

Experiments on electrolysis based on precise observation and analysis of products (Color, Solubility)

Parantap Nandi

AE (Electrical), P.W.D, West Bengal, Ex-Electrical Engineer, WBSEDCL, West Bengal, India

Abstract

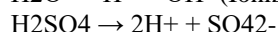
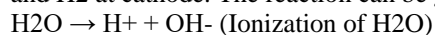
Electrolysis of salts is mainly used for electroplating and electro refining. For this acidic solutions are used (chiefly dilute H_2SO_4). Alkaline solutions are hardly used because metal hydroxides are formed which are mostly insoluble. But precise experiment shows that alkaline solutions can significantly help in metal deposition at cathode as seen case of $SnCl_2 \cdot 2H_2O$ and $(CH_3COO)_2Pb \cdot 3H_2O$ and help in the formation of salts like $(CH_3COO)_2Cu$ which can-not be synthesized generally. Organic compounds like alcohols can form salts by this process salts containing RO^- (R being an alkyl group primary or secondary). If acidic alcohols are electrolyzed, aldehydes and carboxylic acids are formed. So the difference can be easily noticed. Highly covalent aromatic compounds like benzene, toluene e.t.c. can accelerate some reactions, retard some and some times change the products.

In this Paper it has been discussed about the electrolysis of $Ca(NO_3)_2 \cdot 4H_2O$, $SnCl_2 \cdot 2H_2O$, $(CH_3COO)_2Pb \cdot 3H_2O$ in alkaline medium and how organic compounds like benzene can affect the products.

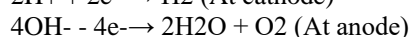
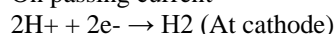
Keywords: $Ca(NO_3)_2 \cdot 4H_2O$; $SnCl_2 \cdot 2H_2O$; $(CH_3COO)_2Pb \cdot 3H_2O$, C_6H_6 , 2 Butanol, NaOH

Introduction

The primary idea of electrolysis comes from the electrolysis of acidulated water with dilute H_2SO_4 and inert electrodes like Platinum, graphite (carbon) which gives O_2 at anode and H_2 at cathode. The reaction can be given as:-



On passing current



Bubbles are formed at both electrodes due to the liberation of gases. But as $d[H_2]/dt = 2d[O_2]/dt$, bubbles of O_2 are formed at a slower rate.

Principle applications of electrolysis include electro refining and electroplating in which cathode and anode are both metals. For instance for electroplating of copper, $CuSO_4$ solution is taken as electrolyte. Sometimes dilute H_2SO_4 is added to increase conductivity.

When salt solutions having cations of high reduction potential like Ca^{2+} are electrolyzed using inert electrodes like graphite, H_2 is liberated at cathode (because the other cation has more negative reduction potential than H_2 which is 0V). At anode O_2 is released but it corrodes graphite into tiny particles. The cathode reaction remains same in all cases. But if metallic electrodes are used, two cases arise:-

1. If anode is inert like platinum, O_2 is released. But anode does not corrode. Only a thin coating of oxide develops.
2. If anode is reactive like copper, O_2 is not obtained. Cu ionizes into Cu^{2+} and combines with OH^- to form pale blue $Cu(OH)_2$. Consequently no bubble is observed.

So if pure salt solution is used, anode ionizes if it is not inert in to hydroxides and H_2 is liberated at cathode. Even if a salt containing a cation having low negative reduction potential like Sn, Pb is used the respective metals can-not be

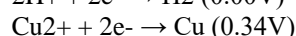
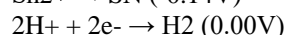
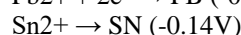
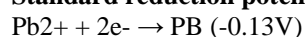
deposited at cathode. H_2 is formed which causes formation of bubbles at cathode. If Sn has to be deposited, $SnCl_2$ solution must be acidified using a suitable acid like HCl.

Experiment reveals that alkalis like NaOH, $Ba(OH)_2 \cdot 8H_2O$ can change the cathode reaction resulting in more than one product at cathode (like H_2 and Sn as will be discussed in this paper).

Salts studied

$Ca(NO_3)_2 \cdot 4H_2O$, $SnCl_2 \cdot 2H_2O$ and $(CH_3COO)_2Pb \cdot 3H_2O$, $Ba(NO_3)_2$.

Standard reduction potentials of various ions studied



Experimental

A. $SnCl_2 \cdot 2H_2O$

1. A mixture of the salt and 4-5 pellets of NaOH were diluted with H_2O .
2. It was electrolyzed using Cu electrodes.
3. Slowly black mass was formed at cathode
4. Cu gradually corrodes.
5. $Ba(OH)_2 \cdot 8H_2O$ if used instead of NaOH, it only slows down the reaction and substantial black mass at cathode is not formed.

B. $Ca(NO_3)_2 \cdot 4H_2O$

1. A mixture of $Ca(NO_3)_2 \cdot 4H_2O$ and NaOH was diluted with H_2O and boiled.
2. The boiling solution was diluted to about 100ml and electrolyzed.
3. Bright blue mass forms at anode and H_2 is liberated at cathode.
4. After some time bubbles start forming at anode while

formation of the bright blue mass almost stops.

- C. $(\text{CH}_3\text{COO})_2\text{Pb} \cdot 3\text{H}_2\text{O}$ (4 separate experiments were performed with this salt)

Experiment A

1. A solution of lead acetate and NaOH was electrolyzed.
2. Black mass is deposited at cathode which reduces the conductivity of Cu.
3. Slowly a clear blue solution forms.
4. Anode corrodes and no bubbles are observed.

Experiment B

1. $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ was used instead of NaOH in experiment (a).
2. No blue solution was formed.
3. Pale blue $\text{Cu}(\text{OH})_2$ was formed which is insoluble.
4. No Black mass was obtained at cathode. Formation of bubbles indicated the production of H_2 at a slow rate.

Experiment C

1. About 20 m.l. alkaline solution of $(\text{CH}_3\text{COO})_2\text{Pb} \cdot 3\text{H}_2\text{O}$ (alkali used was NaOH) was boiled with 2 butanol for 5 minutes.
2. The hot solution was diluted to about 100 M.L. and electrolyzed.
3. Bright green mass forms at anode which slowly dissolves to form a green solution.
4. This color strictly varies from the one obtained in experiment (a).

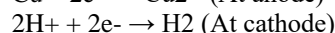
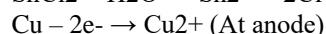
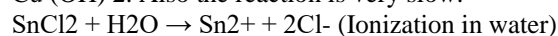
Experiment D

1. $(\text{CH}_3\text{COO})_2\text{Pb} \cdot 3\text{H}_2\text{O}$ and C_6H_6 were boiled.
 2. Two layers of liquids are formed.
 3. The hot liquid is poured in a beaker.
 4. In the same test tube an equal volume (10m.l.) of NaOH is added and boiled.
 5. A brick red mass is formed
 6. It is poured in the beaker, diluted to about 60m.l. and electrolyzed.
 7. Very quick deposition of black mass at cathode occurs.
 8. Anode corrodes very slowly and need not be replaced for a long time. Bubbles are formed at anode.
- D. $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$
1. The salt in its pure state is heated till it melts and starts to boil.
 2. To the boiling mass $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ is added and heated.
 3. The mixture swells and foams and turns yellow.
 4. Little NaOH is added and allowed to react.
 5. After 5 minutes the mass is diluted to 100m.l. and electrolyzed.
 6. Light green mass forms at anode.
 7. It is allowed to stand for about 12 hours. The entire green mass changes to brick red.
 8. Bubbles are formed at cathode.
- E. $\text{Ba}(\text{NO}_3)_2$
1. Alkaline solution of the salt was electrolyzed.
 2. The solution shows very poor conductivity.
 3. A little blue mass at anode is formed. H_2 bubbles at cathode.
- F. $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$
1. Calcium nitrate is heated till it melts and starts boiling.

2. C_6H_6 of an equal volume as the molten salt was mixed with it and boiled.
3. The boiling mass was diluted and with H_2O electrolyzed.
4. The reaction was slower than the electrolysis of pure calcium nitrate solution.
5. Though bubbles were seen forming at cathode, the anode reaction could hardly be detected. This is very different from pure calcium nitrate solution where a pale blue mass of $\text{Cu}(\text{OH})_2$ can be detected within about 10 minutes of switching ON the current.

Contrast noticed when pure salts are used:

$\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ in its neutral solution state gives H_2 at cathode and the anode corrodes to give insoluble mass of pale blue $\text{Cu}(\text{OH})_2$. Also the reaction is very slow.



Every other salt mentioned in this paper shows the same reaction. The only difference lies in their conductivities i.e. calcium nitrate has very high conductivity while lead acetate and stannous chloride show very poor conductivity.

Observations and their explanations

Experiment A

$\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ is fairly soluble in water at S.T.P. Its ionization occurs as:-

$\text{SnCl}_2 + \text{H}_2\text{O} \rightarrow \text{Sn}^{2+} + 2\text{Cl}^-$. As aqueous solution is used, H^+ is also present. Sn^{2+} has more negative reduction potential than H^+ . So cathode reaction is self explanatory, i.e. H^+ is reduced in preference to Sn^{2+} .

Cu has lower oxidation potential than OH^- . So Cu^{2+} and combines with OH^- to give pale blue $\text{Cu}(\text{OH})_2$.

When NaOH is added Na^+ and OH^- increase the conductivity. Cl^- and OH^- migrate to anode. But they have higher oxidation potential than Cu . So anode reaction does not change. But at cathode the reaction gets altered. The ionization of SnCl_2 increases in presence of NaOH as the salt gets hydrolyzed to form $\text{Sn}(\text{OH})_2$. In the solution Sn^{2+} gets oxidized to Sn^{4+} which has a positive reduction potential of 0.15V. So it is easily reduced to Sn^{2+} at first and finally to Sn .

Experiment B

Both $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and NaOH are strong electrolytes. When boiled with water NaNO_3 and $\text{Ca}(\text{OH})_2$ are formed which are also strong. In case of a pure NaOH solution concentration of OH^- is very high. So Cu can not be oxidized. OH^- is oxidized in preference to Cu owing to its high concentration.

For Pure $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ concentration of OH^- is not increased. NO_3^- has high oxidation potential and so Cu ionizes to Cu^{2+} .

When a mixture of both is used, the solution contains H^+ , Ca^{2+} and Na^+ . The reduction potential of Na^+ and Ca^{2+} is very high as compared to H^+ . So H_2 is liberated at cathode and bubbles are observed.

At anode initially Cu ionizes to form bright blue $\text{Cu}(\text{OH})_2$. Though the said hydroxide is slightly soluble, it increases the concentration of OH^- such that OH^- is oxidized at anode and O_2 is formed. $4\text{OH}^- - 4e^- \rightarrow 2\text{H}_2\text{O} + \text{O}_2$. Now bubbles are seen forming at anode.

Experiment C

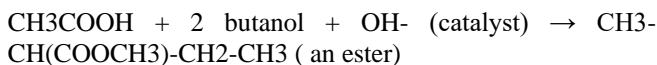
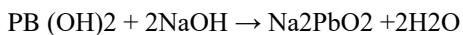
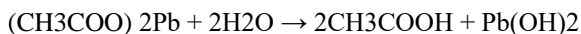
Exp a: $(\text{CH}_3\text{COO})_2\text{Pb} \cdot 3\text{H}_2\text{O}$ in an alkaline medium (NaOH solution) gets hydrolyzed to form CH_3COOH (a weak organic acid) and $\text{Pb}(\text{OH})_2$.

The valency of Pb is 2+ and that of Cu is also 2+. At anode Cu usually forms $\text{Cu}(\text{OH})_2$. $\text{Cu}(\text{OH})_2$ is a base. So it reacts with CH_3COOH to form Blue solution of $(\text{CH}_3\text{COO})_2\text{Cu}$. At cathode Pb^{2+} is deposited as a black mass. The solution contains Cu^{2+} coming from $(\text{CH}_3\text{COO})_2\text{Cu}$ and Pb^{2+} ($\text{Pb}(\text{OH})_2$ is amphoteric, so it reacts with NaOH to form Na_2PbO_2). But concentration of Cu^{2+} is negligible as compared to Pb^{2+} . So Pb^{2+} gets reduced in preference to Cu^{2+} .

If neutral lead acetate is used, hydrolysis is not possible. So at anode $\text{Cu}(\text{OH})_2$ is obtained and H_2 is liberated at cathode. The H^+ (for H_2) and the OH^- for $\text{Cu}(\text{OH})_2$ comes from H_2O . The charges are balanced which need not be explained.

Exp B: $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ is a weak alkali as compared to NaOH. So hydrolysis of $(\text{CH}_3\text{COO})_2\text{Pb} \cdot 3\text{H}_2\text{O}$ cannot take place. Consequently Pb^{2+} can not be deposited and blue solution of $(\text{CH}_3\text{COO})_2\text{Cu}$ is not formed. (In reality it is formed but to such a nominal amount that it can be ignored).

Exp C: $(\text{CH}_3\text{COO})_2\text{Pb} \cdot 3\text{H}_2\text{O} + \text{NaOH} + \text{CH}_3\text{-CH}_2\text{-OH}$ makes the solution both alkaline as well as alcoholic. The following reactions are expected:- OH^-



Also on boiling with strong alkali like NaOH 2butanol gets partly ionized to form 2butoxide ion i.e. H^+ gets separated from OH to give negative charge on O (it is not possible to draw a very neat structure in MS Word). So Cu^{2+} combines with the said ion to form $(\text{CH}_3\text{-CHO-CH}_2\text{-CH}_3)_2\text{Cu}$. CHO is not aldehydic group. Here oxygen and carbon are linked by single bond and Oxygen bears a negative charge. This Oxygen links with Cu. An equilibrium is established between the alcohol and the Cu salt.

Exp D: $(\text{CH}_3\text{COO})_2\text{Pb}$ on heating with C_6H_6 melts and gets denatured. Now when a little amount of concentrated NaOH is added and the mixture is boiled, as usual hydrolysis occurs to give CH_3COOH and $\text{Pb}(\text{OH})_2$. Now due to the presence of C_6H_6 which acts as catalyst Pb^{2+} gets farther oxidized to Pb^{4+} to give brick red PbO_2 . Pb^{4+} has a strong tendency to get reduced (much greater than H^+ , Na^+ which are also present in the solution. So it migrates to cathode readily and gets reduced to Pb^{2+} . As the concentration of Pb^{2+} becomes high around the cathode, it is reduced to neutral Pb.

C_6H_6 being a dielectric increases the concentration of OH^- at the anode which consequently gets oxidized to O_2 . This O_2 tends to convert C_6H_6 into $\text{C}_6\text{H}_5\text{OH}$. Thus anode corrodes at a very slow rate. Hence it is seen that suitable treatment of alkaline lead acetate with highly covalent compound like C_6H_6 not only speeds up the cathode reaction but alters the anode reaction too. But if compounds

Containing oxygen is present, it ionizes and therefore can not act as dielectric. So this reaction does not occur for alcohols.

Experiment D

Both $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ contain water of crystallization. When heated H_2O becomes free. SnCl_2 produces HCl which reacts with NO_3^- from $\text{Ca}(\text{NO}_3)_2$ to liberate NO_2 (yellow). The reaction is similar to synthesis of HNO_3 by laboratory method using H_2SO_4 and KNO_3 . Here some of the HNO_3 decomposes to give NO_2 which remains soluble imparting yellow color.

On addition of NaOH the solution starts to neutralize. Thus the yellow color disappears. When it is diluted the solution contains Na^+ , Ca^{2+} , H^+ and Sn^{2+} . Here H_2 is liberated at cathode just as electrolysis of neutral salt solution. Now in case of alkaline SnCl_2 solution (without Ca^{2+} and NO_3^-) Sn was deposited as was seen in Experiment A. So the presence of these two ions stops the reduction of Sn^{2+} at the cathode.

Anode corrodes into $\text{Cu}(\text{OH})_2$ for sometime. After that OH^- due to excessive concentration starts to get oxidized at anode liberating O_2 . But corrosion of anode doesn't totally stop. Since OH^- is getting oxidized, Cu is no longer able to hold 2 hydroxide ions. So it decomposes to form unstable CuOH which changes to brick red Cu_2O and settles at the bottom. It is insoluble and after about 5 days gets oxidized to black CuO .

Experiment E

Pure solution of $\text{Ba}(\text{NO}_3)_2$ has very poor conductivity. On mixing NaOH, NaNO_3 and $\text{Ba}(\text{OH})_2$ is formed to some extent. Hence conductivity increases slightly. OH^- can not be oxidized because Ba has great affinity for it. $\text{Ba}(\text{OH})_2$ is more soluble than $\text{Ca}(\text{OH})_2$. All these factors do not let OH^- be oxidized at anode. So anode corrodes slowly to pale blue $\text{Cu}(\text{OH})_2$ and H_2 liberates at cathode. This OH^- and H_2 come from water.

Experiment F

$\text{Ca}(\text{NO}_3)_2$ is a very good oxidizing agent as it contains NO_3^- ion. Boiling it with benzene does not produce any considerable reaction. Conductivity of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ is very high. But Presence of viscous C_6H_6 slows down the movement of ions. It does not allow $\text{Cu}(\text{OH})_2$ settle down and so products are not noticeable for a substantial amount of time.

Results and Discussions

Reduction potential of Cu^{2+} is .34V and that of H^+ is 0.00V. So it is evident that Cu can not displace H_2 from acids. When neutral solutions of salts of alkali metals, alkaline earth, or transition metals like Zn are electrolyzed using Cu electrodes, in each and every case anode corrodes into pale blue insoluble $\text{Cu}(\text{OH})_2$ and H_2 is produced at cathode. The salts used as electrolyte i.e. $\text{Ca}(\text{NO}_3)_2$, $\text{Ba}(\text{NO}_3)_2$, SnCl_2 , $(\text{CH}_3\text{COO})_2\text{Pb}$ remain unchanged in mass and composition. If acidic solutions containing HCl, H_2SO_4 are used $\text{Cu}(\text{OH})_2$ gets dissolved to give CuCl_2 or CuSO_4 .

But electrolysis of alkaline solutions using strong alkalis like NaOH can affect the products to a great extent. The principle effects include:-

- Deposition of metal at cathode as in case of alkaline SnCl_2 and $(\text{CH}_3\text{COO})_2\text{Pb}$ which does not occur if neutral solutions are used.
- Synthesis of compounds like $(\text{CH}_3\text{COO})_2\text{Cu}$ and $(\text{CH}_3\text{CHO}\cdot\text{CH}_2\cdot\text{CH}_3)_2\text{Cu}$ which can not be obtained normally.

Farther the reaction can be accelerated, retarded, and anode products can be altered by addition of covalent organic compounds like C_6H_6 e.g. alkaline $(\text{CH}_3\text{COO})_2\text{Pb}$ gives blue solution of $(\text{CH}_3\text{COO})_2\text{Cu}$ but suitable treatment with benzene gives O_2 at anode.

Though electrolysis of CH_3COOH and alcohols can be done, to obtain salts but the reaction is very slow. It results in the evaporation of alcohols because they are highly volatile.

Conclusion

If electrolysis of salt solutions is carried out using metallic electrodes (like Cu as discussed in this paper) give metal hydroxides at anode which are mostly insoluble. On the other hand if inert non-metal graphite is used, O_2 is liberated at anode but it breaks the graphite anode into tiny carbon particles. Hence it has to be periodically replaced. If acidic salt solution along with Cu electrodes is used, $\text{Cu}(\text{OH})_2$ dissolves to give salt of Cu.

Electrolysis of alkaline solution of weakly electropositive metals like Pb, Sn, can cause deposition of the metal at cathode (explanation already given). Not only this, proper treatment with covalent compounds like C_6H_6 can improve the reaction to a great extent by altering speed and anode products. The color of precipitated mass is different for each neutral solution due to absorption of different wavelengths which is beyond the scope of this paper.

The effect of alkalis on solutions is best noticed for metals having negative reduction potential close to zero e.g. Pb, Sn.

Acknowledgement

This research has been financed and encouraged by Mr. P.B. Nandi and Mrs. K. Nandi.

References

1. An Introduction to Electrochemistry by Samuel Glasstone.
2. Electrochemical Methods by Allen J. Bard.
3. Fundamentals of Electrochemistry by V.S Bagotskii.
4. Inorganic Chemistry. Principles of structure and reactivity by James E. Huheey.
5. Organic Chemistry: Principles and Mechanisms by Joel Karty.
6. Classics in total synthesis by K.C. Nicolaou.