

## Dissolved Oxygen Electrodes

### Clark Cell

The Clark cell discovered by Dr. Clark in 1956. This is basically an amperometric cell that is polarised around 800 mV. Reduction of oxygen is achieved between 400 to 1200 mV. Hence the need for a voltage of around 800 mV. In the Clark cell this is provided externally by a battery source.

The Clark cell is built around the popular Ag/AgCl half-cell and a noble metal such as gold, platinum or palladium.

<b>Anode (Ag) reaction</b> (with Electrolyte KCl or KBr)	$2\text{Ag} + 2\text{Cl}^- \rightarrow 2\text{AgCl} + 2\text{e}^-$ (800mV)
<b>Cathode reaction</b> (Platinum, gold, palladium)	$2\text{e}^- + \frac{1}{2}\text{O}_2 + \text{H}_2\text{O} \rightarrow 2\text{OH}^-$
<b>Net result:</b>	$2\text{Ag} + 2\text{e}^- + \frac{1}{2}\text{O}_2 + \text{H}_2\text{O} + 2\text{Cl}^- \rightarrow 2\text{AgCl} + 2\text{OH}^- + 2\text{e}^-$

This means that every time  $\text{O}_2$  is reduced at the cathode, you get 4 electrons i.e. a current is generated directly proportional to the oxygen reduced (consumed) at the cathode.

### Problems Associated With Clark Cells

Assuming a measurement system without any interference i.e. only dissolved oxygen in water, the Clark cell has 4 major problems that limits its use in continuous operation. These 4 problems are:

- Isolation of Anode
- Zero Shift
- Depletion of Chloride
- Warm-up Time

#### Isolation of the Anode

Since the net result of the chemical reaction is AgCl, there will be over time, a build up a AgCl, which coats the anode. When the active area of the anode is covered, the reaction stops. And the oxygen probe stops working. A simple but impractical solution is the cleaning of the anode to remove the AgCl deposit. This reactivates the probe again.

#### Zero Shift

The  $\text{OH}^-$  ions produced move the pH value of the electrolyte towards the alkaline area. The internal electrolyte (which is normally KCl) at around the neutral pH value now moves into the alkaline range. This shifts the electrolyte potential into the negative range and causes a zero shift. This shift is always present and over time, the electrolyte needs to be changed.

#### Depletion of Chloride

The net reaction also consumes  $\text{Cl}^-$  ions. With time, the chloride ions are consumed and the electrolyte needs to be replenished.

#### Warm-Up Time

In Clark cells, an external polarising voltage of approximately 800 mV is applied to the electrode. When the probe is disconnected, the power supply is cut off. On connecting the probe again, the user must wait for the probe to be polarised i.e. for the current loop to be stabilised. This warm up time is approximately 10 minutes. If you measure during this time, there is normally a higher value displayed.

## Galvanic Cell

The galvanic probe principle was by Macreth in 1964. Since then, there have been a few changes. Eutech Instruments is using a modified probe designed by Hoeffner in 1985.

The idea of the galvanic probe is to avoid the external polarization required in the Clark cell. Even though the cell is an amperometric cell and a 800 mV potential difference is required to reduce the oxygen at the cathode, this can be accomplished by using two dissimilar metals. In the presence of an electrolyte, there is an electromotive voltage produced between 2 metals, which is dependent of the difference in the electrochemical series. If we compare lead and gold or lead and silver, the differential voltage is approximately 800 mV.

Hence, a galvanic probe is really a self-polarising amperometric cell. The single biggest advantage is the fact that the cell is now always ready and there is no warm up time. The cell is also a corrosion cell with the corrosion rate determined by the rate of oxygen consumed at the cathode.

Reaction in a galvanic cell is as described below:

<b>Anode reaction</b> (material: Zinc or Lead)	$Zn \rightarrow Zn^{2+} + 2 e^{-}$
<b>Cathode reaction</b>	$2 e^{-} + (\frac{1}{2})O_2 + H_2O \rightarrow 2OH^{-}$
<b>Net reaction:</b>	$Zn + 2 e^{-} + \frac{1}{2} O_2 + H_2O \rightarrow 2 OH^{-} + Zn^{2+} + 2e^{-}$ $Zn + \frac{1}{2} O_2 + H_2O \rightarrow Zn(OH)_2$ (heavily soluble and stable, transparent) $\rightarrow ZnO$ (white precipitate) + $H_2O$
<b>In summary</b>	$Zn + \frac{1}{2} O_2 \rightarrow ZnO$

1 molecule of oxygen produces 4 electrons i.e. there is a direct relationship between the oxygen consumed at the cathode and the current produced by the cell.

## Maintenance of Electrolyte Volume

$H_2O$  is recreated in a galvanic cell i.e. the electrolyte volume is not consumed. Water molecule is replenished and electrolyte will go on forever and there is no need to change unless there is a problem with the membrane. Typical YSI probes need to be replenished (electrolyte) and rinsed (anode) every 2 weeks.

## Anode Maintenance

Two systems are available. The Macreth electrode uses the lead anode and the Hoeffner system the zinc anode.

The net result is the formation of either  $PbO$  or  $ZnO$ . Both are reasonably stable but flake off the anode instead of coating it. This increases the life of the anode and reduces the isolation of the anode.

If ZnO covers the anode and process is stopped. The advantage of the Zn alloy comes in here (beryllium, aluminum etc). There are various oxides formed in addition to Zn. Therefore the layer is not uniform and is porous. The oxide falls off and exposes new Zn metal.

Theoretical lifetime of the anode : approximately 10 years. Practical: depends on O<sub>2</sub> level and temperature; at 10 ppm and 25 °C à 5 years life

## Electrolyte Reaction

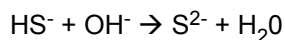
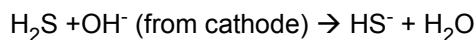
In the Hoeffner cell, the electrolyte is 2M NaCl. The Macreth cells use NaOH as the electrolyte.

## Interference From Gases

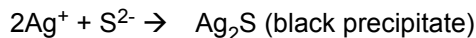
In a dissolved oxygen probe, a gas permeable membrane separates the internal and external environment. The membrane allows any gas to pass through the membrane but does not allow and dissolved elements to pass through i.e. NH<sub>4</sub>, NaOH, HCl etc.

- **SO<sub>2</sub> and H<sub>2</sub>S**

SO<sub>2</sub> is a big problem for most probes. At high pH values it forms H<sub>2</sub>S. This is biggest problem faced by most cells. H<sub>2</sub>S is a by-product of anaerobic respiration. Any organic matter attacked by bacteria produces H<sub>2</sub>S during the decay process. H<sub>2</sub>S is easily recognized by its rotten egg smell. The problem arises when H<sub>2</sub>S passes as a gas into the cell.



Sulfide ions attack silver



The Ag<sup>+</sup> cathode in the Hoeffner electrode is protected by the electrons i.e. negatively charged. As such, it repels the S<sup>2-</sup> ions.

In the Clark cell, there is a silver anode, which it is positively, charged i.e. forms Ag<sup>+</sup> ions. Hence, Clark cells are easily attacked by H<sub>2</sub>S.

- **Ammonia**

Ammonia normally does not exist at neutral pH values. At this pH values, it exists as ammonium ions. In a very high alkaline environment, above pH 11, ammonia is formed and causes a problem as it can permeate the gas membrane. This is a problem with Pb – Ag / Pb – Au galvanic cells as the electrolyte is normally NaOH (pH > 12).

- **Helium and Nitrogen**

Helium and nitrogen diffuse through the membrane but has no effect on the probe. The diffusion carries on until an equilibrium is achieved between the gas on either side of the membrane.

- **CO<sub>2</sub>**

This creates a problem with Hoeffner electrode. Normally, CO<sub>2</sub> level is very low and if the O<sub>2</sub> is 10 times greater than CO<sub>2</sub>, it is OK.

The Hoeffner electrode is not recommended for measuring below 10 % saturation in cases where there is CO<sub>2</sub> present.

### **Stability Of Reading**

Initially, the oxygen in the electrolyte needs to be consumed. This takes around a day.

But the electrode can be used immediately after calibration as this phenomenon only shifts the zero a little.

The real problem is with the replacement of membrane or replenishment of electrolyte. With every change, the probe takes time to achieve mechanical stability.

If there is a slow drift or unstable readings, it means that the membrane is faulty. Replace membrane for better reading.

### **Relationship Between % Saturation And PPM Reading**

The dissolved oxygen probe is really a probe that measures the partial pressure of oxygen in water. At a temperature of 20 °C and an atmospheric pressure of 1013 mbar, saturated water can contain about 9 mg/l of oxygen.

The relationship between oxygen pressure and the oxygen concentration is dependent on a number of factors including:

1. Temperature
2. Atmospheric pressure/altitude
3. Salinity

#### **1. Temperature**

The temperature of the solution has an inverse relationship to the solubility of oxygen. The following table illustrates this fact further:

<b>Temperature °C</b>	<b>Solubility of Oxygen mg/l</b>
0	14.60
20	9.08
25	8.24
40	6.41
50	5.49

As such, the increase in temperature reduces oxygen content. This relationship is non-linear and has been established empirically

#### **2. Atmospheric Pressure / Altitude**

Due to the fact that the oxygen pressure reduces at higher altitude, the solubility of oxygen reduces with increase in altitude (or reduction of atmospheric pressure).

### 3. Salinity

Salinity has an inverse relationship to oxygen solubility. As the salinity of the solution increases, the solubility of oxygen reduces.

In essence, if we need to find the concentration of dissolved oxygen in water, we need to perform the following steps:

1. measure oxygen saturation in sample
2. measure temperature of sample
3. check on maximum oxygen solubility at sample temperature
4. calculate oxygen concentration in mg/l without altitude (pressure) and salinity correction
5. apply altitude correction factor
6. apply salinity correction factor

In the case of the Eutech's CyberScan DO100 meter, all you need to do is to press the MODE key to switch from percent saturation to concentration mode.

### Eutech Instruments' DO Electrode

#### CyberScan DO 100 or CyberScan DO300/310 Handheld Meter

Anode	Zinc
Cathode	Silver
Membrane	25 micron HDPE
Flow rate requirement	5 cm / sec
Electrolyte	NaCl based
Anode lifetime	5 years

If there is a problem with the frequent drifts, clean anode with a blade or emery paper.

#### alpha DO 1000 – General Purpose Probe (Type I)

Anode	Zinc
Cathode	Silver
Membrane	50 micron HDPE
Electrolyte	Type 1: NaCl
Type 1	0.5 to 50 ppm, general purpose
Typical applications	Aquaculture

#### alpha DO 1000 – Low Oxygen (Type 2)

Anode	Lead
Cathode	Silver
Membrane	50 micron HDPE
Electrolyte	

	Type 2: Na <sub>2</sub> CO <sub>3</sub> , sodium carbonate
Type 2 (Macreth principle)	0 to 15 ppm, low oxygen for long periods of time
Typical applications	Biological systems