Chapter 3
Dissolved Oxygen

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3.1 Introduction

Dissolved oxygen (DO) plays a vital role in many industrial[1,2], physiological,[3,4] and environmental processes. The electrochemistry is greatly influenced by the amount of dissolved oxygen because of the reduction of molecular oxygen. Monitoring the percentage of oxygen in cell cultures allows us to screen drugs, cell growth, as well as toxicity analysis. Measurement of dissolved oxygen in the blood reflects the hemoglobin-binding sites occupied by oxygen. If the level of oxygen saturation is low which is called hypoxemia this medical condition is an indication of carbon monoxide poisoning or chronic obstructive pulmonary disease (COPD).[5]

A number of chemical and biological reactions in water also depend on the amount of dissolved oxygen. Monitoring the oxygen in ground or wastewater is an important test in water quality and waste treatment.[6,7] The quality of water can easily be assessed by the concentration of dissolved oxygen since the metabolic activity and growth rate of microorganisms and aerobic cells depend on their oxygen consumption.[8]

The oxygen present in water systems is due to atmospheric aeration and photosynthetic activity. These common sources maintain an adequate level of oxygen in the aqueous environment which is necessary for the existence and growth of all

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forms of life in water. If the concentration of oxygen in aquatic systems falls below 2 mg/L for some time then it can cause the dying of large fish.[9] Thus, the amount of dissolved oxygen is a vital parameter to assess water quality.

The DO level should be kept high in order to maintain freshwater streams for swimming or fishing. If the oxygen level drops too low then fish will suffocate and the aqueous environment will be quite favorable for harmful bacteria. There should also be an optimum level of dissolved oxygen in the wastewater treatment process control because the solids in wastewater are allowed to settle and bacteria are added to decompose this solid. If the concentration of oxygen is quite higher than the optimum level more energy is required for aeration and processes will become expensive. If the dissolved oxygen level is low the aerobic bacteria will die and decomposition ceases.

3.2 Membrane-Covered Electrodes

Selectivity can be introduced to an electrode by covering it with a membrane. This membrane helps the specific analyte in reaching the electrode surface and leaves other substances behind. In addition, these membranes also eliminate the problem of electrode poisoning. The best known example is the Clark electrode which is covered with a polytetrafluoroethylene (PTFE) membrane. This porous membrane assists the diffusion of oxygen only. A platinum or gold electrode is first covered with a thin layer of electrolyte. Then, a PTFE porous membrane is placed over it which hinders other species except oxygen to permeate to the electrode, thus avoiding its poisoning. A potential is applied to the working electrode to reduce oxygen. A silver disc serves as a reference electrode.

3.2.1 Clark's Electrode

Leland C. Clark developed this well-known oxygen sensor in 1956 which is widely used for physiological, industrial, and environmental analysis. It is an amperometric sensor which consists of a working electrode, a reference electrode, and the electrolyte as shown in Fig. 3.1.

The working electrode (cathode) is made of noble metals such as platinum or gold, so the cathode material does not take part in the chemical reaction, whereas the anode is Ag in KCl. A negative potential is applied to cathode relative to the anode (reference electrode) in order to reduce the dissolved oxygen present in the solution by the following reaction:

$$O_2 + 2H_2O + 2e^- \rightarrow H_2O_2 + 2OH^-$$

$$H_2O_2 + 2e^- \rightarrow 2OH^-$$

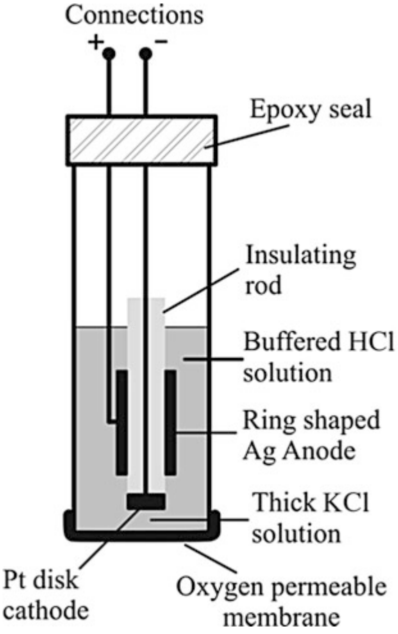

Fig. 3.1 Clark oxygen sensor

The electrode surface is isolated by the oxygen-permeable polymeric membrane in order to avoid the interference of any electroactive species present in the solution along with DO. As a result, only dissolved oxygen present in the sample will diffuse through the membrane and be reduced at the cathode surface due to a negative external potential which will produce an electric current. At a specific value of polarization potential which depends on the cathode material the current is linearly proportional to the oxygen concentration.

3.2.2 Pt-LaF$_3$-Sensing Membrane

Xingbo and co-workers designed a device to determine the DO content[10] with a sensor based on metal insulator semiconductor field effect (MISFET) structure. A LaF$_3$ crystal exhibits extraordinary sensing capability towards oxygen which makes it an attractive material for researchers.[11] In order to fabricate the device, carbon paste with a Pt-LaF$_3$ mixture film was used as a sensing membrane. The sensor was assessed with different oxygen concentrations (5–12 ppm) and output voltage signals were obtained at different temperatures and different biases. The device with Pt-LaF$_3$ sensor film exhibited excellent sensitivity towards DO concentrations. The sensor responded to a change in oxygen concentration producing a gate voltage shift of the MISFET which was used to measure DO concentrations. The gate of the sensor device was developed by following N-type metal oxide semiconductor (NMOS) technology. Then, the sensing film of Pt-LaF_3 was prepared by a carbon paste film. Paraffin wax was used as an adhesive and by melting it at 60 °C it was spread equally on the surface of the gate which helped in preparing the film with the sensing mixture after drying.

The device was operated at a constant drain-source current and voltage. The measurement was carried out with a feedback loop by regulating the reference voltage.[12] The sensor output signals in terms of gate voltage shift were measured as a function of the DO concentration by a digital voltmeter.

LaF_3 was also employed as solid electrolyte while using Pt as a sensing electrode to develop a potentiometric oxygen sensor.[13]

3.2.3 PIDS or TiO_2 Membrane-Coated Sensor

A potentiometric sensor was developed by Martinez-Manez and co-workers in thick film technology.[14] RuO_2 was used as sensitive material whereas this active electrode surface was covered with a semipermeable polymeric (poly-isophthalamide diphenylsulfone, PIDS) or ceramic-based (TiO_2) membrane. The measurement of DO could only be carried out effectively if other redox processes were excluded except the desired reaction which was produced by oxygen.[15] This was achieved by covering the active electrode with a semipermeable polymeric or ceramic membrane which allowed to pass DO and excluded any other redox-active species present in solution. A schematic view of the DO potentiometric sensor is displayed in Fig. 3.2.

This DO electrode consisted of (1) a substrate made of isolating material, (2) a layer of conductive material with (2a) as the terminal side of this material, (3) a layer of sensitive material (RuO_2), (4) a layer of a polymer or ceramic as oxygen-permeable membrane, and (5) an isolating layer exposing the active and terminal sides and covering the rest. The response of the TiO_2-coated RuO_2 electrode was monitored in the presence of oxygen in an aqueous environment. Variations in the

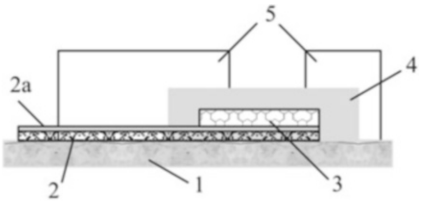

Fig. 3.2 Schematic representation of MISFET for dissolved oxygen electrode: (1) substrate, (2) layer of conductive material, (2a) terminal area, (3) layer of material sensible to oxygen, (4) layer consisting of a membrane ideally permeable to oxygen and non-permeable to ions, and (5) isolating layer, adapted from reference [14]

emf of the active electrode versus an Ag/AgCl reference electrode as a function of DO concentrations in water were obtained. A linear response with a Nernstian slope of 59.4 mV per decade was observed in 0.5–8 ppm DO concentration range. This reaction involved only one electron per oxygen molecule in the reduction process indicating that superoxide (O_2^-) was produced by the reaction $O_2 + 1e^- = O_2^-$.

Excellent emf variations were observed if the active electrode was covered with an oxygen-permeable membrane because the typical interfering species was the proton. Non-coated active electrodes gave a linear response against proton concentrations in comparison to the oxygen-permeable membrane-coated electrode which showed a much lower variation of the potential against pH. The PIDS-coated RuO_2 also exhibited a linear response as a function of DO concentrations in the range from 0.8 to 8 ppm and showed negligible influence from pH, but the only drawback was the inferior adherence of the PIDS membrane in comparison to the titania membrane.

3.3 Modified Electrodes

Aside from covering their surface with a membrane, electrodes can be modified with an electroactive species. These modifiers act as mediators which help with the electron transfer between the analyte and the electrode. Moreover, this modification also helps in lowering the potential needed to reduce oxygen at the electrode surface. The modified electrodes can be prepared by direct adsorption of electroactive species or by physically covering the electrode surface. In some cases, linkers are also employed in order to immobilize the mediators to the electrode surface. Chapter 16.2 of the volume 1 is dedicated to the many different aspects of modified electrodes.

3.3.1 Poly(Nile Blue)-Modified Electrode

Electrodes modified with electroactive polymers exhibit considerable sensitivity and may lower the reduction potential for the detection of oxygen.[16] Actually, the direct reduction of oxygen at solid electrodes requires a highly negative potential. Electroactive metal complexes such as metal-porphyrins or metal-free organic compounds can act as electron transfer mediators and are suitable for electrode modification to determine oxygen.[17] Nile blue is a well-known electroactive mediator for electron transfer. Poly(nile blue) film can easily be immobilized on a glassy carbon electrode by electropolymerization. The resulting layer is very stable which is attributed to the presence of conjugated aromatic rings in the dye. The poly(nile blue) layer possesses significant affinity for dissolved oxygen. By the electrocatalytic activity of this compound oxygen is reduced in a two-electron-two-proton process at a lower potential as shown in Fig. 3.3.[18]

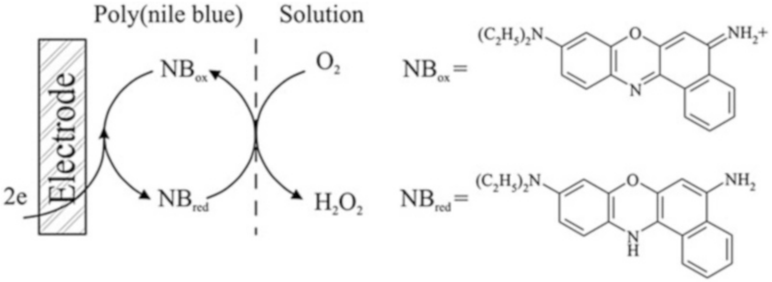

Fig. 3.3 Electrocatalytic action of poly(nile blue) for the reduction of oxygen, adapted from reference [18]

3.3.2 Metalloporphyrin-Modified Electrode

Porphyrins and metalloporphyrins possess distinct properties which make them attractive as a class of material suitable for modifying electrodes.[19] These properties include electrocatalytic activity, or photoreactivity. Hydrolysis and subsequent condensation of silanes with metalloporphyrins create a silica matrix in which metalloporphyrins are covalently bound. The iron(III)-tetra-o-ureaphenyl-porphyrino silica matrix ((o)-FeTUPPS) is an excellent mediator for electron transfer; it is obtained by anchoring iron porphyrin tetraurea to a silica matrix[20]; the resulting layer is highly stable due to the covalent attachment of the porphyrin to the silica backbone.[21]

Modification of the electrode surface with (o)-FeTUPPS leads to the formation of active sites available for the reduction of oxygen which occurs at a less negative potential in comparison to the unmodified graphite electrode. If metalloporphyrins are used for electrode modification, then the reduction of dissolved oxygen can occur via two mechanisms: reduction of oxygen to hydrogen peroxide by a transfer of two electrons, or direct reduction to water when four electrons take part in the process. (o)-FeTUPPS as a modifier catalyzes the two-electron process which leads to the formation of H_2O_2 which is determined by a rotating disk electrode.

3.3.3 Cobalt Tetrasulfonate Phthalocyanine (CoTSPc)-Modified Electrode

In another approach, a DO sensor was proposed by modifying a glassy carbon (GC) electrode with cobalt tetrasulfonate phthalocyanine (CoTSPc).[22] The direct reduction of oxygen at a solid electrode is a slow process and also requires a high negative potential which can be lowered by electron transfer mediators that can shuttle the electrons between oxygen and electrode. Among these mediators, phthalocyanines acquired a lot of attention because of their catalytic ability and stability.[23,24] CoTSPc was immobilized by using a poly-L-lysine (PLL) film which acted as an excellent stabilizer for CoTSPc modifier.[25] This polyelectrolyte avoids leaching of the electrocatalyst due to ion-pair attraction between the amino group of PLL and the sulfonic acid group of CoTSPc. The PLL film alone does not create any effect in reducing dissolved oxygen; the catalytic effect is solely attributed to $[Co(II)TSPc]^{4-}$ as the active site present in the PLL film.

The influence of CoTSPc and PLL amount in the sensor response was analyzed and best results were obtained when using 0.8 mmol L^{-1} of CoTSPc and 0.12 mmol L^{-1} of PLL. The measurements were carried out by differential pulse voltammetry (DPV) and chronoamperometry. With the latter technique a linear response was observed for 0.2–8 mg L^{-1} DO in solution.

In the DPV measurements, the peak current increased with scan rates from 0.005 to 0.02 V s^{-1} but accompanied by a broadening of peaks. Best sensitivity was achieved with a pulse amplitude of 0.075 V and a scan rate of 0.02 V s^{-1}. The DPV measurements showed a linear response at optimized conditions for concentrations from 0.2 to 8 mg L^{-1} oxygen in solution. The device with modified GC exhibited excellent catalytic activity and shifted the reduction potential of DO by 200 mV towards less negative value.

3.3.4 Vitamin B_{12}-Modified Electrode

Cobalt-based macrocyclic complexes are some of the catalysts that exhibit significant catalytic activity against DO.[26] Vitamin B_{12} is a cobalt-based complex and inherits excellent electrocatalytic properties.[27] It can be easily screen printed to modify the electrode providing DO sensors better than the Clark-type electrode. The latter should be covered with a permeable membrane and must be properly maintained. Modifying the electrode with vitamin B_{12} creates a membrane-free DO sensor. Tedious maintenance is not required with this kind of sensor. Moreover, poisoning of the membrane is not an issue anymore. The electrochemical behavior of the vitamin B_{12}-modified electrode involved in the reduction of oxygen can be explained by the following equations[28]:

$$\text{Electrode-vitamin } B_{12}\left(Co^{III}\right) + e^- \rightarrow \text{Electrode-vitamin } B_{12}\left(Co^{II}\right)$$

$$\text{Vitamin } B_{12}\left(Co^{II}\right) + O_2 + 2H^+ \rightarrow \text{Vitamin } B_{12}\left(Co^{III}\right) + H_2O_2$$

$$\text{Vitamin } B_{12}\left(Co^{II}\right) + H_2O_2 + 2H^+ \rightarrow \text{Vitamin } B_{12}\left(Co^{III}\right) + 2H_2O$$

These equations clearly show the electrocatalytic properties of vitamin B_{12}. The electrocatalytic reduction of oxygen leads to the formation of hydrogen peroxide by the electrode; H_2O_2 is then further reduced to water molecules by vitamin B_{12}.

3.3.5 Manganese Phthalocyanine-Modified Electrode

A mixed oxide matrix comprises a porous framework which makes it a perfect substrate for the immobilization of electroactive species.[29] The surface of the mixed oxide network is covered with hydroxyl (-OH) groups which allow functionalization with electroactive species. The electrochemical properties, electrical conductivity, as well as stability of transition metal complexes make them a promising candidate for designing an electrochemical sensor for dissolved oxygen.[30] These properties are associated with the electrons of conjugated bonds and on the central metal atom as well. The manganese phthalocyanine (MnPc) complex can be immobilized on a porous network of a mixed oxide matrix consisting of SiO_2/SnO_2[31] to which the mechanical stability of the film is attributed. Chemical stability results from the strong confinement of electroactive species in the pores of the oxide framework which prevents its leaching over a long time when being in contact with the solution. Moreover, the confinement of metal complexes in the pores ensures a homogeneous layer of electroactive species over the whole-electrode surface.

The reduction of oxygen can occur in two different ways, either involving two electrons yielding H_2O_2 or through reduction to water with four electrons:

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$$

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$$

The estimation of the number of electrons involved in oxygen reduction and the product obtained can be assessed by rotating ring-disk electrode experiments. This technique proved the involvement of four electrons when MnPc complex was used for the modification of electrodes.

3.3.6 Poly(Methylene Blue)-Modified Electrode

Some organic dyes show high electroactivity which makes them useful electron mediators.[32] The electrochemical activity of dyes, such as methylene blue, methylene green, neutral red, and pyronin B, is attributed to their conjugated ring structure.[33] Modification of electrodes with these electroactive compounds (e.g., methylene blue) for the detection of dissolved oxygen yields excellent results. However, problems are associated with their anchoring on the electrode surface because they will leach if they are not properly attached. Many organic dyes can be immobilized on the electrode surface by carbon nanotubes, zeolite, Nafion, silane, or electropolymerization.

Electrodes which are modified with a dye-polymer exhibit usually good stability, conductivity, and enhanced electrochemical sensing behavior. Among a lot of other significant properties silica nanoparticles possess a large surface area and open space for the immobilization of organic dyes without affecting their inherent properties. These nanostructures incorporate dye molecules inside their matrix avoiding their leaching. The dye molecules trapped in silica nanoparticles are able to form a polymer which will form a nanocomposite called polymer(dye)-doped silica nanoparticles. The nanocomposite is electrocatalytically active and exhibits conductive properties as well. The reduction of oxygen in such a nanostructured environment involves three steps[34]:

1. Diffusion of oxygen molecules into the polymeric structure
2. Adsorption of oxygen molecules at the active sites
3. Reduction of oxygen with the aid of the electrocatalyst

Hence, the mechanism of oxygen reduction on polymethylene blue-doped silica nanoparticles (PMB@SiO_2) is described by the following reaction sequence[35]:

Oxygen diffuses into the polymeric structure and subsequently adsorbs at the active sites. Afterwards, it is reduced via electron transfer by the following equation:

$$O_2(ad) + 2H^+ + 2e^- \rightarrow H_2O_2$$

where the reduced leuco form of methylene blue (LMB) acts as the catalyst:

$$\text{Electrode-SiO}_2\text{-poly(LMB)} - ne^- - nH^+ \rightarrow \text{Electrode-SiO}_2\text{-poly(MB}^\bullet\text{)}$$

The overall reaction can be summarized as

$$\text{Electrode-SiO}_2\text{-poly(LMB)} + O_2(aq) \rightarrow \text{Electrode-SiO}_2\text{-poly(MB}^\bullet\text{)} + H_2O_2$$

Leucomethylene blue is regenerated again from the deprotonated form of methylene blue ($MB^\bullet$) by electrochemical reduction:

$$\text{Electrode-SiO}_2\text{-poly(MB}^\bullet\text{)} - ne^- - nH^+ \rightarrow \text{Electrode-SiO}_2\text{-poly(LMB)}$$

3.3.7 Nickel-Salen-Modified Electrode

Electrocatalysts which assist multi-electron transfers are of great interest for the reduction of oxygen because this process involves multiple electron transfer steps.[36] These electrocatalysts facilitate crossing over the activation energy barriers involved in this process.

Transition metal complexes with Schiff bases as ligands attracted a great interest in this respect. These metal complexes can easily be immobilized on electrode surfaces via electropolymerization[37] generating an electrically conductive polymeric film.[38] The reactivity of metal complexes depends on the nature of the metal as well as on the ligand attached.

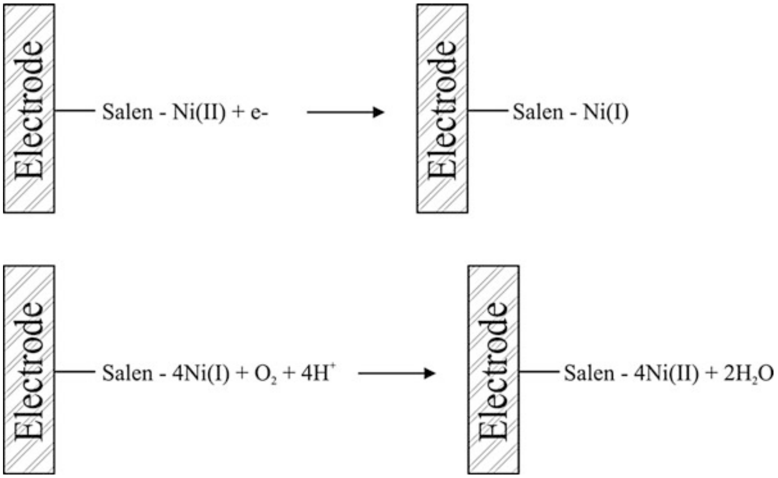

Fig. 3.4 The reduction mechanism of oxygen at Ni-salen-modified platinum electrode, adapted from reference (41)

A thin film of Ni-salen (salen = N,N'-ethylenebis(salicylideneiminato)) polymer on a platinum electrode exhibits a high rate of electron transfer and can be the platform for a highly sensitive system for the determination of oxygen.[39]

The Ni-salen polymer promotes the reduction of oxygen via the Ni(II)/Ni (I) redox couple. Oxygen is reduced directly to water involving four electrons at a significantly decreased potential.[40] The reduction proceeds in two steps as shown in Fig. 3.4 [41]:

1. Ni(II) is reduced to Ni(I).
2. Ni(I) reduces oxygen and is oxidized to Ni(II).

The output of the sensor will be in the form of current which is controlled by oxygen diffusion.

3.3.8 Anthraquinone-Modified Electrode

The high overpotential of the oxygen reduction can be significantly lowered with electrocatalysts which also improve the speed of electron transfer.[42] p-Quinones are recognized as such type of compounds which can transfer electrons in biological systems. Thus, among others, anthraquinones attract considerable interest in this respect because of their p-quinoid substructure which can be easily reduced. In addition, anthraquinones are also conductive and can be shaped into monolayers. Thus, anthraquinones can be used for the modification of electrodes for the reversible electron transfer which is attributed to the p-quinones group.[43] However, these electrocatalysts require to be attached covalently; otherwise these they cannot be used for long-term operation.

The anthraquinone moieties on the surface of electrode show excellent electrocatalytic ability towards oxygen. The reaction involves the reduction of anthraquinone to dihydranthraquinone via two electrons and two protons.[44] Afterwards, dihydranthraquinone reacts with oxygen and converts it to hydrogen peroxide while anthraquinone is regenerated.

3.4 Miniaturized Dissolved Oxygen Sensors

3.4.1 Solid-State Oxygen Sensor

McLaughlin and co-workers designed a microfabricated solid-state oxygen sensor.[45] The device consisted of microfabricated electrodes overlaid by a solid-state proton conductive matrix. It was further encapsulated in a bio-inert polytetrafluoroethylene (PTFE) film. The sensor characteristics exhibited a linear response to oxygen over a concentration range from 0 to 601 μM. It was a Clark-type oxygen sensor matrix consisting of a matrix working electrodes with diameters of 10, 20, 40, and 80 μm; each element of the matrix consisted of a working, reference, and counter electrode having a surface area ratio of 1:5:25 in order to gain higher current density at the working electrode (Fig. 3.5). Afterwards, a proton conductive matrix (PCM) was deposited on the electrode matrix which was a Nafion-perfluorinated ion-exchange resin. The hydrophobic structure of the PCM was permeable to oxygen whereas its hydrophilic region acted as proton transport site. The device was finally encapsulated with a bio-inert PTFE film which was oxygen permeable.

The fabricated sensor device reduced dissolved oxygen electrochemically and monitored the resulting current. This sensor could also be used to measure the oxygen concentration in blood because the electrodes were encapsulated in a bio-inert oxygen-permeable PTFE membrane. The electrochemical reduction of

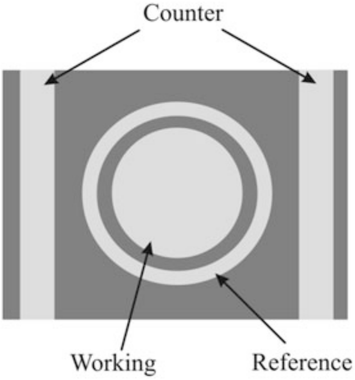

Fig. 3.5 Illustration of an element of the matrix of electrodes, adapted from reference [45]

oxygen is a two-step process which occurs at the working electrode whereas the counter electrode converts it back into reactants.[46]

The mechanism of the oxygen reduction at the working electrode (cathode) is described in the following two equations:

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$$

$$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$$

The products formed at working electrode are converted back into reactants at the counter electrode (anode) by the following process:

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^-$$

This sensor is better than a conventional Clark's device because there is no net consumption of any electrode. Both cyclic voltammetric and chronoamperometric measurements were carried out to analyze the performance of the microfabricated DO sensor. Good linearity was observed when using 80 μm diameter electrode sets.

3.4.2 Microelectrodes

Microelectrodes are among the most advanced, reliable, and excellent sensing systems.[47] A needle-type microelectrode array (MEA) was also designed for measuring the concentration of dissolved oxygen in solution.[48] The MEA was fabricated by following microelectromechanical system (MEMS) technologies. The needle-type nature of the DO sensor allowed the device to penetrate into the environmental sample. The microelectrodes were made of gold due to its potential use in measuring DO[49] as well as a large number of other analytes.[50] The DO-MEA consisted of four 1 cm long electrically isolated microelectrodes. The DO microelectrodes were characterized by using a calibration cell with a commercial Ag/AgCl reference electrode.

The microelectrode array was polarized before calibration with a negative voltage to reduce the amount of oxygen to zero on the cathode of the microelectrode surface which eliminated any disturbances caused by any residual oxygen. Different salinities of water samples produced different sensitivities of the microelectrode array.

The developed dissolved oxygen sensor was capable to operate in multi-species aerobic films.[51] The horizontal and vertical movement of the microelectrodes was controlled by a micromanipulator. Thus, the MEA could measure microprofiles of dissolved oxygen in biofilms. The results depicted that the DO concentration was high at an interface of air–saline solution due to oxygen diffusion. The DO concentration decreased within the saline-biofilm.

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