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An experiment on electrolysis at high voltage D.C

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Electrolysis finds a variety of industrial applications viz. electroplating, electro refining and synthesis of certain chemicals. Most of these processes rely on low voltage and high current. Some typical chemicals can be synthesized only above a certain minimum value of current. Voltage is generally not important in such cases. Anything between 6-12V D.C is good enough. The process (electrolysis) under ordinary circumstances is not carried out at high voltages ($>100V$). But such high voltages may be easily obtained from a simple rectifier circuit even at home. When applied across a solution such high voltages cause currents in the range of mA to flow through the circuit. The high resistance of the solution restricts the current to such a low value. Hydrogen can be easily synthesized by such method. Various other compounds having varying chemical properties can also be prepared by electrolyzing proper solutions using metal electrodes. Co (NO₃)₂.6H₂O, FeCl₃ (anhydrous), CdCl₂ & NaCl were electrolyzed with copper electrodes at such high voltages and the behaviors of the products were studied.

Keyword: Electrolysis; Electrolytes; Voltage; Current.

1. Introduction

Low voltage-high current electrolysis finds a variety of applications in the industry as well as in the laboratory. Industrial applications include electroplating and electro refining while in the laboratory it may be used in the synthesis of chemicals. Examples include:—

1. Kolbe's electrolytic method is used to prepare hydrocarbons like ethane.
2. Chemicals like ClO₂ are prepared by electrolysis of NaClO₂ solution.
3. Electrolysis of brine yields NaOH.
4. Electrolysis of molten PbBr₂ gives Br₂ at cathode.
5. NaClO₃ is prepared by electrolysis of hot NaCl solution.
6. Electroplating of silver is done using Na [Ag (CN)₂] and articles are electroplated with nickel using NiSO₄.

Now, whether of commercial purposes or for laboratory synthesis electrolysis is not carried out at high voltage D.C. Voltages between 6-12V is

mostly used. An electrolyte has high resistance. Hence it should be able to limit current when high voltage is applied across it.

A half wave was used to provide high voltage D.C from ordinary domestic supply (230V-50Hz A.C). It was applied to various solutions like FeCl₃ (anhydrous), NaHSO₄.H₂O etc. It was noticed that the current was low (in the range of mA). Cu was used as electrodes and electricity was passed. The color of the product was carefully noted. The resultant solution was treated with dilute H₂SO₄ and the solubility was tested. The NaCl solution which is a strong electrolyte was used to compare the conductivity of the solutions in taking the ratio of initial current.

2. Materials and methods

2.1 Chemicals

1. Co(NO₃)₂. 6H₂O
2. FeCl₃ (anhydrous)
3. CdCl₂
4. NaHSO₄. H₂O
5. NaCl

6. Dilute H_2SO_4

2.2 Instruments

1. 230V-50Hz supply
2. Pn junction diode
3. Digital multimeter
4. Good quality Cu wires

3. Experimental

A half wave rectifier was constructed using a single diode and supplied from a 230V-50Hz A.C supply. This was used as a *high voltage D.C* source. As is the nature of a half wave rectifier circuit the output no load voltage was *103V D.C*. No filter (capacitor filter etc.) was used because it was unnecessary. The current was recorded using a digital multimeter. The entire experiment was divided into five sections.

Experiment no. 1

A solution of $Co(NO_3)_2 \cdot 6H_2O$ was added to 80ml. water in a beaker. The mixture was stirred and a light red solution was formed. Electricity was passed at high voltage as discussed above and the current was recorded. $\Delta I/\Delta t$ was calculated taking $\Delta t = 290s$. After the experiment was over the *resultant mixture was made acidic by the addition of dilute H_2SO_4* .

Experiment no. 2

A solution of $FeCl_3$ was prepared in 80 ml. water at

room temperature. *No acid was added*. A brown solution was formed. The remaining steps were same as above.

Experiment no. 3

A solution of $CdCl_2$ was prepared in 80ml. water. *The solution was not adulterated with acid*. A whitish solution was obtained. This was electrolyzed at high voltage.

Experiment no. 4

Sodium bisulfate monohydrate i.e. $NaHSO_4 \cdot H_2O$ was dissolved in 80 ml. water. A clear solution was obtained. The remaining procedure was same as above with only one exception. Since $NaHSO_4$ is *acidic itself dilute H_2SO_4 was not added*.

Experiment no. 5

A solution of $NaCl$ was electrolyzed in the same process and the end product was made acidic by the addition of H_2SO_4 .

The initial current in each case was compared with that of $NaCl$ solution. Since $NaCl$ is a strong electrolyte and its solution is neutral, it was considered as a reference.

4. Observations

The following table shows the respective currents in the solutions and the values of $\Delta I/\Delta t$:—

Table no.1

Solution	Initial current I_0 (mA)	Final current I_f (mA)	$\Delta I/\Delta t$ (mA/s)	I_0/I_{0NaCl}
$Co(NO_3)_2 \cdot 6H_2O$	34	52	.06206	.12142
$CdCl_2$	42.6	61.2	.06413	.15214
$FeCl_3$	11.7	11.4	*	.04178
$NaHSO_4$	70.8	78.5	.02655	.25285
$NaCl$	280	380	.34822	1

* $FeCl_3$ is a very *weak electrolyte*. Since current is very small heating given by $H=I^2Rt$ is also small. Hence resistance of the solution remains unaltered and so current remains almost constant.

The table given below shows the color of the solution, product and its solubility in acid:—

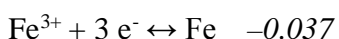
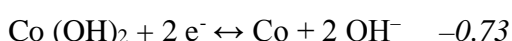
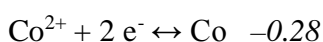
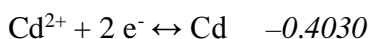
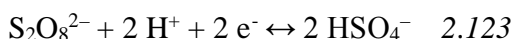
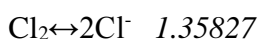
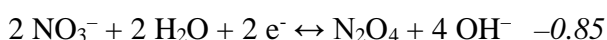
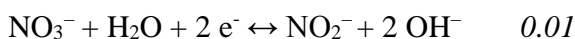
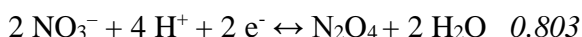
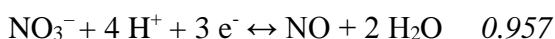
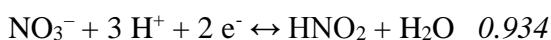
Table no.2

Solution	Initial color	Color of precipitate	Solubility in dil. H ₂ SO ₄
Co(NO ₃) ₂ .6H ₂ O	Red	Deep blue mass at cathode later changes to greenish grey.	Insoluble
CdCl ₂	White	Black mass at cathode. Final color pale blue**	Soluble to give a clear blue solution
FeCl ₃	Brown	Brown	Slightly soluble
NaHSO ₄	Colorless	Clear blue solution (No ppt.)	—
NaCl	Colorless	Yellow	Soluble to give a blue solution

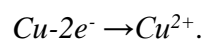
** At first both black and a white scummy mass are formed at the cathode. The white mass on exposure to air turns pale blue.

5. Results and discussions

In every case we notice that the current through the solution is very low. The solutions themselves are very dilute. So the discharge of the ions will be on the basis of their position in the electrochemical series. The anions used are NO₃⁻, Cl⁻, and HSO₄⁻. The electrode potentials are:—



The values given above clearly indicate that *the anions* will not take part in the anode reaction. Hence, in every case copper ionizes to give blue copper ions.



Again a question arises that with which anion Cu^{2+} combine so as to maintain equilibrium. For each solution the conditions are different which have been discussed under:—

Co (NO₃)₂.6H₂O— Both Co²⁺ (in the hydrated state) and H⁺ (from water) migrate to anode. Hydrogen is evolved ($2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2\uparrow$). But Co²⁺ is also reduced to Co. That's why a deep blue color appears at the cathode. This may also absorb impurities on its surface which reflect the particular wavelength. Also partial formation of $\text{Co}(\text{OH})_2$ is possible.

CdCl₂— Hydrogen is formed at cathode. But a few Cd²⁺ migrate to anode and get reduced to Cd ($\text{Cd}^{2+} + 2\text{e}^- \rightarrow \text{Cd}$). *Cu* ionizes at anode to form Cu⁺ (white scummy mass). On exposure to air it gets oxidized to pale blue $\text{Cu}(\text{OH})_2$. Addition of H₂SO₄ results in the formation of blue solution of CuSO_4 .

FeCl₃—Fe³⁺ migrates to cathode but is not reduced. Hydrogen is produced at cathode (reaction already given). $\text{Cu}(\text{OH})_2$ is formed along with reddish

brown $Fe(OH)_3$. Hence the overall color of the precipitate is brown. On addition of acid $Fe_2(SO_4)_3$ is obtained along with small amount of $CuSO_4$.

$NaHSO_4.H_2O$ — *Solution is itself acidic* in nature and turns litmus paper red. Hydrogen is liberated at cathode without any exception. The ionized Cu^{2+} at anode first forms $Cu(OH)_2$ and after wards becomes soluble due to presence of H^+ . Hence *no precipitate* is observed.

$NaCl$ — Solution is a *strong electrolyte* and hence both current and $\Delta I/\Delta t$ are much larger than the remaining solutions. Here also Cu ionizes to give mixtures of Cu_2O (predominant) and $Cu(OH)_2$ which on reaction with H_2SO_4 form $CuSO_4$.

On the basis of the experiment and observations made we may infer the following:—

- A. Electrolysis may be carried at high voltage and low current using a half wave rectifier and domestic supply.
- B. The current is in the range of mA and $\Delta I/\Delta t$ is also small.
- C. The solution gets heated up for currents more than 50 mA. In these cases a water bath should be used for efficient operation.
- D. Relatively weak electrolytes can be electrolyzed at high voltage. For e.g. $NaCl$ which is a strong electrolyte conducts a large amount of current and makes the reaction difficult to control.
- E. The method is cheap and power consumption is low (except for strong electrolytes).

6. Conclusion

High voltage electrolysis has unique characteristics. The current through the solution is low and power consumption is small. Some useful compounds can be synthesized by this method while the conductivity of solutions may be studied. It is seen that the products are different for the same electrode and depend on the solution used. This method is extremely suitable for electrolysis of relatively weak electrolytes where the current is not more than 100 mA.

7. Acknowledgements

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8. References

The electrode potentials have been taken from 'ELECTROCHEMICAL SERIES', Petr Vany'sek © 2000 by CRC PRESS LLC.