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ISSN (Online): 2455-7838
SJIF Impact Factor (2015): 3.476

EPRA International Journal of Research & Development (IJRD)

Volume:1, Issue:7, September 2016

Published By :
EPRA Journals

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SJIF Impact Factor: 3.476 **ISSN: 2455-7838(Online)**
EPRA International Journal of Research and Development (IJRD)
Volume: 1 | Issue : 7 | September | 2016

EXPERIMENTS ON ELECTROLYSIS USING A.C AT SUPPLY VOLTAGE (230V-50Hz)

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ABSTRACT

Electrolysis with direct current has numerous applications owing to the well defined polarity of D.C. But alternating current has almost no application. Due to the availability of A.C and numerous other reasons A.C could provide a good alternative in the field of electrolysis. A few solutions like nickel sulfate; copper chloride, lead acetate etc. show reactions on the application of alternating electric field between two active electrodes such as iron. Such reactions do not occur at all or occur very slowly in the absence of such a field. So alternating current may accelerate some specific reactions. As every electrolyte has negative temperature coefficient of resistance, the increased temperature results in passage of higher current thereby accelerating the reaction. However these reactions are highly selective in nature. Also the current through the solution has to be carefully and properly controlled. In this paper investigations using alternating current (at supply voltage and frequency) on electrolytic solutions have been outlined.

KEYWORDS: *Electrolysis; A.C; Cathode; Anode; Frequency; Voltage*

INTRODUCTION

The terms electrolysis and direct current often complement each other. Direct current can cause '*splitting up*' of a conducting solution (e.g. brine) in to its constituents and form new products. The reverse process is also feasible i.e. reaction between an electrolyte and an attackable electrode may result in the production of direct current. This very principle is used for the manufacture of batteries. The mentioned facts may be expounded using two simple examples:—

A. When D.C is passed through brine using copper electrodes, pale blue scummy mass is obtained at anode and hydrogen bubbles are observed at cathode. This is nothing but simple electrolysis phenomena (reactions are explained later).
B. In a lead acid battery dilute H_2SO_4 reacts with PbO_2(positive plate) and Pb (negative) plates to produce direct current.

The entire phenomenon of *electrolysis relies on the fixed polarity of D.C.* The sources of electrolysis are generally *low voltage and high current D.C sources* so as to pass a high amount of charge through the solution.

Now the general question which comes to our mind is that can alternating current be used for such applications? The question is justified due to the following merits of A.C:—

a. These days most of the supplies are A.C.
b. A.C can be easily transformed to achieve any voltage level using suitable transformers.
c. A.C voltage regulators are cheap and easily available.
d. It does not require bulky rectifier circuits and filters.
e. A.C can be easily generated using convenient alternators and can be easily transmitted to the load centre without incurring much power loss.

But the single demerit which out weighs all its merits in the field of electrolysis is associated with the basic definition of A.C, i.e. it has a definite frequency. The '*indefinite*' polarity of A.C does not allow the electrolysis process to have a well defined anode and cathode. So ion migration and discharge is theoretically not possible. *The ion's inertia does not allow it to get discharged because the moment an ion starts migrating to an electrode (say anode) its polarity changes*.

But not withstanding the above facts the solution still retains its conductivity. This allows passage of alternating current through a column of the solution just like current can pass through a piece of wire.

And now the question that haunts us is what are the effects of passing alternating current through an electrolyte? Surely enough the effects will differ from those seen on passage of D.C. This is illustrated by considering the passage of 230V-50Hz '*wall current*' through a solution of brine (common salt in water). The effects may be classified as:—

I. **Physical effects:** As soon as the circuit is closed a lot of sparking occurs at each electrode and the solution tends to spurt out. The temperature rise is very rapid. In a few minutes the solution reaches its boiling point.

II. **Chemical effects:** Theoretically there *should not be any chemical effect* as the current is alternating in nature. But practically many significant changes occur in the solution and thee depend on the choice of electrodes, the nature of the electrolyte which will be discussed later.

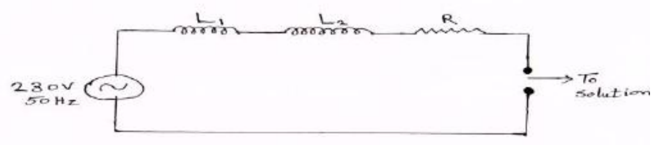
Thus the chemical effects are what we may refer to as '*highly selective*'. But when practiced with utmost care, A.C can accelerate a few chemical reactions and yield quick and useful products. In a way A.C can be thought to act as a '*catalyst***' to enhance the rate of certain reactions.

***By definition a catalyst is a chemical compound which alters the rate of chemical reaction by providing an alternate path for the reaction. Catalyst forms an unstable intermediate which dissociates in to products.*

MATERIALS AND REAGENTS REQUIRED

A. Domestic supply 230V-50Hz
B. Incandescent lamps rated 250V having power of 25W
C. Good quality iron, copper and solder (for electrodes)
D. H_2SO_4 (20% solution)
E. HNO_3 (20% solution)
F. HCl (10% solution)
G. $NiSO_4$
H. $KMnO_4$
I. $K_2Cr_2O_7$
J. $CuCl_2$
K. $Pb(CH_3COO)_2$
L. Choke of CFL (inductive type; either copper or aluminum)
M. Power factor meter

EXPERIMENTAL SETUP



CHEMICALS DESCRIPTION

Chemical formula	Mol. Weight (g/mol)	Solubility (g/100ml)	pK_a	pK_b
$NaHSO_4$	138.07	28.5	1.99	_
$NiSO_4.7H_2O$	280.86	77.5	4.5	_
$CuCl_2.2H_2O$	170.48	75.7	_	_
$PbCrO_4$	323.2	Negligible	_	_
$Pb(CH_3COO)_2.3H_2O$	379.33	69.5	_	_
$K_2Cr_2O_7$	294.185	4.9 (at 0˚C)	_	_
$KMnO_4$	158.034	6.4	_	_
$C_{10}H_{16}N_2O_8$	292.24	_	1.782	12.215
HCl	36.5	Miscible completely	-6.3	_
H_2SO_4	98.079	do	-3,1.99	_
HNO_3	63.01	do	-1.4	_

Experimental: The entire experiment was performed at standard domestic supply voltage of 230V-50Hz single phase A.C. If such a voltage is directly applied across an electrolyte severe sparks will be produced at either electrode which will cause:—

- Extreme heat
- Noise
- Vibration

All such effects will make the reaction go beyond control. So at first a control circuit is necessary. Hence the circuit shown in the figure was designed.

Here the two inductors prevent any fluctuation in current through the solution which could have adverse effects and the incandescent lamp acts as a current limiting resistor. It is true that the inductors result in poor power factor but it is not a matter of high importance in this experiment.

The D.C resistance of the choke was measured using a high precision and was 60±.1Ω.

The solutions were prepared and each solution measured 80ml. The electrode separation was kept fixed at 2.5cm. Electricity was separately passed through each of the solutions using the circuit mentioned above and the following table was tabulated:—

Solution	V_{L1}	V_{L2}	V_R	$V_{Soln.}$	Δt(˚C)	Observed P.F	Calculated P.F
$NaHSO_4$	47V	61.6V	190.7V	2.5V	1	.75	.782
$CuCl_2$	50.3V	65.7V	176.6V	8V	1	.73	.747
$NiSO_4$	50.8V	66.2V	175.8V	10.6V	1.7	.73	.764
Titriplex	44.5V	58.1V	148.2V	33.6V	5	.71	.736
HNO_3	51.2V	68.3V	181.8V	2.3V	1	.72	.745
HCl	51V	67.5V	185V	.8V	0	.73	.752
H_2SO_4	52V	67.8V	190.9V	.4V	0	.76	.7744
$Ba(OH)_2+PbCrO_4$	51.2V	66.3V	183.5V	10.8V	2	.76	.786
HNO_3+KMnO_4	51V	69V	182V	2.2V	1	.73	.746
$HNO_3+K_2Cr_2O_7$	52V	69.2V	180V	2.4V	1	.72	.738
$HCl+KMnO_4$	50V	68V	186V	.75V	0	.74	.756
$HCl+K_2Cr_2O_7$	51V	69V	187V	.75V	0	.74	.759
$H_2SO_4+KMnO_4$	51.5V	67.9V	191V	.35V	0	.76	.774
$H_2SO_4+K_2Cr_2O_7$	52V	67.7V	192V	.36V	0	.77	.778
Pure H_2O*	40V	52V	140V	45V	15	.7	.748

*Pure water was used as a comparison, to see how other electrolytes behave when compared to it.

Observations: The visual effects of each solution have been discussed separately.

$NaHSO_4$

As soon as current is switched on bubbles start coming out of both electrodes. Small amount of green mass sticks to the electrodes. The final solution turns faded green. No precipitate is observed. The heat generation is very small not sufficient to raise the solution temperature.

$CuCl_2.2H_2O$

No bubbles are noticed. Brown mass is deposited on the electrodes very quickly. Solution turns from pale blue to dull green (resembling freshly prepared $FeSO_4$). The temperature rises slightly.

$NiSO_4.6\text{-}7H_2O$

No bubbles are visible. Yellow mass collects at each electrode. Ultimately yellow precipitate is obtained and the solution fades in color. The solution temperature increases slightly.

Titriplex

Bubbles are observed at both electrodes. The solution first changes to pale green and finally to pale yellow. Clearly Fe^{2+} is being changed to Fe^{3+}. Due to high solution resistance the voltage drop across the solution is high and its temperature increases.

HNO_3

No bubble is observed at either electrode. The solution gradually turns yellow. Temperature rise is insignificant.

H_2SO_4

Dense bubbles are observed at both electrodes. The evolution of bubbles decreases with time. So color change is observed. No significant temperature rise is recorded.

HCl

Almost same observations as sulfuric acid are made.

$Pb(CH_3COO)_2$

Tiny bubbles are observed at either electrode. Glittering particles of Pb stick to the electrodes. The solution turns yellowish orange. A small amount of white precipitate settles at the bottom due to the hydrolysis of lead acetate. Significant temperature rise is recorded.

$PbCrO_4+Ba(OH)_2$

When electrolyzed using copper electrodes brick red precipitate of PbO_2 is obtained. The same observation is made using Fe electrodes.

$KMnO_4+HCl$

Dense bubbles are observed as soon as the circuit is switched on. The purple color of KMnO4 changes to red, then to green and finally gets decolorized. Due to the presence of HCl the resistance of the solution is very low and there is almost no temperature rise. The decolorized solution is stable and does not undergo further change of color.

$KMnO_4+H_2SO_4$

Same observations as that of HCl are made.

$KMnO_4+HNO_3$

The reaction is comparatively slower as compared to the above two. However ultimately the solution gets decolorized. On continuous passage of current the solution turns yellow. The voltage drop is slightly higher as compared to the above two solutions.

$K_2Cr_2O_7+HCl$

Bubbles are observed at both electrodes and the solution changes to green. The green color remains stable and does not change further. No temperature rise is observed.

$K_2Cr_2O_7+H_2SO_4$

Same observations as above are made.

$K_2Cr_2O_7+HNO_3$

Insoluble greenish brown mass is formed. The voltage drop is higher as compared to the above two solutions. The difference is undoubtedly *due to the lower conductivity of HNO_3, the highly oxidizing nature of NO_3^- ions.*

For pure water the voltage drop is high (as high as 40V) and as a result water evaporates quickly. The electrodes turn light green due to the formation of insoluble Fe^{2+} whose concentration is not very high.

In case of solder electrodes a 'double' reaction is visible due to the presence of both Pb and Sn in the alloy. Pb does not show much tendency of reactions except for when the temperature of the solution becomes high due to self heating ($H=I^2Rt$). So lead particles are visible as glittering particles at the surface of the solution and later sinks to the bottom. Sn shows a tendency to react with the solutions but Sn^{2+} and Sn^{4+} both is white. So white solutions are obtained. The solutions get hydrolyzed very quickly to give insoluble $Sn(OH)_2$ which floats as a scummy mass. Only in HCl solution the precipitate dissolves to give soluble $SnCl_2$.

Copper as is expected is most stable in +2 oxidation state. So it gives blue or bluish green solutions in most cases. However the reaction rates shown by copper electrodes are lower compared to Fe or solder.

RESULTS AND DISCUSSIONS

All the solutions *except H_2SO_4 and HCl are unreactive to iron*. HNO_3 has the tendency of rendering iron inert due to the formation of oxide coating. In any reaction a certain amount of energy however small is required. This energy may be in the form of heat ($2Pb_3O_4 \rightarrow 6PbO + O_2$), light (photosynthesis), sound ($C_2H_2 \rightarrow 2C+H_2$) etc. The reactions which occur at room temperature use thermal energy of the molecules. In this paper all the experiments have been performed with alternating current as the source of energy.

Though alternating in nature the electrodes become positive or negative for a fraction of a second. This time though very small is enough to cause ionization of a metal. The phenomenon becomes very clear if we study the electrolysis of sodium bisulfate using iron electrodes and alternating current at 50Hz. In the absence of field no visible reaction occurs. But when an alternating potential is of 2.5V (refer to table) is applied bubbles are observed. This is because Fe is rendered positive for a fraction of a second alternately. During this time Fe loses electrons to give Fe^{2+}. The bubbles observed at the electrodes are *bubbles of H_2 & O_2*. Their formation may be expounded as:–

- H_2 is formed *partly due to the acidic nature of $NaHSO_4$ and partly due to the electrolysis of water*. $Fe + 2H^+ \rightarrow Fe^{2+} + H_2\uparrow$ & $2H^+ + 2e^- \rightarrow H_2\uparrow$.
- O_2 is formed due to the electrolysis of water. $4OH^- - 4e^- \rightarrow 2H_2O + O_2\uparrow$

The same explanations hold for $CuCl_2$, $NiSO_4$ and titriplex.

In HNO_3 bubbles are not observed because normally it does not liberate H_2 from dilute acids *except for magnesium and manganese due to its oxidizing nature*. But the presence of electric field prevents Fe electrodes from becoming passive. So ultimately the solution will contain ferric nitrate i.e. $Fe(NO_3)_3$ turning the solution yellowish brown. As HNO_3 is *highly oxidizing*, even low concentration of the acid can provide *nascent oxygen* in the solution. This being highly reactive oxidizes iron to Fe_3O_4 and renders it passive. But on application of alternating potential between two iron electrodes the following reactions occur:—

$Fe - 3e- \rightarrow Fe^{3+}$

$Fe^{3+} + 3OH^- \rightarrow Fe(OH)_3$

$2H^+ + [O] \rightarrow H_2O$

$Fe(OH)_3 + 3HNO_3 \rightarrow Fe(NO_3)_3 + 3H_2O$

When it comes to HCl and H_2SO_4, alternating current increases the rate of the reaction. This is evident from the fact that as soon as electric field is applied the intensity of bubbles increases which is clearly visible to the naked eye. Again the rendering of the iron positive even for a minute amount of time is responsible for this. On application of D.C voltage from a battery, bubbles are still visible at both electrodes. But the solution slowly turns green due to the slow dissolution of Fe^{2+} at the anode. The anode only gets thinner and there is no corrosion of the cathode. This is due to the fact that the cathode is permanently negative and it shows no tendency of ionization. The liberation of H_2 may be attributed as $2H^+ + 2e^- \rightarrow H_2\uparrow$. This is strictly different from A.C.

Acidified solutions of $KMnO_4$ get decolorized very quickly on applying alternating potential between the electrodes with the liberation of a large volume of H_2 gas. In absence of electric field the reaction occurs very slowly. Potassium permanganate being a strong oxidizing agent has a tendency to react with concentrated HCl at elevated temperatures according to the reaction:—

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

At normal temperature and in presence of dilute acid (10% as used in this experiment) no reaction occurs and the purple color of MnO_4^- remains intact. Dilute sulfuric acid also has no effect on permanganate solution. Actually *$KMnO_4$ and H_2SO_4 both are strong oxidizing agents. Here sulfur is in the +6 oxidation state while Mn is in the +7 oxidation state. For a reaction to occur a reducing agent is highly necessary. In the presence of alternating current H_2 is liberated which is primarily in the form of nascent hydrogen and this causes decolorization of $KMnO_4$ to give a clear solution of $MnSO_4$.*

Acidified dichromate also behaves much like permanganate and develops green color due to the formation of Cr^{3+}. Normally the reaction that occurs between potassium dichromate and concentrated HCl on heating is given as:—

$2K_2Cr_2O_7 + 14HCl \rightarrow 2KCl + 2CrCl_3 + 3Cl_2 + 7H_2O$

But no reaction occurs between potassium dichromate and dilute HCl. On applying alternating field chlorine is still not liberated but the solution turns green due to the formation of $CrCl_3$. H_2 is formed instead of chlorine.

The voltage drop in case of titriplex and barium hydroxide solution along with $PbCrO_4$ is large owing to their high resistance. This causes temperature rise and hence evaporation of the solution. A very special phenomenon occurs when passing through a solution of lead chromate and barium hydroxide. It is known that *CrO_4^{2-} remain stable in alkaline media*. But even in the OH^- released from $Ba(OH)_2$, *PbO_2 is formed which is visible as a brick red layer at the bottom of the solution*. The power factor of the entire process lies in the range of .7 to .8.

It is observed that voltage drop across nitric acid solutions are comparatively higher as compared to other acids. Also the products formed as a result of electrolysis of HNO_3 solutions have a lower tendency to become soluble.

The currents in the separate experiments were all in the range of 50 to 80mA which implies that the current is very low when compared with the conventional electrolysis using D.C is considered.

All the electrolytes especially the weaker ones may be associated with a *small amount of capacitance*. When alternating current at 50Hz is passed the capacitive reactance ($X_C=1/2\pi fC$) may be quite large. This has the effect of diminishing the circuit current and also changing the phase between the voltage and the current. But experimentally it has been seen that it does not affect the nature of the chemical reaction. So for practical purposes the capacitance effect has been neglected in this paper. Also the observed power factor closely agrees with the calculated one. So the negligence of capacitance effect in the analysis is correct.

CONCLUSION

Normally supply current or '*wall current*' is not utilized under any circumstances for electrolysis because the continuously changing polarity of the electrodes prevents effective ionic discharge. But experiments show that *alternating current can either accelerate reaction rates or 'start' reactions*. But direct application of wall current across any solution is dangerous as it causes heavy currents and uncontrollable reaction rates. So a suitable apparatus or a 'control circuit' as we may call it must be designed. In this experiment such a control circuit was designed using *two chokes (inductors) in series with a 25W incandescent lamp*. However for experimental convenience under different conditions other components like resistors may be used. The important points have been summarized under:—

1. An electric potential (alternating) of 2-5V* between electrodes is enough to cause reaction in maximum cases.
2. *'Moderately reactive'* metals such as iron are more suitable for these experiments because their reactivity is not very high like Zn (to cause 'self reactions') nor very low like copper to cause no reaction at all.
3. For solutions like titriplex where the solution resistance is high, a water bath may be used or the wattage of the current controlling lamp has to be suitably decreased because temperature rise may cause side reactions.
4. The power factor is low due to the presence of inductors. But it is not of great importance until the power factor goes below .7.
5. This method is *extremely useful where fast manufacture of hydrogen is required*. Any suitable iron piece (need not be of high purity) may be used as electrodes in an acid solution (except HNO_3).
6. Most of the power loss occurs in the current limiting resistor. But as the resistor is of low wattage the power loss is not exorbitant.
7. The current in these experiments is low, typically less than 100mA.
8. While carrying out the experiment it is necessary to ensure that not only voltage across the solution has to be kept as low as possible (<1V for very strong electrolytes) the current through the solutions should be maintained at least above 65mA. This is generally not possible in step down transformers. So a control circuit is absolutely necessary which can minimize the voltage as well as maintain the current at a desired level.

**Applying 2-5VAC using a step down transformer may not cause expected reactions. This is because solution resistances being high, only a few mA current (<10mA) can pass through the solution. At high voltage (230V) basically the incandescent lamp draws the necessary current and the solution being in series with the lamp is subjected to the same amount of current. The difference is that while application of 2V directly across the solution (using transformer) allows only less than 10mA to pass through the solution, the circuit used in the experiment provides a large current of 80mA. So direct application of 2-5V A.C is not sufficient to cause reaction. This is different from D.C where this much voltage is enough to cause reactions.*

So overall the process is very cheap and easy to conduct. Since A.C is easily available it can be used to generate useful compounds & hasten reactions. Also the process is clean and safe.

Acknowledgements: I'd express my gratitude to Mr. P.B Nandi and Mrs. K. Nandi for financing and constantly encouraging this experiment.

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