

Experimental research on the behavior of electrolytes at high frequencies

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Abstract: Traditional electrolysis using direct current as a power source finds numerous applications. The electrodes having definite polarities make ionization/discharge possible. Generally, heavy currents at low voltages are used. Electrolysis using power frequency sinusoidal voltage can yield substantial products as has been proved experimentally. This relies on high voltages low currents of the order of mA. High frequency alternating currents of the order of several tens of kilohertz if harnessed carefully *should* be able to cause ionization/discharge as the case may be. This may pave the way for hydrogen production using suitable electrodes where current remains in the range of mA, unlike conventional electrolysis experiments. However, the low mobility of heavy ions may impose significant difficulties. This may be overcome using techniques such as *heterogeneous supply* and *auxiliary electrodes*. The choice of the materials used for the electrodes is very important. In this paper, electrolysis techniques using high-frequency voltage, waves have been expounded.

Keywords: Electrolysis; Electrolyte; Auxiliary electrode; Conductivity; Mobility.

Introduction: 'Electrolysis' is the *splitting up* of a conducting chemical compound in to its constituents on the passage of electricity through it using suitable electrodes (*preferably inert*). The conducting state may be reached either by dissolving the compound in water (*universal solvent*) or by melting it. In both cases the compound dissociates into ions; followed by their migration to the oppositely charged electrodes. However the discharge at the electrodes depends on several factors viz:-

1. The position of the respective ion in the electrochemical series.
2. The type of electrode used i.e. its electrode potential compared with the discharge potential of the ion.
3. The ionic concentration of the solution (i.e. the molarity of the solution).
4. The nature and quantity of 'stray' ions present.

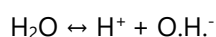
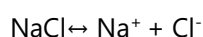
Here the term stray ions refer to the impurity ions which may be present in the dissolved state. For e.g. commercial sodium chloride contains traces of Mg^{2+} , K^+ etc.

The conventional technique of electrolysis veritably relies on direct current where the electrodes have *fixed* polarities. In case of alternating current the electrodes' polarity changes with time. Again alternating current may be broadly classified in to two categories:-

- a) Low frequency/ power frequency alternating current (50-60Hz).
- b) High frequency/ communication frequency alternating current (>20 KHz).

The effect of the former on electrolytes has been studied ^[1]. The waveforms of the voltage and current were sinusoidal. In the later case the rate of change of the electrodes' polarity is very high. *The ions being relatively heavy and immobile ought not to be able to alter their directions of migration at such high speeds*. This should result in *local concentration of the heavy ions* leading to *no discharge at all* which is the theoretical case. The entire energy supplied at the electrodes must be dissipated as heat which would ultimately lead to temperature rise of the solution.

A study of mechanism of electrolysis is necessary before proceeding further. Considering a simple experiment of electrolysis of brine solution using a battery as a power source:-



Assuming absence of stray ions, two cases may arise.

Case 1 (electrodes are reactive for e.g. copper).



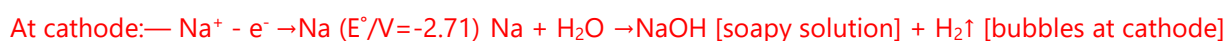
The following reactions are observed:—



Other active metals like iron, zinc etc. result in similar reactions resulting in the formation of insoluble hydroxides at anode along with liberation of hydrogen gas at the cathode.

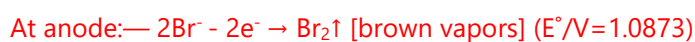
In the above experiment both O.H.^- and Cl^- migrate to the anode. But $2\text{Cl}^- - 2\text{e}^- \rightarrow \text{Cl}_2$ $E^\circ/V = 1.35827$, can not be oxidized. But copper, which has far less E°/V value, is oxidized to Cu^{2+} ions.

Case 2 (electrodes are of graphite)



Chlorine being a very strong oxidant attacks the graphite electrode requiring its periodic replacement. The carbon particles finally settle at the bottom resulting in black sediment. A part of the chlorine formed reacts with water to form hydrochloric acid according to the reaction $2\text{H}_2\text{O} + 2\text{Cl}_2 \rightarrow 4\text{HCl} + \text{O}_2\uparrow$. HCl is neutralized by NaOH giving back NaCl and water. As a result we get strong odour of chlorine during the electrolysis process.

Electrolysis of molten salts is somewhat *simpler* due to the absence of *side reactions* that occur owing to the presence of water. Considering for e.g. the electrolysis of molten lead bromide at temperatures above 373°C



The source of power in the above case is D.C.

Electrolysis using low energy pulses obtained from a pre charged capacitor (the charging source removed) can be used to ionize active metals giving ionic concentrations of the order of micromoles^[2]. Under this condition the capacitor acts just like a battery maintaining the electrodes at fixed potentials.

A pure D.C source may be represented by a *unit step function*. In this case the trajectories of both voltage and current remain parallel to the time axis and hence these quantities have constant amplitude at all instants of time.

On the other hand pulsating D.C obtained from a rectifier has different values at different instants of time. So the voltage between the electrodes is different at different instants of time. Assuming the electrolyte to be purely resistive and ignoring capacitive effects, the *solution current follows the voltage waveform*. The continuous variations of the voltage and current values are responsible for the creation of '*local disturbances*' which leads to a chaotic condition amongst the molecules. The ultimate effect is the production of heat leading to solution temperature rise. This could engender side reactions and inhibit migration/ionization/discharge or all. As the current strength varies, the charge transfer at each instant varies. But as the current may be represented by an average value, so can the charge. The situation gets a little better on the inclusion of a capacitor (2200 μF and above) across the rectifier terminals. This can smoothen the voltage waveform at low values of voltages. But electrolytic capacitors having high capacitances are difficult to equip for high voltages. Hence the voltage disturbances become very prominent at high values due to the difficulty encountered in smoothening. This results in a reduction in the efficiency of charge transfer. However, ionization and discharge are still possible as has been observed experimentally^[3]. All these studies have been based on the sinusoidal nature of the A.C waveform.

H^+ is the lightest ion having the smallest ionic radius. Its mobility is higher compared to other larger ions, it *should be able to follow the rapid variations of electrode polarity*. Therefore its discharge as hydrogen *should not* be altogether impossible at high frequencies. Keeping in view the said property, experiments were conducted which have been elaborated in the succeeding sections.

Chemicals and Apparatus required:

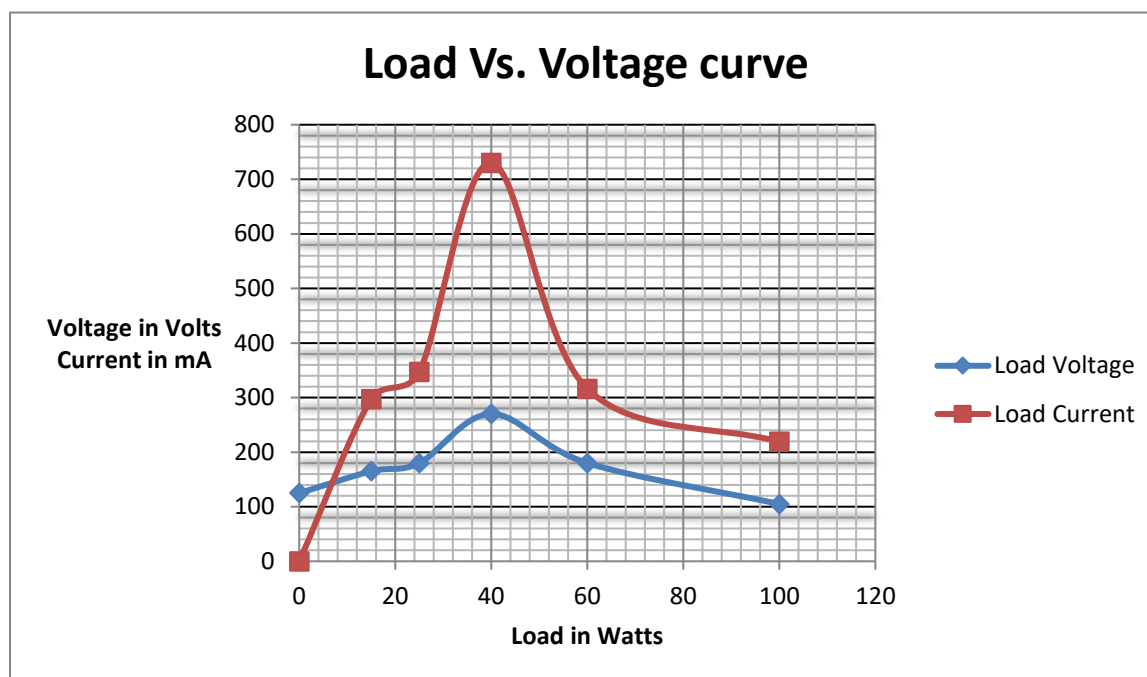


1. Glacial acetic acid (99% pure)
2. Oxalic acid dehydrate crystals
3. Sodium Chloride
4. Potassium Iodide
5. Nitric acid (68% pure)
6. Potassium Permanganate crystals
7. Barium hydroxide octahydrate crystals
8. Hydrogen Peroxide (6% solution)
9. 36W fluorescent tube equipped with electronic ballast
10. Analog multimeter
11. High accuracy milliammeter
12. Thermometer
13. Aluminum wires
14. Copper wires
15. Incandescent lamps (15W, 25W, 40W, 60W, 100W)
16. Electronic voltage regulator equipped with triac
17. 230V/50Hz Single phase A.C. supply.
18. 5V/2A D.C supply

Experimental: The essence of the experiments described in this paper is vested in the application of a voltage waveform characterized by a high frequency of the order of KHz along with high amplitude of the waveform (>150V). This is very different from the *conventional method of electrolysis* relying on *low voltages and high currents*. The high voltage is essential in order to provide enough instantaneous positive potential at the electrodes so as to ensure ionization despite rapid polarity change. The crux of the hurdle lies in finding a source which would satisfy the above mentioned criteria. Small transistorized oscillator circuits are capable of generating high frequencies but the voltage magnitude is quite low. Moreover they are susceptible to overloads. With a view to overcoming the odds electronic ballast normally used for powering 40/36W tube lights was resorted to as a power source. A brief description of the working of such ballast is essential before proceeding further.

Electronic ballast as the name suggests solely relies on an electronic circuit which takes power frequency input at 230V/50Hz. It then rectifies it to D.C voltage. After necessary filtration, the output is fed in to a half bridge resonant converter. The resultant output of this converter is a typical square wave having a frequency in the range of 20-80 KHz. The high frequency results in noiseless operation of the tube light and increases its life. The high frequency voltage exists across the gas column between the two ends of the tube light which can be measured by a multimeter with its ends connected between the two metallic ends of a lighted tube light. An auxiliary load like an incandescent lamp may be easily powered using this voltage as long as the tube light is operating. In this case the auxiliary load acts in parallel with the load offered by the glowing gas column. The voltage across the gas column depends on the magnitude of the auxiliary load applied. A curve was plotted describing the variation of voltage with the wattage of the external load applied across the gas column.

Graph No. 1



It is observed that the voltage first increases with increase in load, shoots up to a maximum and then decreases again. The voltage reaches its maximum when the magnitude of the auxiliary load approximately equals that offered by the glowing gas column. It can be further inferred that the current almost follows the variation of voltage at all instants.

For the experiments electrodes made of commercial aluminum were used. The reasons behind this choice were:-

1. Aluminum, being above hydrogen in the electrochemical series ($\text{Al}^{3+} + 3\text{e}^- \leftrightarrow \text{Al} \text{ E}^\circ/\text{V} = -1.662$) is capable of displacing hydrogen from acids as well as water. So it would be easier to detect whether ionization is accelerated on the passage of high frequency current as is observed with D.C.
2. Being amphoteric, it can also react with alkalis like sodium hydroxide.
3. On ionization aluminum does not form colored insoluble precipitates like those of copper or iron.
4. Aluminum has the property of attaining passivity under the influence of strong oxidizers like nitric acid due to the formation of oxide layer on its surface. So it would not be out of point to see the effect of high frequency voltage on this oxide layer.
5. Aluminum has the tendency to liberate I_2 on passage of current through a solution of potassium iodide.

Hence Aluminum was considered most suitable for conducting the experiments. Copper was used as *auxiliary electrode* as will be described later.

The entire procedure of experimentation was divided in to a series of experiments.

Experiment 1A

1l. water at room temperature of 22.6°C was used as the electrolyte for the experiment. The water being almost pure was devoid of impurity ions and hence possessed poor conductivity and was found to be neutral ($\text{pH}=7$). The 230V/50Hz supply to the fluorescent tube was switched ON with both electrodes removed from the solution. Instantly the tube light attained full brightness. Slowly the electrodes were inserted in to the electrolyte by gradually lowering in to the depths of the liquid. The lumen output of the tube light decreased slightly. An initial current of 235mA was found to pass through the solution. The voltage between the electrodes was 175V. Very tiny bubbles were observed at both electrodes. After an hour the solution temperature shot up to 25.6°C . Evidently not much power was being absorbed by the solution. A final steady current of 350mA was recorded.

Experiment 1B

The above experiment was repeated by adulterating the solution with 10ml. 99% glacial acetic acid. The reasons behind the usage of acetic acid were:—

- i. It is a water soluble organic acid.
- ii. To supply H^+ ions without allowing the pH to fall vigorously as is observed with mineral acids like HCl.
- iii. To increase the conductivity of the solution slightly by supplying low concentration of H^+ and CH_3COO^- ions.

Bubbles were visible at both electrodes along with an initial current of 250mA and electrode voltage of 180V. No bubble could be detected at either electrode once the current was switched OFF. So evidently it was the passage of current which was responsible for the evolution of bubbles. After an hour a temperature hike of $4^\circ C$ was recorded. According to the relation $P=VI$, (considering unity P.F) a power of 40W was being supplied to the solution. Yet the temperature rise was appreciably low.

Experiment 1C

The solution used in Experiment 1B was mixed with 5g. sodium chloride with a view to increasing conductivity without altering the pH value. On inserting the electrodes in to the solution the tube light extinguished completely. An initial current of 350mA was recorded. Large bubbles were observed at each electrode. The temperature rise after an hour was $15^\circ C$. Evidently a large power was getting dissipated as heat. But surprisingly with increase in temperature the current decreased by 70mA. This is contrary to the fact that electrolytic conductivity increases with rise in temperature.

All these experiments yielded identical results except for the fact that the temperature rise in each case was different.

Experiment 2

A solution was prepared by dissolving 10ml. 6% hydrogen peroxide with 1l. water. Hydrogen peroxide was used not to increase conductivity but to render the solution oxidizing. Due to availability of 'extractable' oxygen within the molecule of hydrogen peroxide, oxidation of the electrodes ought to be facilitated. Aluminum would react with this oxygen forming thin oxide layer rendering it passive preventing further reaction. As a result *pure oxygen gas should result at the electrodes*. Indeed bubbles were observed at both electrodes which ceased once the current was switched OFF. An initial current of 240mA was recorded. The vol. of bubbles increased with the passage of time i.e. the bubbles got bigger. After an hour a current 300mA with a temperature rise of $5.3^\circ C$ was recorded. On removal of the electrodes from the solution it was observed that both had tarnished, vestiges of the oxide layer formation.

Experiment 3

Electrolyte comprising of 1l. water mixed with 5g. K.I. was used. On insertion of the electrodes in to the solution the lumen output decreased considerably with an initial current of 374mA passing through the solution. Dense bubbling was observed at one of the electrodes while tiny bubbles were observed at the other. As the solution temperature increased, the tube light extinguished. An overall temperature rise of $16^\circ C$ was detected. The solution current dropped by 50mA. However bubbles at the electrodes never ceased.

Experiment 4

1l. M/20 solution of oxalic acid dihydrate (Molecular Wt.=126) was electrolyzed. Dense bubbles were observed at one of the electrodes while bubbling at the other electrode was almost negligible with an initial current of 456mA. As time elapsed the solution assumed a milky appearance. Temperature rise after an hour was $16.8^\circ C$ and the current dropped to 282mA. The bubbling stopped instantly once the current was switched OFF. On allowing the solution to stand for an hour after removal of the electrodes, the solution slowly resumed its clear appearance.

All the experiments described above are based on *two electrode system* having resemblance to a D.C. system. The reaction rates get altered on the insertion of *auxiliary electrodes*. An auxiliary electrode may be defined as an additional electrode of a metal other than the one used in the main electrodes charged from a separate

source having a different voltage and frequency as compared with the main electrode system. An auxiliary electrode may be charged in three different ways viz.

1. A 230V/50Hz live line through an inductance if the need be.
2. A D.C source such as a rectifier.
3. An earth electrode.

Experiment 5

M/20 solution of oxalic acid dihydrate, 1l. by volume was prepared. It was ascertained that the solution was devoid of any insoluble mass in any form. On inserting the electrodes in to the solution the lumen output of the tube light decreased while bubbles were visible at one of the electrodes. Now a copper electrode charged by a 230V/50Hz live wire was inserted in to the solution. Instantly the intensity of bubbles at the aluminium electrode increased to a great extent. Bubbles were also visible at the copper electrode (auxiliary). In a matter of minutes the solution turned milky. The bubbling disappeared once the power from both sources was switched OFF. So indeed it was the passage of current which was responsible for the production of water insoluble gas causing the appearance of bubbles. Temperature rise of 22.8°C after an hour was recorded. On allowing the solution to stand, brown mass deposited on the aluminum electrodes while the copper electrode developed a whitish coating.

Experiment 6

A 1l. dilute nitric acid solution was prepared by dissolving 30ml. 68% nitric acid in 970ml. water. Aluminum would not liberate hydrogen from nitric acid due to passivity. To test the hypothesis an uncharged aluminium rod was immersed in the solution for a long time. Indeed no visible reaction could be detected. The rod was removed and the electrodes were inserted in to the solution. The glow of the tube light decreased but no bubble was visible at either electrode. On inserting an auxiliary copper electrode charged by a 230V/50Hz live wire large bubbles started evolving from one of the aluminum electrodes. Dense bubbles were also observed from the copper electrode. On removal of the copper electrode, bubbling continued at the aluminium electrode though with a decreased intensity. The inclusion of the auxiliary electrode had initiated the bubbling process but its removal didn't stop the bubbling. So water insoluble gas must have resulted which was escaping as bubbles. Nothing but the passage of current was responsible for the gas formation.

Experiment 7

In this experiment the aluminum electrodes were replaced by copper. Solution of hydrogen peroxide was used as electrolyte. Aluminum was used as auxiliary electrode and it was connected to earth. On inserting all the three electrodes in to the solution at the same time, the brightness of the fluorescent tube decreased slightly. Bubbles were visible from the aluminium electrode and from one of the copper electrodes. Slowly pale blue mass collected on the surface of the copper electrode which resembled copper hydroxide. The current varied from 250-300mA with an electrode voltage of 75V. The temperature rise after an hour was 10°C. The pale blue mass was scraped off and was divided in to two parts A and B. To part A ammonium hydroxide solution was added which resulted in deep blue color confirming the presence of Cu^{2+} ions. Part B was kept exposed to atmosphere which gave bright green crystals of basic copper carbonate. So indeed the pale blue mass was that of $\text{Cu}(\text{OH})_2$.

Experiment 8

All the above experiments were carried out using conventional D.C. supply in order to bring out the difference in reactions between the two. For this the electrodes were charged from a 5V D.C. source. No auxiliary electrode was used in any case.

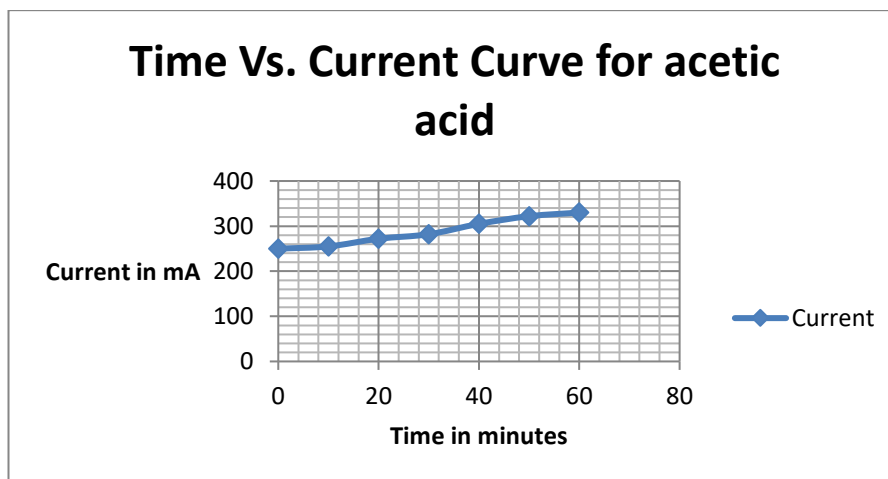
Since the fluorescent lamp along with the electronic ballast arrangement was only used as a source of supplying high frequency square wave voltage, no study on the electrical behavior of the circuit such as variation of lumen output, power factor etc. was made.

Observations: Weak electrolytes like water allow high frequency currents to pass through them without appreciable dissipation of heat. The high frequency current is capable of discharging gases like hydrogen and

oxygen at the electrodes. These gases may be collected by downward displacement of water as was done in the above experiments.

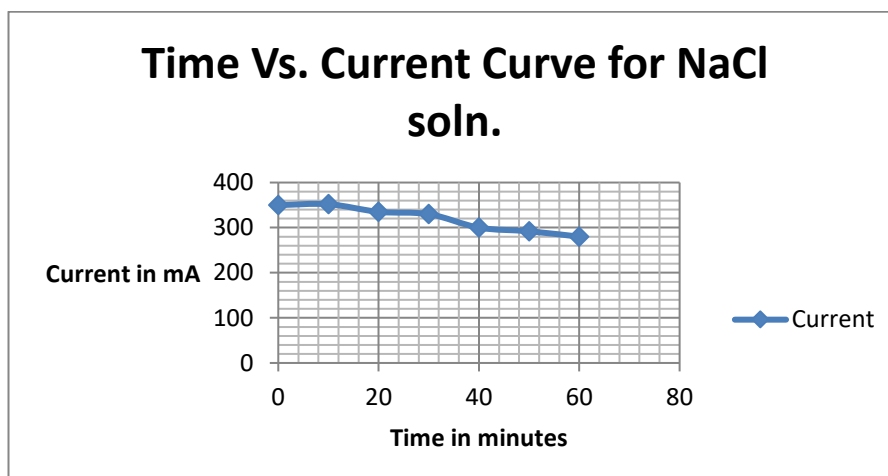
Hydrogen generation is enhanced by the addition of weak organic acids like acetic acid capable of supplying low concentration of H^+ ions. Due to increase in conductivity of the solution, the temperature rise is slightly more when compared with that in case of pure water. Current in both situations increases *monotonically* with time.

Graph No. 2



The situation is much altered on the addition of strong electrolytes like sodium chloride which are capable of maintaining the solution neutrality and at the same time causing rapid discharge of gases. The rate of rise of temperature is higher but the conductivity falls with increase in temperature. The formed gases at the electrodes just like the former case may be collected by the downward displacement of water. A plot of current with time is shown:—

Graph No. 3



Hydrogen Peroxide doesn't increase conductivity. It only serves an *oxygen supplying agent*. The predominant products are hydrogen and oxygen; the source of oxygen being both water and hydrogen peroxide. Aluminium electrodes due to formation of inert oxide layer do not ionize thereby facilitating the process of gas generation. However copper having no such oxide layer ionizes as pale blue copper hydroxide which is confirmed on the addition of ammonium hydroxide resulting in deep blue complex. However the principle products are oxygen and hydrogen (visible as bubbles at the electrode surface); copper hydroxide may be considered as a byproduct. Current increases monotonically with time.

Potassium iodide being a strong electrolyte increases the conductivity appreciably. Unlike low frequency A.C. no iodine is liberated. Large hydrogen bubbles are visible which when collected and ignited burn with a characteristic pop sound. Tiny oxygen bubbles are liberated at the other electrode. The solution possesses positive resistance characteristics i.e. conductivity falls with rise in temperature. Rate of temperature rise is slightly more when compared with that of NaCl solution.

Oxalic acid solution behaves alike to acetic acid solution except for the fact that aluminium dissolves as insoluble aluminium oxalate thereby imparting a milky appearance. The insoluble mass settles down and the solution regains its clear nature.

Hence all the experiments conducted employing a 'two electrode system' resulted in oxygen and hydrogen as the principle products. Side reactions may lead to appearance of byproducts having concentrations of the order of micromoles.

Table no.1

S.No.	Solution used	Electrode used	ΔT ($^{\circ}C$)	I_0 (mA)	I_f (mA)	Observation with HF A.C	Observation with DC
1	Pure water	Aluminium	3	235	350	Tiny bubbles of oxygen and hydrogen at both electrode	Insoluble $Al(OH)_3$ along with hydrogen and oxygen at the respective electrodes
2	Acetic acid		5	250	330	Tiny bubbles of oxygen and hydrogen at both electrode	Bubbles at both electrode along with gradual dissolution of aluminium as aluminium acetate
3	Sodium Chloride	Aluminium	15	350	280	Large bubbles of oxygen and hydrogen at both electrode.	Formation of hydrogen at cathode along with dissolution of anode as insoluble aluminium hydroxide
4	H_2O_2	Aluminium	5.3	240	300	Bubbles of hydrogen and oxygen at both electrode	Bubbles of oxygen at anode and hydrogen at cathode
6	KI	Aluminium	16	374	324	Large bubbles at one electrode and tiny ones at the other	Bubbles at both electrodes along with liberation of yellow iodine at anode rendering the solution temporarily yellow

7	Oxalic acid	Aluminium	15	282	350	Large bubbles at both electrode along with dissolution of aluminium as white insoluble aluminium hydroxide	Large bubbles at both electrode along with dissolution of aluminium as white insoluble aluminium hydroxide
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Table no. 2

S.No.	Solution used	Main Electrode used	Auxiliary electrode used	Main electrode current in mA	ΔT ($^{\circ}C$) after 1hr.	Observation	Major products
1	Oxalic acid	Aluminium	Copper charged to 230V/50Hz	300	16.8	Dense bubbles at the copper electrode and at one of the aluminium electrodes. Tiny (almost no) bubble at the other aluminium electrode. Brown deposition on the aluminium electrode and white deposition at the copper electrode	Oxygen, Hydrogen and aluminium oxalate
2	Nitric acid	Aluminium	Copper charged to 230V/50Hz	500	20	Large bubbles at the copper electrode and one of the aluminium electrodes. Gradual dissolution of the other aluminium electrode and the copper electrode	Oxygen, Hydrogen
3	Hydrogen peroxide	Copper	Aluminium connected to earth	310	15	Large bubbles at each electrode. Aluminium gets tarnished. Indigo blue mass obtained at the copper electrode.	Oxygen, Hydrogen

4	NaCl	Aluminium	Copper charged at -90V.D.C	550	25	Bubbles at the copper electrode along with dissolution of both aluminium electrode	Hydrogen and aluminium hydroxide which dissolves on addition of NaOH
5	K.I.	Aluminium	Copper connected to earth	540	25	Large bubbles at each electrode. Yellow deposition at one of the aluminium electrodes.	Oxygen, Hydrogen and elemental iodine which turns the solution temporarily yellow. The yellow color fades gradually.

Results and discussions: Electrolysis at high frequencies like 20-60 KHz is not altogether impossible. Unlike D.C electrolysis, high frequencies also seek for the application of high voltages between the electrodes. This is feasible using both homogenous two electrode system as well as heterogeneous three electrode system where an auxiliary electrode plays a vital part. The important results have been summarized under:-

- i. High frequencies at high voltages mostly generate oxygen and hydrogen as predominant products at the electrodes which become evident from the continuous evolution of bubbles at the electrodes. Both of these gases may be collected by downward displacement of water.
- ii. High voltage is essential for providing sufficient electric field strength which in turn would facilitate migration despite high frequencies and low ionic mobilities.
- iii. Inert electrodes like graphite or electrodes those possess the property of attaining passivity are best suited for the discharge of gases from their surface.
- iv. Reactive electrodes like copper and iron also give hydrogen and oxygen as the major products along with insoluble hydroxides e.g. copper hydroxide in micro molar concentrations. These insoluble hydroxides may be treated as by products.
- v. The reason behind the generation of hydrogen can be imparted to the high mobility and small ionic radius of H^+ ions whose source is nothing but water itself. Being the lightest ion it is capable of *following* the rapid changes in the electrodes' polarity. The reaction mechanism is simple and is alike to D.C i.e. $H^+ + 2e^- \rightarrow H_2\uparrow$.
- vi. Due to discharge of protons as hydrogen gas, $O.H.^-$ ions become free and their concentration in the solution gradually increases. But the solution has to remain electrically neutral. Again due to passivation by oxide layer aluminium is unable to ionize and combine with the free hydroxyl ions. Therefore the $O.H.^-$ ions are oxidized according to the reaction $4OH^- - 4e^- \rightarrow 2H_2O + O_2\uparrow$. The electrical neutrality is thus restored.
- vii. If reactive electrodes like copper are used, the metal *tries* to follow the frequency variation and in the process only a small part of it ionizes as Cu^{2+} which in turn combines with the free $O.H.^-$ ions leading to the formation of insoluble hydroxides. However the major portion of $O.H.^-$ ions is discharged as oxygen. This is totally contradictory to D.C electrolysis where no discharge of oxygen occurs and only insoluble hydroxides are formed at anode.
- viii. The rate of temperature rise is more for strong electrolytes as compared with that of weak electrolytes.
- ix. The conductivity of strong electrolytes decreases with rise in temperature while that of weak electrolytes decreases with increase in temperature.

- x. The reason behind the above is the facilitation of ionization with temperature rise for weak electrolytes and increase in collision with temperature for strong electrolytes.
- xi. The exception to the above is a solution of oxalic acid which despite being a weak electrolyte, high frequency conductivity falls with temperature rise.
- xii. Auxiliary electrodes charged at 50Hz enhances the rate of discharge of gases. Basically the frequency of the auxiliary electrode being much lower compared with the main electrodes, a D.C characteristic is imparted to the entire system. So insoluble metal hydroxides are obtained at the surface of the auxiliary electrode (if reactive).
- xiii. If D.C is used for charging the auxiliary electrode, the main electrodes attain a polarity opposite to that of the auxiliary electrode. In this case the unidirectional D.C wave is superimposed on the high frequency A.C square wave and the D.C component dominates.
- xiv. Organic acids like oxalic acid lead to the formation of salts of aluminium along with the deposition of metallic copper on the aluminium surface. In this case the electrodes possess a what may be called '*dual polarity*'. Aluminium acts as anode and ionizes to produce insoluble aluminium salt and at the same time it acts as cathode thereby reducing Cu^{2+} to metallic copper by supplying electrons.
- xv. A three electrode system having aluminium as one of the electrodes is capable of liberating iodine from a solution of potassium iodide just like D.C. However a two electrode system comprising only the main electrodes gives only oxygen and hydrogen even if the main electrodes are made of aluminium.
- xvi. The system of electrolysis works best for weak electrolytes because strong electrolytes having high conductivities have the propensity of overburdening the delicate high frequency generating apparatus like electronic ballast whose components are highly susceptible to overloads.

Therefore it may be concluded that high frequency square wave is capable of discharging gases at the electrodes and also ionizing metals like copper and other metals which are below hydrogen in the electrochemical series and hence normally can't displace hydrogen from acids.

Conclusion: High frequency (20-60KHz) square voltage waveforms having sufficiently large amplitude are capable of discharging hydrogen and oxygen as the predominant products from aqueous solutions. '*Passive*' electrodes like aluminium having a thin layer of aluminium oxide or graphite are best suited for the purpose. However high frequency voltage waves are incapable of ionizing active metals when used as electrodes. Therefore precipitation of insoluble metallic hydroxides is minimal unlike D.C electrolysis. The essence of electrolysis at high frequencies is the high mobility of H^+ ions having small ionic radius. This in turn facilitates the generation of hydrogen and oxygen at the electrodes. The apparatus required for supplying such high frequency voltages is quite inexpensive but is susceptible to overloads. This makes weak electrolytes having poor conductivities ideal for the experiments. The current remains below 300mA. This technique may pave the way for hydrogen production in the future while supplying electrical loads like fluorescent tube lights.

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