International Journal of Chemical Science
Online ISSN: 2523-2843, Print ISSN: 2523-6075
Impact Factor: RJIF 5.22
www.chemicaljournals.com
Volume 1; Issue 2; November 2017; Page No. 45-47

Preparation of di oxygen (O_2) from water using nitrate (NO_3-) ion and partially inert iron (Fe) electrodes

Parantap Nandi
Electrical engineer, University of Calcutta, West Bengal, India

Abstract

Preparation of H2 is possible by electrolysis of neutral aqueous solutions of every salt of the alkali metals as well as alkaline earth metals. Any conductor (both inert and active) can serve as the electrodes; e.g. when common salt solution (NaCl) is electrolyzed using Cu wires (acting as the electrodes) and a battery, H2 is invariably liberated at cathode. This is evident from the fact that as soon as the current is switched ON, bubbles start forming at cathode.

But O2 is never obtained. Every time the metallic anode ionizes to give the corresponding hydroxides which are generally insoluble. In the above example Cu anode ionizes to Cu2+ and combines with OH- to give insoluble Cu(OH)2. This occurs for any salt (chlorides, nitrates, nitrites, sulphates e.t.c) of alkali or alkaline earth metals. Concentration of the solutions can make no difference. H2 is liberated at cathode and metal hydroxide is obtained at anode. So the anode needs to be replaced. This happens because metals like Cu, Ni, Zn all have a greater tendency to lose electrons than OH-.

The only way to obtain O2 is to use an inert anode like graphite, platinum (Pt).

But Ca(NO3)2.4H2O and rusted Fe can alter the picture. When a highly concentrated solution of calcium nitrate (made saturated by heating) is electrolyzed using old Fe (may be nails) having rust on their surface, O2 is obtained at anode. Fe becomes partly inert as will be discussed in the subsequent headings. Very pure Fe(OH)3 is also obtained as a by product which can be easily reduced to Fe.

Keywords: Ca(NO3)2.4H2O, Pb3O4, PbO2, HgO

Introduction

The common processes of preparation of O2 in the laboratory include:-

A. Heating oxides like red lead, lead di oxide, mercuric oxide etc. The corresponding reactions occur as:-
   $2Pb3O4 \rightarrow 6PbO + O2$
   $2PbO2 \rightarrow 2PbO + O2$
   $2HgO \rightarrow 2Hg + O2$
B. Heating salts like chlorates, per chlorates, nitrates of transition metals (but not alkali metals).
   $2KClO3 \rightarrow 2KCl + 3O2$
   $2Pb(NO3)2 \rightarrow 2PbO + 4NO2 + O2$
C. Treatment of peroxides with water.
   $2Na2O2 + 2H2O \rightarrow 4NaOH + O2$
D. The most common process is to heat H2O2 in presence of MnO2 as catalyst.
   $2H2O2 \rightarrow 2H2O + O2$
E. Electrolysis of acidified water (usually containing a few drops of dilute H2SO4) with Pt electrodes where O2 is liberated at anode.
   $4OH- - 4e- \rightarrow 2H2O + O2$ (The red – means subtraction)

But the above procedures are not very advantageous because:-

a. The named oxides, salts and peroxides are all very expensive.
b. In most cases the entire O2 in the compound can not be obtained. This is clearly visible from the decomposition of red lead where we see that the major part of the oxygen remains combined with Pb. The same is noticed in case of Pb(NO3)2.
c. If electrolysis is adopted, inert electrode is a must. Every inert electrode has its own disadvantage. Pt is highly expensive. Graphite is soft and there fore breaks into tiny black particles. So it needs to be replaced at regular intervals. The graphite used in lead pencils is a poor conductor and the reaction becomes slow.
d. In case of Cu(NO3)2, in addition to the problems mentioned in point b high temperature is required which leads to wastage of fuel.
e. The most important problem is that a given mass of a compound always yields a fixed mass of O2.

But if an alkaline earth metal nitrate Ca(NO3)2.4H2O is used as electrolyte and rusted Fe as electrodes, O2 can be obtained at anode. The salt mentioned is very cheap in comparison to the oxides or salts and Fe is probably the cheapest metal. Rusty iron nails are found at homes! They can serve as electrodes very well.

A highly concentrated solution of Ca(NO3)2.4H2O containing excess of the salt, if electrolyzed using rusted Fe (may be a nail) liberates O2 at anode. Here the experimental rate of formation of O2 is almost equal to the theoretical one i.e. $\frac{1}{2} d[H2]/dt = d[O2]/dt$.

The iron nail is not brittle unlike graphite. So even a very thin nail having diameter of only about 1.5 mm can be used for a fortnight or even more.

Iron reacts very slowly forming yellow $Fe(NO_3)_3$ without affecting liberation of O_2. As seen in the case of Fe^{3+} salts, ferric nitrate also gets hydrolyzed to form insoluble $Fe(OH)_3$ which when allowed to stand settles at the bottom. This can be filtered out and treated with HNO_3 to give $Fe(NO_3)_3$.

After the entire H_2O has been used up, $Ca(NO_3)_2$ may be recovered unchanged in mass as it does not take part in the reaction.. Though some O_2 of H_2O is used up in the formation of $Fe(OH)_3$, it does not matter because both water and iron are very cheap and easy to find. $Fe(OH)_3$ can converted back to pure Fe (about 99%).

Experimental

60 ml of water was taken in a 100ml beaker. 30 cc of $Ca(NO_3)_2.4H_2O$ was added. A saturated solution was prepared by stirring and mild heating. When the temperature was about 50°C heating was stopped.

Two rusted iron nails about 2mm in diameter and 5cm long were just washed with tap water and used as electrodes. Current was supplied from a 9V battery.

For about 30s nothing could be seen but after that bubbles started forming both at anode and cathode.

After the experiment was over, the solution was allowed to stand and insoluble $Fe(OH)_3$ settled at the bottom which was filtered out with a filter paper and dried in bright sunlight. $Ca(NO_3)_2$ was obtained by evaporation. This is almost pure except a very low concentration of Fe^{3+} which was not precipitated. But strictly speaking, this concentration is so minute that it can be easily neglected and $Ca(NO_3)_2$ can be reused.

**This experiment works best when the battery is 7-9V. But if very large quantity of O_2 is desired, a 6V, 4-6A rechargeable battery is preferable.

Observations

$Ca(NO_3)_2.4H_2O$ is a deliquescent salt and dissolves very easily to form a clear colorless solution. After about 30s of switching ON the current bubbles are observed at both electrodes. As stated in reaction dynamics H_2 bubbles form a bit more vigorously than O_2. But O_2 also forms at a pretty fast rate and can be easily seen by the naked eye.

Slowly the solution turns yellow due to ionization of Fe in to Fe^{3+} but it does not affect the rate of O_2 formation. It remains same throughout the entire duration of the reaction.

When current is switched OFF and the solution is allowed to stand, $Fe(NO_3)_3$ begins to get hydrolyzed to form insoluble $Fe(OH)_3$ which settles to the bottom forming a yellow precipitate.

Explanations

NO_3^- is a very strong oxidizing agent. When $Ca(NO_3)_2.4H_2O$ is added to water it ionizes as:-

$$Ca(NO_3)_2.4H_2O \rightarrow Ca^{2+} + 2NO_3^-.$$

Ca^{2+} has high negative reduction potential of-2.868V whereas that of H^+ is 0.00V. So the liberation of H_2 at cathode in preference to Ca^{2+} despite high concentration of Ca^{2+} is self explanatory.

OH^- and NO_3^- both migrate to anode. NO_3^- is highly oxidizing and since OH^- is available Fe_2O_3 (rust) develops a coating of Fe_3O_4. This reaction is some what similar to reaction between Fe with concentrated HNO_3 which renders Fe inert by forming a coating of Fe_3O_4. So high concentration of OH^- and NO_3^- in the vicinity of anode produces HNO_3 and O^{2-} (oxide ion). The oxide ion oxidizes Fe anode into passive Fe_3O_4. This electrode is about 75% inert and helps in oxidation of OH^- in to O_2 (oxygen gas).

Only 10% NO_3^- can combine with Fe and become $Fe(NO_3)_3$. This is because though Fe_3O_4 is inert, the anode remains positive. So a small fraction of Fe loses electrons and forms Fe^{3+}. This also highlights the high oxidizing ability of NO_3^-.

In every other solution e.g. $CaCl_2$, Fe^{2+} is first observed (mostly dirty green in appearance).

$Fe(NO_3)_3$ is hydrolyzed in to $Fe(OH)_3$ and so the quantity of Ca^{2+} and NO_3^- remain same as the initial concentration.

Mechanism of the reaction

$$Ca(NO_3)_2.4H_2O \rightarrow Ca^{2+} + 2NO_3^- + 4H_2O$$

A small portion of the salt gets hydrolyzed as:-

$$Ca(NO_3)_2 + 2H_2O \rightarrow Ca(OH)_2 + 2HNO_3$$

But as H^+ is repelled by anode, the ions in its vicinity are NO_3^- and OH^-. NO_3^- can not be oxidized in a concentrated solution. So OH^- must be oxidized. As anode is passive as discussed earlier Fe can not ionize easily to form Fe^{3+}. This provides an opportunity for the negative OH^- to lose electrons.

$4OH^- - 4e^- \rightarrow 2H_2O + O_2$ (Main reaction at anode)

Formation of $Fe(NO_3)_3$ may be considered as a side reaction. Most of the Fe (about 90%) is unionized. Ferric nitrate ultimately forms very pure $Fe(OH)_3$ from which iron can be recovered very easily.

*** From observations and analysis of the reaction it is evident that:-

Quantity of H_2O is reduced due to its decomposition.

A small amount of Fe is wasted as $Fe(OH)_3$.

$Ca(NO_3)_2$ can be recovered.

Results

Every soluble salt (chlorides, nitrates, nitrites etc) of alkali and alkaline earth metals when electrolyzed can give H_2 at cathode irrespective of the electrode used (inert or reactive). But liberation of O_2 is possible only when anode is inert (Pt, graphite). Their disadvantage lies in the fact that:-

a. Pt is extremely expensive.
b. Graphite is very soft. Though it is inert, it is broken to tiny bits which float in the solution. So it needs to be replaced at regular intervals. Also graphite used in lead pencils is a poor conductor. This slows the reaction. The graphite used in batteries is not easily available. Handling thin graphite rods of diameter~ 1mm is very difficult as it is very brittle.

High oxidizing property of NO_3^- ion and the passive character of Fe_3O_4 (a mixed oxide) makes liberation of O_2 at anode possible during electrolysis of a concentrated solution of $Ca(NO_3)_2$.

This property of NO_3^- is very unique as no other anion is capable of showing the above reaction.

But concentration of NO_3^- should be **more** than the metal ion. For this reason alkaline earth metal nitrates are more favorable than alkali metal nitrates.

$Ca(NO_3)_2$ can be recovered very easily. $Fe(OH)_3$ is obtained in very pure form. The corrosion of Fe is very slow and so anode does not need frequent replacement.

Significance of this phenomenon:

1. The main significance is in the reduction of expense.
2. The electrode is very easily available(it is found in almost every house as nail etc)
3. Unlike graphite, conductivity of Fe is high.
4. A piece of Fe (nail for instance) of 2mm diameter serves the purpose of about 20 such graphite rods of same diameter. So no doubt it is long lasting.

Conclusion

For production of O_2 by electrolysis, inert electrodes are required. They are very expensive as in Pt or they are very fragile and difficult to handle as in graphite. Moreover graphite needs replacement frequently and its conductivity is also low.

The unique oxidizing property of NO_3^- and inertness Fe_3O_4 can be of assistance. Here O_2 is easily liberated at anode.

But this method is applicable only to nitrates, esp. alkaline earth metal nitrates (e.g. Calcium nitrate as used in this experiment). The following must be kept in mind:-

a. The nitrate solution must be very concentrated.
b. The iron must contain only Fe_2O_3. Traces of impurities e.g. saline water or other salt will not let Fe turn in to Fe_3O_4. So Fe will ionize at anode (in case of impurities) and consequently O_2 won't be obtained.

Acknowledgement

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

References

1. Modern's abc OF Chemistry by Dr. SP Jauhar.