copper ionizes at anode to give Cu2+ ions which forms a slight pale blue mass. On application of high voltage the ions gain sufficient energy so as to liberate O2 at anode which comes from the oxidation of hydroxyl ions under application of high electric field.

NaHSO4 is an acid salt of H2SO4 and its solution is acidic. Its solution has high conductivity. So CuSO4 is formed which dissolves instantly. Due to the acidic nature and presence of dissolved Cu2+ the solution behaves just like the one used in electroplating of copper using acidified copper sulfate. Both Cu2+ and H+ migrate to cathode and both are reduced. Hence a blackish brown mass of copper is obtained at at cathode which has sufficient amount of conductivity.

Potassium dichromate is not a good electrolyte and neither is acetic acid a strong acid, so a mixture of KCl potassium dichromate and acetic acid behave like ordinary KCl solution and formation of Cu(OH)2 takes place which remains un dissolved.

$CuCl_2$ acidified with HCl and acetic acid behaves like acidified copper sulfate and liberates H_2 and copper at cathode. But under high voltage sufficient electric field exists for the liberation of O_2 at anode along with ionization of copper.

$Ca(NO_3)_2$ itself has a very good conductivity. Ca^{2+} is highly electropositive. Under high voltage conditions the reaction behaves similar as D.C arc welding. An arc appears at cathode and voltage across the solution increases gradually. This is due to the combined effect of:—

1. High initial electric field.
2. High electropositive nature of Ca^{2+}
3. Low radius of Ca^{2+}.
4. Easy excitation of Ca to Ca^{2+}.

The sparks are red due to the characteristic color of Ca^{2+}.

$KMnO_4$ is a very strong oxidizing agent and it has a tendency to oxidize HCl to Cl2 according to the reaction:-

$2KMnO_4 + 16HCl \rightarrow 2KCl + 2MnCl_2 + 5Cl_2\uparrow + 8H_2O$

When electrolyzed in a solution of NaCl a reaction occurs which oxidizes NaCl to $NaClO_3$ and a small amount of Cl_2 is also obtained. $KMnO_4$ first changes to MnO_2 and finally to $MnCl_2$. The oxidation state changes in steps from +7 to +6, then to +4 and finally to +2. This can be proved by carefully observing the color changes (from purple to dark red then to green then brown and finally colorless).

SnCl2 gives Sn deposit at cathode along with liberation of H2. The deposited tin particles appear as a blackish metallic mass. At anode copper ionizes to give its ions.

Isopropyl alcohol is a very poor electrolyte and this result in a very large voltage across the electrolyte. Due to high electric field O_2 is obtained at anode with H_2 at cathode. This is not observed at low voltage. In the later case H2 is obtained at cathode and pale blue $Cu(OH)_2$ is obtained at anode due to low field.

Conclusion

The important aspects and results have been concluded under:—

1. Electrolysis using rectified wall current (240V-50Hz) with a current limiting resistor is feasible and controllable.
2. Such a process provides a high potential gradient and hence high energy to the ions.
3. As the resistance of the electrolyte decreases the voltage across it drops greatly.
4. Owing to the fall in voltage with decrease in resistance the voltage across the electrolyte, the heat produced is less in strong electrolytes (calcium nitrate) as compared to weak electrolytes (oxalic acid).
5. Owing to the availability of high energy the reactions are very fast.
6. The high voltage gradient causes O2 liberation at the anode in most cases even in the presence of active electrodes like Copper, a phenomenon which is absent under low voltage conditions.

This method of electrolysis under high voltage gradient under controlled conditions can reduce expense in terms of expensive converters, batteries e.t.c. The only limitation is the energy loss in the external current limiting resistor. However this process can't be used in processes where high current density is required.

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References

Modern's abc of Chemistry By Dr. S.P Jauhar, Modern Publishers.