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An experiment on electrolysis utilizing low energy capacitive pulses

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Abstract

Electrolysis relies on the migration of ions towards oppositely charged electrodes (anode and cathode) under the influence of applied electric field. This (the field) is obtained from a D.C source rated for a suitable voltage and current supplying capability. The energy supplied to the electrolyte is high of the order of Joules (may be in the order of hundreds or thousands). The supply is maintained continuous. All these occur when the supply is D.C. The fixed and well defined polarity of D.C allows the ions to migrate in a definite manner. But A.C does not have a fixed polarity. Yet A.C can charge a capacitor. A charged capacitor when kept open circuited retains the charge for a very long time. Energy is stored in the electrostatic field. This energy is very small in magnitude ranging from µJ to a few mJ. When discharged using a resistive load, the energy dissipates in the load without oscillation. If the load is an electrolyte, the released energy causes electrolysis of the solution. This paper describes the characteristics of electrolysis using capacitive discharges under low energy conditions.

Keywords: electrolysis, energy, charge, capacitor, ions

Introduction

Electrolysis is the '*splitting up*' of a chemical compound on passage of electricity. The compound known as electrolyte is either in the molten or aqueous solution state. The ions migrate to oppositely charged electrodes. Thereafter the ion gets discharged or the electrode gets ionized depending on the following factors:—

- Charge on the electrode.
- Position of the ion in the electrochemical series.
- The concentration of ions in the solution.
- The nature of the electrodes used.

The simplest example is electrolysis of acidulated water using inert electrodes. The reactions may be given as under:—

$H_2O \xrightarrow{ionization} H^+ + OH^-$
At cathode—
$2H^+ + 2e^- \rightarrow H_2$
At anode—
$4OH^- - 4e^- \rightarrow 2H_2O + O_2$
Overall reaction—
$2H_2O \rightarrow 2H_2 + O_2$

This is an example of discharge of gases at oppositely charged electrodes. Electrolysis of NaCl solution gives the following reactions:—

$NaCl \xrightarrow{ionization} Na^+ + Cl^-$
$H_2O \xrightarrow{ionization} H^+ + OH^-$
At cathode—
$2H^+ + 2e^- \rightarrow H_2$
At anode
$Cu - 2e- \rightarrow Cu^{2+}$
$Cu^{2+} + 2OH^- \rightarrow Cu(OH)_2$ (pale blue ppt.)

This is an example of ionization at anode. The energy required by the process is supplied by a D.C source like a lead-acid battery or an A.C-D.C converter. Generally *low voltage high current sources are preferred*. Taking an example if a 12V battery supplies 1A, assuming internal resistance to be negligible, the power supplied to the electrolyte is P=VI i.e. 12W. Putting in another way *the electrolyte receives energy at the rate of 12J every second*. Charge is given by Q=It. So 1C charge passes every second. Hence the yield of products is very fast. Industrial systems e.g. electroplating require even higher current (and hence power) of say 100A. In this case 100C charge is delivered every second and 1200 J energy is received by the electrolyte (taking voltage 12V). Hence energy supplied is very large.

A capacitor is a device which can store energy in an electrostatic field. In D.C circuits capacitor gets charged to the potential of the source and blocks further flow of current. *When A.C is applied the capacitor charges, discharges and then charges in the reverse direction*. When the circuit is kept closed, the charging and discharging continues and the capacitor supplies reactive power to the source and hence improves power factor.

When a capacitor is connected to A.C and the switch is opened, *the final potential attained by it depends on the instant at which the switch is opened*. The polarity of the terminals also depends on the instant at which the switch is opened. So each terminal can be of either polarity (positive or negative). But *once the switch is opened the polarity remains fixed*. Under this condition one terminal is positive while the other is negative. When a circuit is made using this charged capacitor current flows from positive terminal to negative terminal through the external circuit. Hence a sensitive PMMC ammeter shows a deflection. Once the entire charge is released, the potential reduces to zero and the capacitor is discharged.

After charging and removal of the A.C source, the capacitor has a definite positive and negative plate. The stored charge is given by Q=CV. Let a capacitor of 2.5µF be charged so that the final potential is 100V. So it stores 250µC charge. The energy given by $E=1/2CV^2$ is 1.25mJ. Under this condition if the terminals are dipped in an electrolyte, the energy is released in to the electrolyte.

As the terminals have a fixed polarity, this low energy ‘should’ electrolyze the solution. *The rate of energy release depends on the resistance of the electrolyte while the energy received by it remains same*. Hence though the source is A.C, the ultimate thing is low energy D.C. The succeeding sections deal with electrolysis at such low energy level.

Materials and Chemicals required

1. 9V 6F22 battery
2. 230/12V, 3A transformer
3. 2.5µF capacitor
4. Digital multimeter
5. Stopwatch
6. NaCl
7. Dilute HCl
8. Sodium bicarbonate
9. Acetic acid
10. Sodium hydroxide
11. Ammonium hydroxide

Experimental

Before proceeding with the original experiment a brief overview of conventional electrolysis using a pure D.C source was made. Strong solution of NaCl was electrolyzed using a 9V battery an iron electrodes of crossectional area 2.4X4.7cm^2. As soon as the switch was closed, bubbles started evolving from the cathode and the solution started turning ‘ugly’ yellow. A current of 350mA was recorded. So energy was being supplied @ 9x.35J every second. The reactions occurring at the electrodes were:—

$NaCl \xrightarrow{ionization} Na^+ + Cl^-$

$H_2O \xrightarrow{ionization} H^+ + OH^-$

At cathode—

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

At anode—

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

$Fe - 2e^- \rightarrow Fe^{2+} + 2OH^- \rightarrow Fe(OH)_2$

So basically a mixture of ferrous and ferric hydroxide was being obtained which imparted ugly yellow color to the solution along with evolution of hydrogen (evident from evolution of bubbles) when energy was being supplied @ 9x.35J every second.

A 230V-50Hz single phase A.C supply was used to charge a capacitor. The capacitance was varied from 2.5-10µF with an increment of 2.5µF every time. The capacitor was charged by closing ‘S_1’ and discharged by closing ‘S_2’. *The two switches were never simultaneously closed* (other wise the supply would directly appear across the solution). During each ‘cycle’ of switching first ‘S_1’ was closed with ‘S_2’ open. Then ‘S_1’ was opened and ‘S_2’ was closed. The entire process was called ‘*one switching operation*’.

The two terminals were connected to Fe electrodes of area 2.4X4.7 cm^2. These electrodes were dipped in concentrated NaCl solution and the switching operation was started. ‘S_1’ was turned ON for 1s and then OFF. After opening ‘S_1’, ‘S_2’ was closed for 2s. The analogy behind this was that an ideal capacitor should get charged instantaneously. But in 1s there are 50 cycles of A.C. So *it is possible that the capacitor is charged to an ‘intermediate’ voltage level rather than the rated r.m.s voltage of 230V* (the explanation already given). It is also possible that the capacitor voltage is greater than 230V depending on the instant at which the switch was opened. *No voltmeter was connected across the capacitor. This is because however high the resistance of the voltmeter might be, the capacitor would ‘tend’ to lose a part of its charge (and hence energy) by dissipating it in the voltmeter*. To prove this a separate capacitor was charged by a D.C source of 100V. It was then disconnected and its terminals were connected to a high resolution voltmeter. The capacitor showed 100V at the time of connection but the voltage gradually decayed to 0V. The interval was only 110 seconds. Hence no voltmeter was used. Now coming back to the experiment, after charging the capacitor ‘S_1’ was opened and ‘S_2’ was closed for 2s. Again ‘S2’ was opened and ‘S_1’ was closed for 1s. The process was repeated. Initially nothing is apparent. But after 100 switching operations, a pale yellow color develops in the solution and the electrodes develop a black coating. As the switching is continued, the yellow color gradually deepens and after 200 switching cycles appreciable yellow mass develops. When allowed to stand yellow ppt. settles at the bottom. To this dilute HCl was added. A greenish solution was developed. The solution is kept in an airtight condition for 1 day. After this excess NaOH was added. Reddish brown ppt. settles at the bottom.

The above experiment was repeated using cylindrical copper electrodes of 1.5mm^2. After 150 switching operations pale blue mass started accumulating at the electrodes. This blue mass was allowed to settle and dilute HCl just enough to solubilize the ppt. was added. It resulted in a blue solution. Again after keeping the solution under airtight condition for a day, NaOH was added. The pale blue ppt. was recovered. To this excess ammonium hydroxide was added. A deep blue solution was obtained.

Another experiment was tried using acetic acid as the electrolyte. This was chosen because *acetic acid is a weak electrolyte and hence offers high resistance*. It is also easily available. *Iron electrodes were not used in this experiment because Fe being higher in the electrochemical series than hydrogen would it self react with acetic acid forming ferric acetate* and hence the results of the experiment can’t be made out. So copper electrodes of 1.5mm^2 were used. Copper being below hydrogen in the electrochemical series would not react with acetic acid under ordinary conditions. The switching operation was started using 10% acetic acid and copper electrodes. As acetic acid offers high resistance as compared to NaCl solution, it would pass less current and hence it would take larger time to pass the same charge than in NaCl solution. So 'S_1' was closed for 1s and then opened. But 'S_2' was closed for 4s to allow complete discharge of the capacitor through the solution. It took 400 switching operations to turn the solution from colorless to pale blue. After 600 switching operations the hue was quite visible. Now to the blue solution sodium bicarbonate was added to neutralize the excess acid. The solution was now kept in an air tight container for 1 day and ammonium hydroxide was added. A deep blue solution was obtained.

The above experiments were repeated using 5, 7.5 and 10μF capacitor adding every time a 2.5μF capacitor in parallel.

The above experiments depict conditions where voltages are high and capacitances are low. The results were compared with low voltage high capacitance conditions. Hence the above experiments were repeated using a 9V battery as the source and a capacitor of 4700μF. As the source is pure D.C there is no question of an 'intermediate voltage' as depicted in the earlier cases. The capacitor would always be charged to 9V.

In the above experiments Fe and Cu electrodes were used because:—

a. Both Fe and Cu give colored ions and hence detection is easy.
b. They are easily available.

N.B. The above experiments are to be conducted using exactly identical electrodes in terms of metal, length and crossection should be used. This is because either terminal may be positive during the course of the reaction and hence if electrodes are different, more than one product will be formed and the experiment may apparently give no result. Hence both electrodes should be exactly similar.

Another experiment was carried out with a view to convert the energy stored in the capacitor in to high voltage pulses and then release the energy (and hence charge) in to the solution. This could obviously be accomplished with an inductive circuit. Since $e=-L\frac{dI}{dt}$, if switching is very fast, $\frac{dI}{dt}$ will be very large resulting in a high voltage short duration pulse.

A transformer was used in conjunction with a capacitor. The capacitor after being charged was made to release its energy through the LV winding of the transformer. The high $\frac{dI}{dt}$ (due to the low resistance and fast switching) 'should' result in a very high voltage pulse at the HV (230V) winding. Fe electrodes were connected to the HV terminal and these were dipped in strong NaCl solution. As usual 'S_1' was closed for 1s and opened. 'S_2' was closed and opened very fast in order to allow a high $\frac{dI}{dt}$. After 800 switching operations very pale yellow hue was observed in the solution. Again just like the previous experiments dilute HCl was added to solubilize the ppt. This was kept in airtight condition for 1 day and NaOH was added. A reddish brown ppt. was obtained. When Fe electrodes were replaced with copper, a pale blue scummy mass at each electrode was obtained after 800 switching operations. Addition of HCl resulted in a blue solution. After keeping airtight for one day, ammonium hydroxide was added which produced a deep blue solution.

The above experiment was repeated using acetic acid and copper electrodes. The solution started attaining a blue hue after 650 switching operations. The reason behind using copper electrodes with acetic acid has been already explained. The excess acid was neutralized using sodium bicarbonate. It was kept in airtight condition for 1 day and ammonium hydroxide was added. This resulted in a deep blue solution. These experiments (using transformer) were repeated with capacitances of 5, 7.5 and 10μF by adding a 2.5μF capacitor in parallel every time.

Observations

In conventional electrolysis the effects are clearly visible to the naked eye. The reactions are quite fast and the products are easily obtained. But in this experiment of charging and discharging, the effects are hard to observe but nevertheless observable. The striking contrast between the two methods is in the magnitude of current. *While in conventional electrolysis current is given by* $I=\frac{V}{R}$, *R being the resistance of the electrolyte, the current in the presented method is very small compared with the theoretical value obtained by the previously mentioned equation*. Strong NaCl solution offers a resistance of around 25±2Ω. As the capacitor is charged to ≈200V a current of 8A should be available on discharge of the capacitor through the solution. But practically the current is in the range of μA. This is very small compared to the expected value. So clearly *the relation I=V/R does not hold under such a condition*. The reason behind this is the capacitor itself. The capacitor offers very high input impedance and hence restricts the flow of current. Another reason is the extremely low magnitude of charge accumulated on the capacitor plates. Since charge is of the order of micro Coulombs and t is in the order of seconds, current stays in the range of μA. Due to the low magnitude of current no spark and noise are observed. The low energy supplied causes slow electrolysis of the solution. A table summing up the observations is given:—

Table 1

Capacitance (μF)	Solution	Electrodes	Current (μA)	No. of switching	Final product
2.5	NaCl	Fe	250	200	$Fe(OH)_3$
	NaCl	Cu	250	200	$Cu(OH)_2$
	Acetic acid	Cu	50	600	Copper acetate
5	NaCl	Fe	450	200	$Fe(OH)_3$
	NaCl	Cu	450	200	$Cu(OH)_2$
	Acetic acid	Cu	100	600	Copper acetate
7.5	NaCl	Fe	800	200	$Fe(OH)_3$
	NaCl	Cu	800	200	$Cu(OH)_2$
	Acetic acid	Cu	150	600	Copper acetate
10	NaCl	Fe	1350	200	$Fe(OH)_3$
	NaCl	Cu	1350	200	$Cu(OH)_2$
	Acetic acid	Cu	250	600	Copper acetate

So the current is in the range of μA. Moreover it is evident that *the current does not double on doubling the capacitance though theoretically this should be the case*. In each case iron and copper are found to ionize. The possible reactions are:—

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

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

The addition of NaOH to Fe^{3+} hives reddish brown ppt of $Fe(OH)_3$ and confirms its existence. On the other hand formation of deep blue complex $[Cu(NH_3)_4]^{2+}$ on addition of ammonium hydroxide confirms the existence of Cu^{2+}. Since the solutions were initially free from Fe and Cu, the formation of $Fe(OH)_3$ and $[Cu(NH_3)_4](OH)_2$ indicate the ionization at the electrodes on the discharge of the capacitor.

Now coming to the experiment using the transformer, discharge at the LV winding 'must' result in a high voltage pulse at the HV side and therefore 'should' result in an increase in the rate of reaction. But this is not so due to the following reasons:—

1. Since the energy supplied is very low it is mostly supplied in copper losses in the LV winding. So despite supplying high voltage, it is incapable of providing sufficient power.
2. The resistance of the HV side is very large compared to that of NaCl solution. So maximum voltage drops across the HV winding and energy is lost in this winding.
3. Acetic acid gives better performance in comparison to NaCl because it has high resistance compared to the HV winding and voltage drop is possible across the solution.
4. The capacitor connected to the LV winding is unable to sustain oscillations due to availability of low energy and its subsequent wastage in the form of copper loss.

Results and discussions

Instead of relying on a constant D.C power supply as in the case of conventional electrolysis, this paper presents an alternative method using charging and discharging a capacitor. Though the source is A.C., after getting charged one of the plates becomes positive while the other becomes negative. Hence the capacitor now has 'well defined' polarity and it starts behaving as if it were a D.C source. The energy available is very low. The following important results have been summed up:—

1. As the capacitor is rated in μF it stores only a small charge and hence small energy. The energy, however small is capable of producing electrochemical effects in electrolytes.
2. These electrochemical effects are not instantaneous and may be termed as 'long term' effects as it takes much longer time than conventional method.
3. There is no heating of the solution at such low energy magnitudes and hence there is no possibility of side reactions owing to excitation by heat energy.
4. The current during discharge does not obey the normal formula I=V/R. The practical value is many times smaller than the theoretical value. Several factors are responsible for this.
5. On increasing the magnitude of capacitance the stored charge and hence energy released show proportional increase but the current does not. The *current increases but not in direct proportion to the increase in capacitance*.
6. Since the charging current in a capacitor leads the applied voltage by 90˚, the power factor is almost zero leading. So reactive power may be supplied to the source.
7. Though high voltage pulses may be obtained using a transformer in conjunction, it is not of much use because the low magnitude of energy is used in supplying losses in the transformer and little energy is left for the solution.

So basically this paper presents the method of electrolysis using electrostatic charges stored on the plates of a capacitor. This method might find applications in areas where very low concentration of ions are required. These ions may be in the form of insoluble hydroxides e.g. ferric and cupric hydroxide or as soluble salts. *Low concentrations of soluble salts of metals 'less reactive' metals like copper which don't react with acids under ordinary conditions may be easily synthesized using this method*. One such salt is copper acetate. The energy consumption is also low. It is true that this method of '*interrupted electrolysis*' would require more time than usually required but it will draw very minute energy from the mains. The various losses which occur during conventional electrolysis like power loss in the internal resistance of the battery, losses in the transformer, diodes and self heating of the electrolyte and poor power factors of large converters are absent in this method. So it is not at all wasteful. *Solutions in micro molar concentrations or even less may be easily synthesized without excessive loss of energy*. This also eliminates the necessity of expensive conversion equipment.

Conclusion

Electrolysis can be performed using static charges providing low energy. This leads to ion formation in micro molar concentrations. The source need not be D.C. *A capacitor is the key feature of such electrolysis using static charges*. Heat is not lost in the electrolyte. The VARs supplied in charging the capacitor provide active power for electrolysis. So in a way the line supplies leading VARs but the capacitor supplies power in micro Watts. This process also helps in the improvement of power factor. But as the operation of the capacitor is not continuous, the power factor improvement can’t be relied upon. However ionization is possible at the electrodes in the presence of low energy. This should find application in the synthesis of micro molar solutions.

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