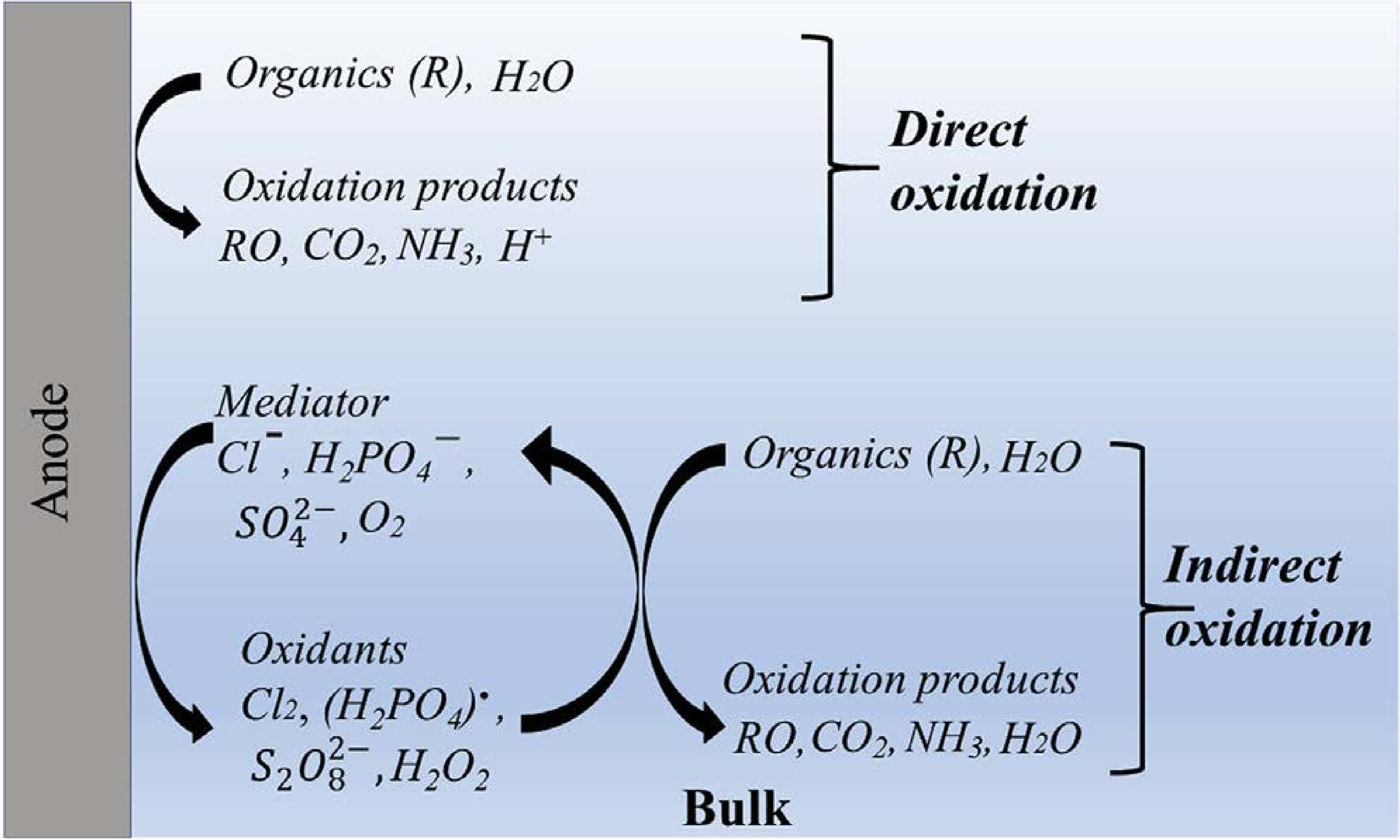
CEE 597T

Electrochemical Water and Wastewater Treatment

UNIT 4
ELECTROCHEMICAL OXIDATION:
Direct And Indirect Electrochemical Oxidation, Electrode Materials

ELECTROOXIDATION OF ORGANIC MATERIALS

- Electrochemical oxidation (EO) is a chemical reaction, involving the loss of one or more electrons by an atom or a molecule at the anode surface made of catalyst material during the passage of direct electric current through the electrochemical systems (anode, cathode, and an electrolyte solution).
- Electrochemical oxidation has been applied successfully to degrade different organic pollutants and disinfect drinking water and municipal wastewaters. Also many industrial wastewaters, such as textile, olive oil, pulp and paper mill and tannery effluents have been treated successfully by this technique.
- There are two main mechanisms for EO of organic compounds in water. They are direct and indirect mechanisms:



Anode

Organics (R), H_2O

Oxidation products

RO, CO_2, NH_3, H^+

Direct oxidation

Mediator

$Cl^-, H_2PO_4^-, SO_4^{2-}, O_2$

Organics (R), H_2O

Indirect oxidation

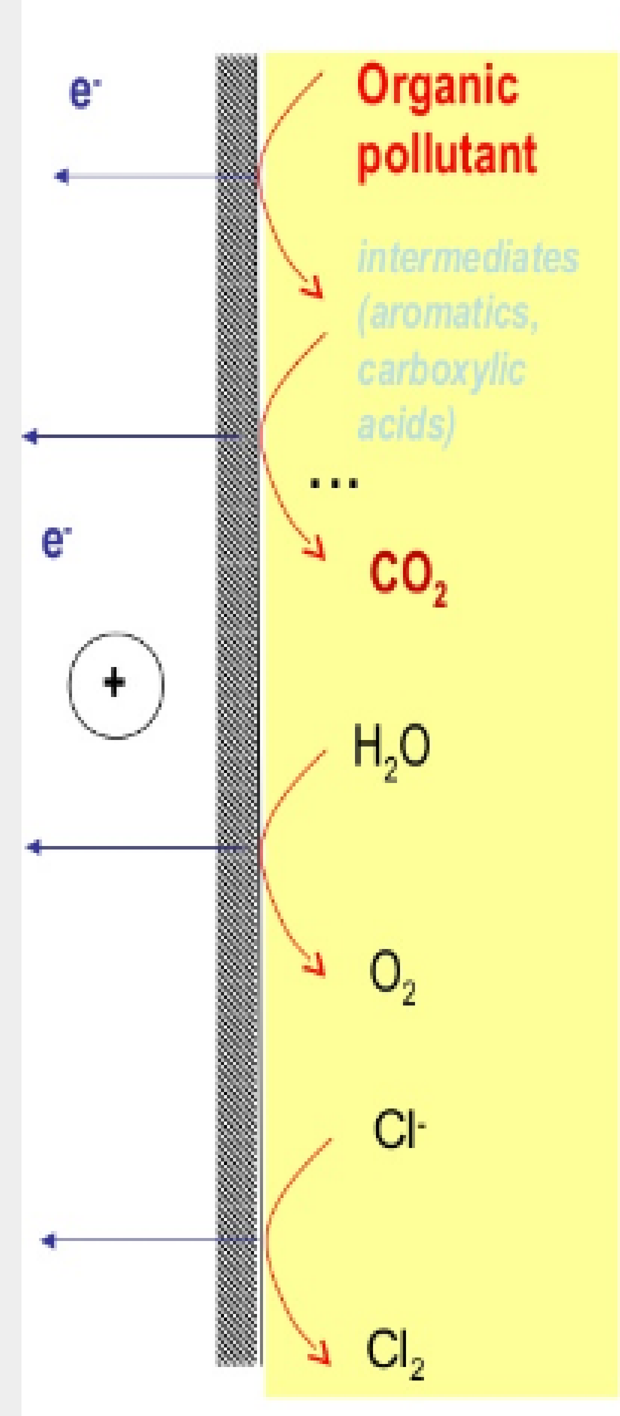
Oxidants

$Cl_2, (H_2PO_4)^\bullet, S_2O_8^{2-}, H_2O_2$

Oxidation products

RO, CO_2, NH_3, H_2O

Bulk



DIRECT ELECTOROXIDATION

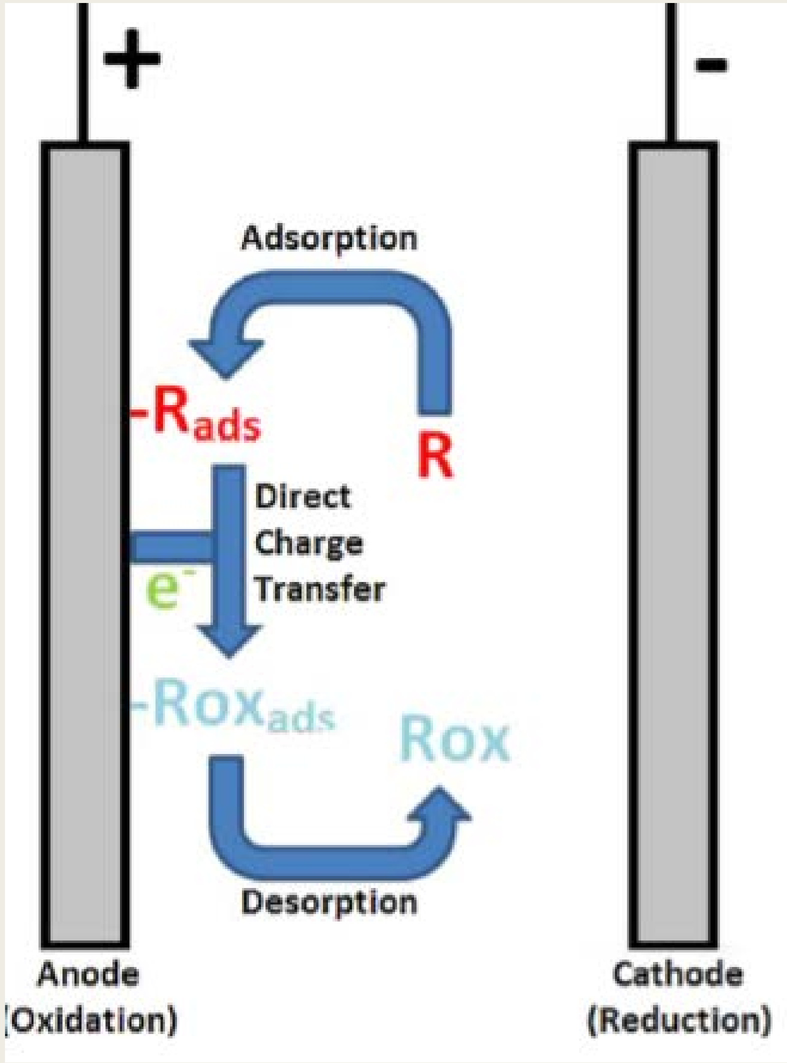
*Direct electrooxidation consist of the direct oxidation of a pollutant on the surface of the anode. To be oxidized the organic must arrive to the anodic surface and interact with this surface. This means that **electrocatalytic properties of the surface** towards the oxidation of organics can play an important role in the process.

*Likewise, it means that in certain conditions mass transfer can control the rate and the efficiency of the electrochemical process.

*The potentials required for the oxidation of organics are usually high. This implies that water can be oxidized and the generation of oxygen is the main side reaction. This is a non desired reaction and it influences dramatically on the efficiencies.

*Frequently the potential is high enough to promote the formation of stable oxidants, through the oxidation of other species contained in the wastewater. This can have a beneficial effect on the efficiency as these oxidants can oxidize the pollutant in all the volume of wastewater.

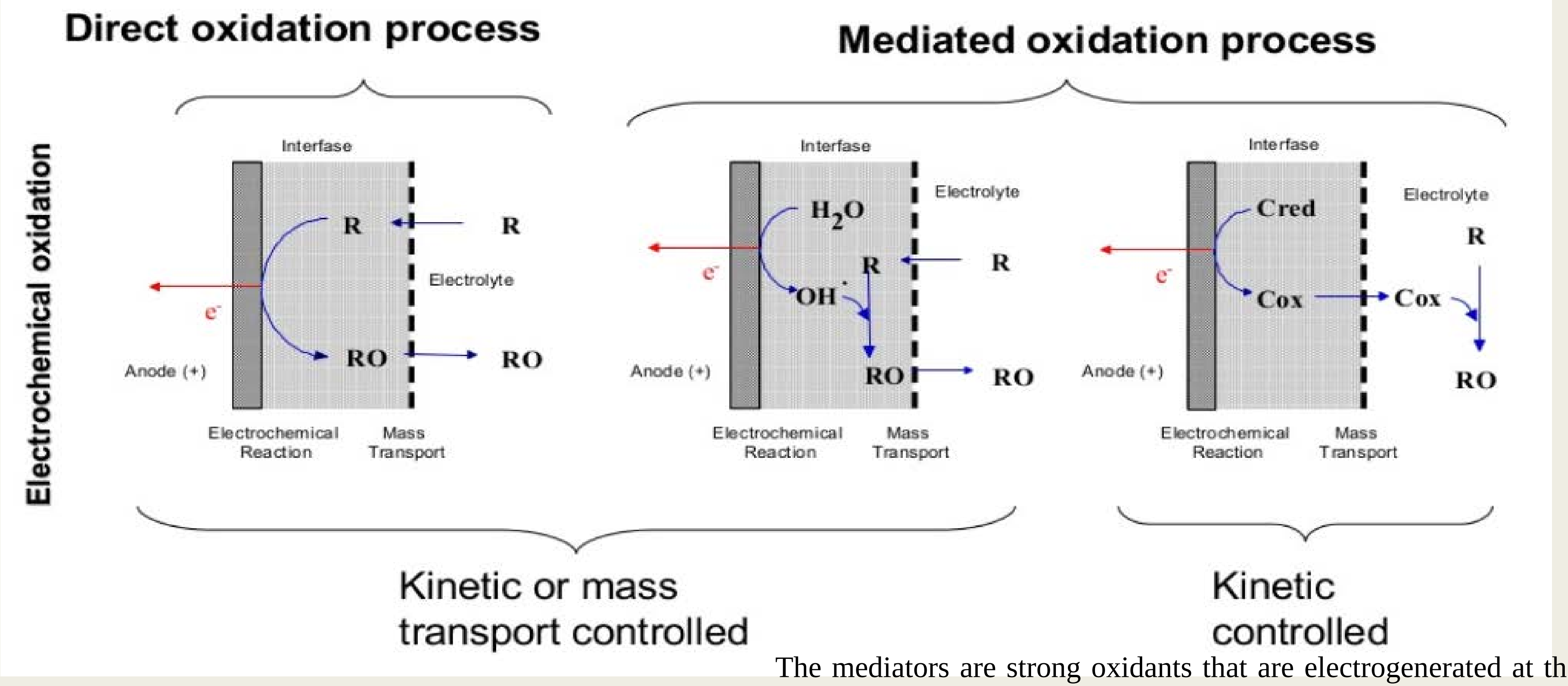
- The direct anodic oxidation or electrolysis occurs directly on the anode (M) and involves direct charge transfer reactions between the anode surface and the organic pollutants involved.
- The mechanism only involves the mediation of the electrons, which are capable in oxidizing some organic pollutants at defined potentials more negative the oxygen evolution reaction (OER) potential.
- The direct electrolysis usually requires prior adsorption of pollutants onto the anode surface, which is the rate-limiting process and does not lead to the overall combustion of organic pollutants.
- In direct electrolysis, the pollutants are oxidized after adsorption on the anode surface without the involvement of any substances other than the electron, which is a “clean reagent”:
- $R_{ads} - ze^{-} \rightarrow P_{ads}$



- Direct electrooxidation is theoretically possible at low potentials, before oxygen evolution, but the reaction rate usually has low kinetics that depends on the electrocatalytic activity of the anode.
- High electrochemical rates have been observed using noble metals such as Pt and Pd, and metal-oxide anodes such as iridium dioxide, ruthenium-titanium dioxide, and iridium-titanium dioxide.
- However, the main problem of electrooxidation at a fixed anodic potential before oxygen evolution is a decrease in the catalytic activity, commonly called the poisoning effect, due to the formation of a polymer layer on the anode surface.
- This deactivation, which depends on the adsorption properties of the anode surface and concentration and nature of the organic compounds, is more accentuated in the presence of aromatic organic substrates such as phenol, chlorophenols, naphthol and pyridine.

INDIRECT ELECTROOXIDATION

- The indirect EO processes are mediated by the in situ electro-generation of highly oxidant species at the electrode surface. Different kinds of oxidant species can be generated by the EO process (i) reactive oxygen species and (ii) chlorine active species.



- Not all pollutants are electroactive.
- During the anodic oxidation, fouling can occur at the anode surface, which can affect or block the transfer of electrons.
- The rate of organic removal is limited by mass transfer, due to the depletion of organic matter in the solution. This limitation by mass transfer leads to a decrease in the current efficiency during electrolysis, which greatly enhances the energetic cost.

The mediators are strong oxidants that are electrogenerated at the electrode from water (hydroxyl radicals), oxygen (ozone and hydrogen peroxide), or from salts (active chlorine or peroxocompounds). Salts may already be present in the effluent, or they can be added to render the solution conductive. The electrogenerated mediators can be classified into one of the following two groups:

(i) Very reactive species with strong oxidizing power. For this case, the chemical reaction with organics is not selective and complete mineralization can be reached. Oxidation is irreversible. The use of a divided electrochemical cell is not required, but the technological implementation is more simple. Moreover, reusing treated wastewater might be considered. The hydroxyl radicals, produced by direct water oxidation, belong to this group. Their half-life is very low (10^{-9} s in water), and their action takes place exclusively close to the anode. Unlike direct oxidation, consequently, this process has mass transfer limitations.

(ii) The other oxidants belong to the selective oxidants group.

Electro-generation of reactive oxygen species

- Reactive oxygen species (ROS) are reactive chemical species containing oxygen such as hydrogen peroxide (H_2O_2), ozone (O_3), or hydroxyl radical (•OH). Their chemical reactivity is due to the oxygen molecule's unpaired electron.
- The generation of such oxidants strongly depends on several key reaction parameters. electrode material,

electrolyte composition,

applied current (or voltage),

pH, and

temperature.

- The anode material is the key parameter. Because all oxidants are formed at high potentials, the competitive reaction is the formation of oxygen. An anode material with a high oxygen overpotential is required.

- The indirect EO by reactive oxygen species is based on the electro-generation of adsorbed hydroxyl radical (•OH) (E◦ = 2.8 V/SHE) onto the anode surface as an intermediate of the OER (1)

Anode: $M + H_2O \rightarrow M(\bullet OH) + H^+ + e^-$ (1)

where, M is referred the anode and M(•OH) is the adsorbed hydroxyl radical.Reaction between an organic compound R and hydroxyl radicals (loosely adsorbed on the anode) takes places close to the anode's surface.(n:the number of electrons involved in the oxidation reaction of R).

$R_{(aq)} + M(\bullet OH)_{n/2} \rightarrow M + \text{Oxidation products} + n/2\ H^+ + n/2\ e^-$ (2)

However, the inevitable competitive reactions (3) and (4) that consume the radical species leading to oxygen evolution are also feasible.

$M(\bullet OH) + H_2O \rightarrow M + O_2 + 3\ H^+ + 3\ e^-$ (3)

$2M(\bullet OH) \rightarrow 2\ M + O_2 + 2\ H^+ + 2\ e^-$ (4)

- In order to produce greater amounts of M(•OH), anodes with high overpotential for OER should be used to promote reaction (1) and to avoid the parasitic reactions (3) and (4). Electrodes for wastewater treatment can be classified under two groups regarding to high overpotential oxygen evolution : “active” and “non-active” anodes.
- The different performance of these anodes is related to the enthalpy of adsorption of the OH radicals onto the anode surface. Physisorbed species are more oxidant than the strongly chemisorbed ones that are represented by reaction (1) and reaction (5), respectively.

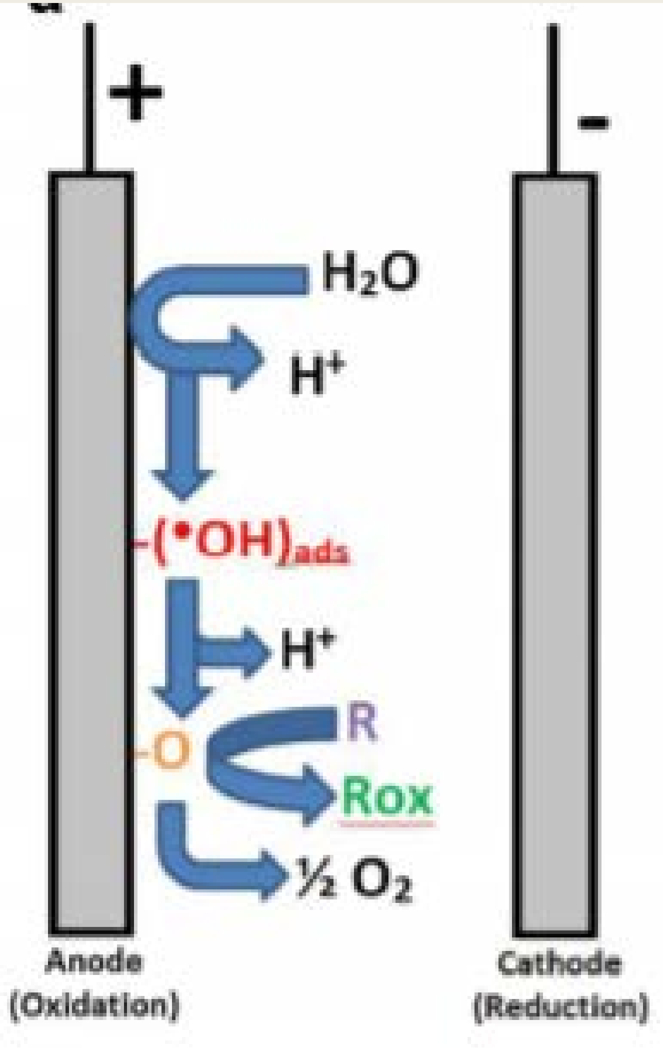
$$\mathrm{M(\bullet OH)} \rightarrow \mathrm{MO} + \mathrm{H}^{+} + e^{-} \qquad (5)$$

where, MO represents the oxidant species of the so-called higher oxide that is generated onto the anode surface by the chemisorption of OH radicals

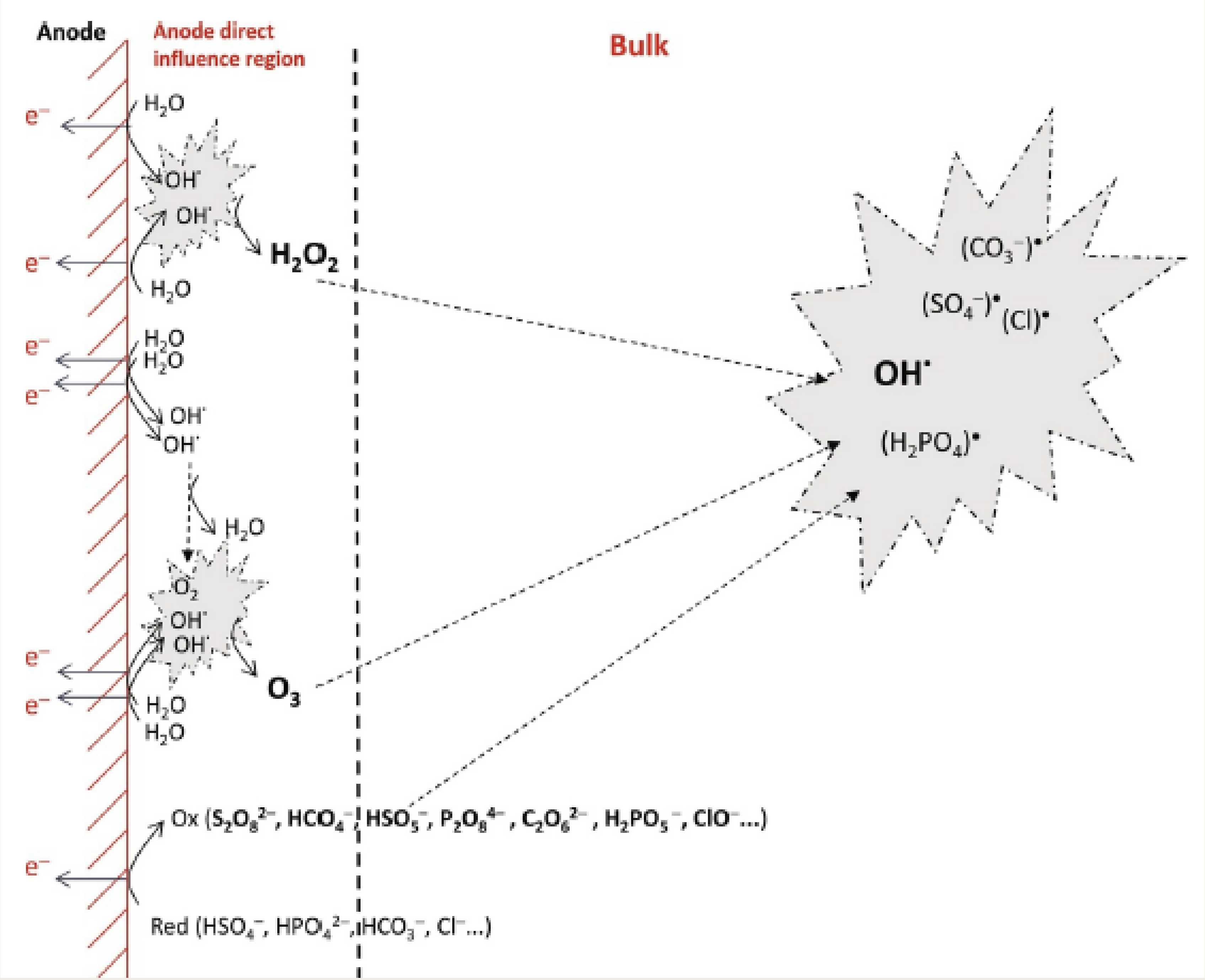
!The active anodes are only capable in inducing the electrochemical conversion of organics into more biodegradable molecules such as short-chain carboxylic acids, but they cannot achieve complete mineralization or organics combustion into carbon dioxide (CO_2)

- This occurs because higher oxidation states are available for these metal or metal oxide anodes above the standard potential for OER (E◦ = 1.23 V/SHE), leading to the preferential formation of chemisorbed active oxygen species MO by the concatenated reactions (1) and (5). Following this, the oxidation is mediated by the reaction of pollutants with the chemisorbed MO.

! Characteristic active anodic materials are platinum (Pt), dimensionally stable anodes (DSA) of ruthenium (IV) oxide (RuO_2), iridium (IV) oxide (IrO_2), and other mixtures of metal oxides.

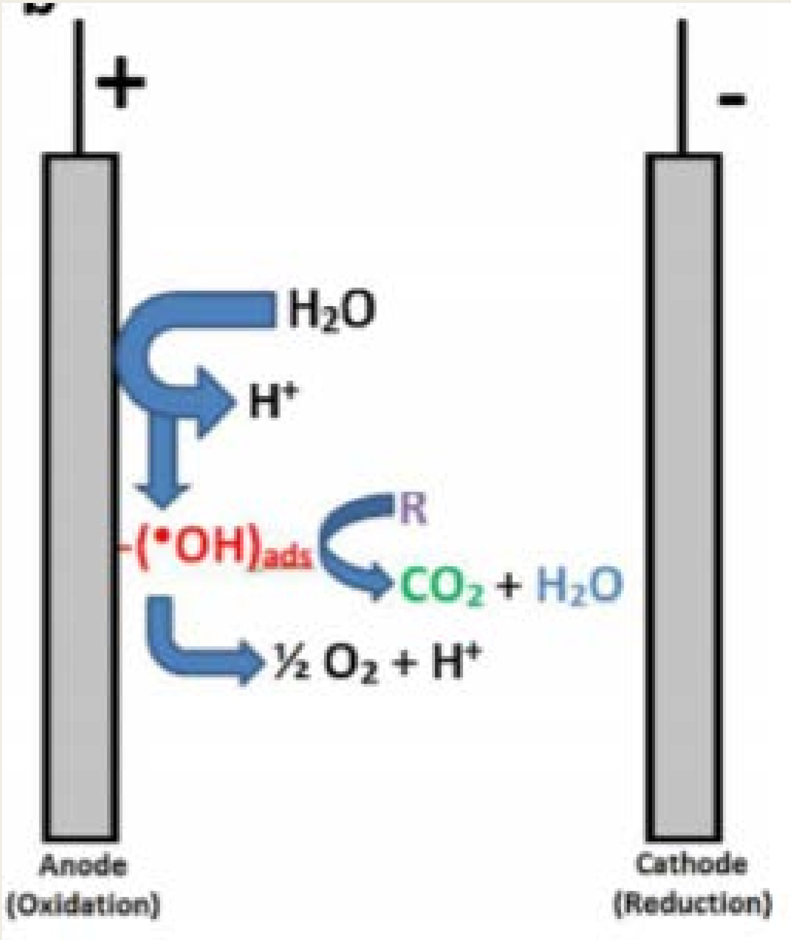


Scheme of the main routes associated with the anodic formation of oxidants



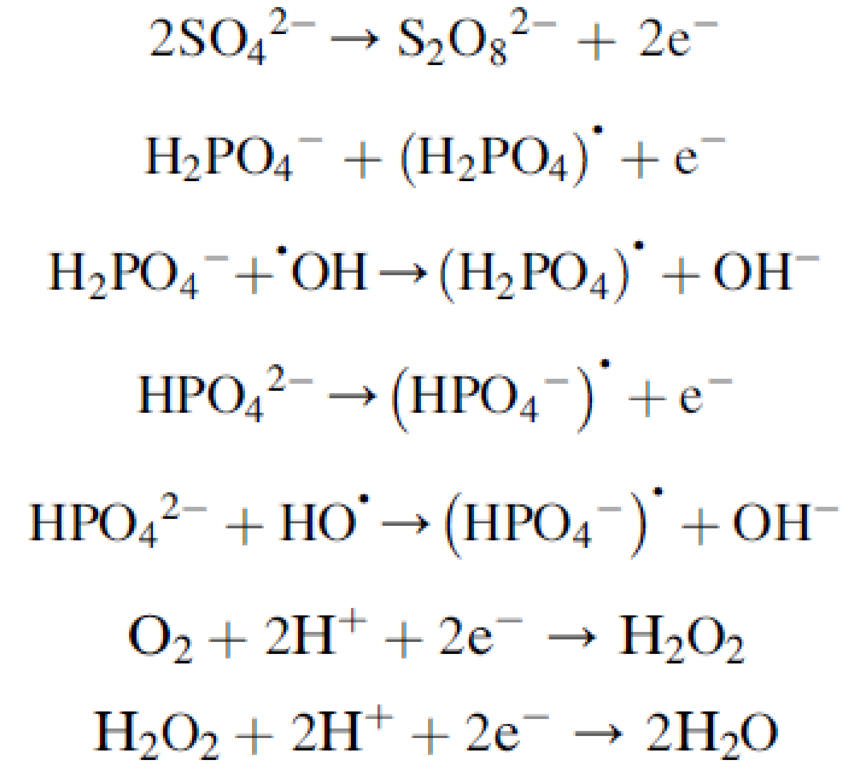
- As for the non-active anodes, the $OH^{\cdot}$ radicals that are electro-generated by reaction (1) remained physisorbed on the anode surface.
- The physisorbed $OH^{\cdot}$ radicals present a major lability, reactivity, and a higher oxidant power for the complete electrochemical incineration of organic pollutants into CO_2.

! Characteristic non-active anodic materials are lead (IV) oxide (PbO_2), tin (IV) oxide (SnO_2) and boron-doped diamond.



Other reactive oxygen species

- One of the main disadvantages of EO of organics with electrogenerated ClO- ions is the formation of toxic chlorinated intermediates especially while working in acidic medium. Therefore, EO by other reactive species is of interest.
- Indirect EO of organic compounds can be enhanced by electro-Fenton reactions, electrogeneration of hydrogen peroxide, peroxodisulfate, peroxidiphosphate, and ozone.



$$2SO_4^{2-} \rightarrow S_2O_8^{2-} + 2e^-$$

$$H_2PO_4^- + (H_2PO_4)^\bullet + e^-$$

$$H_2PO_4^- + {}^\bullet OH \rightarrow (H_2PO_4)^\bullet + OH^-$$

$$HPO_4^{2-} \rightarrow (HPO_4^-)^\bullet + e^-$$

$$HPO_4^{2-} + HO^\bullet \rightarrow (HPO_4^-)^\bullet + OH^-$$

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

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

Cathode

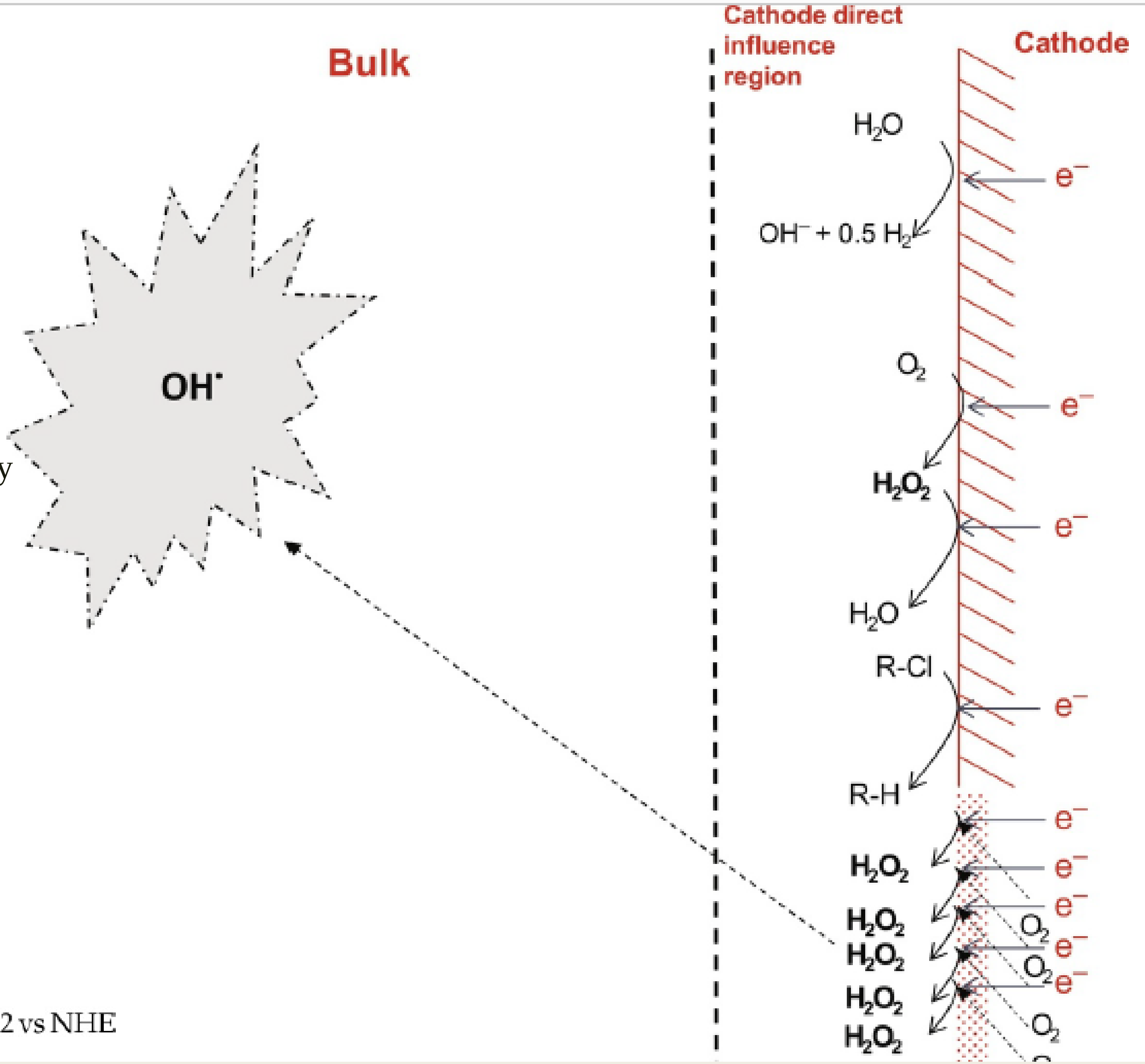
- Typically, water reduction to form hydrogen is the most important cathodic reaction. This reaction has no impact on the remediation of wastewater and, for this reason, materials with low overpotencials are typically used in order to try to attain low cell voltages and, at least, to not increase the operation cost of the wastewater treatment unnecessarily.

- Typically, water reduction to form hydrogen is the most important cathodic reaction.

$$H_2O + e^- \rightarrow 1/2\,H_2 + OH^-$$

- This reaction has no impact on the remediation of wastewater and, for this reason, materials with low overpotencials are typically used in order to try to attain low cell voltages.
- In fact, there are two potentially important ways to use the cathode during the electrolysis of wastewater: the reductive dehalogenation and the production of hydrogen peroxide.
- Reductive dehalogenation of organohalogenated compounds is not the most important cathodic process. The cathodic generation of hydrogen peroxide by the two-electron reduction of oxygen (directly injected as pure gas or bubbled air) ocur at the cathode surface in acidic/neutral media.

$$O_2 + 2e^- + 2H^+ \rightarrow H_2O_2 \quad E^0 = 0.682\ \mathrm{vs\ NHE}$$



Electro-generation of chlorine active species

- The oxidation by electrochemically in situ generated chlorine active species is the other indirect EO process mostly applied to remove organic pollutants.
- The principles are related to the oxidation of chloride anion on the anode that releases chlorine (6). When the electrogenerated chlorine diffuses away from the anode, it is quickly hydrolysed yielding HClO and Cl− by disproportionation (7), with the hypochlorous acid in acid-base equilibrium with hypochlorite anionic species by reaction (8) with pKa = 7.55

Anode: $2Cl^- \rightarrow Cl_2(aq) + 2e^-$ (6)

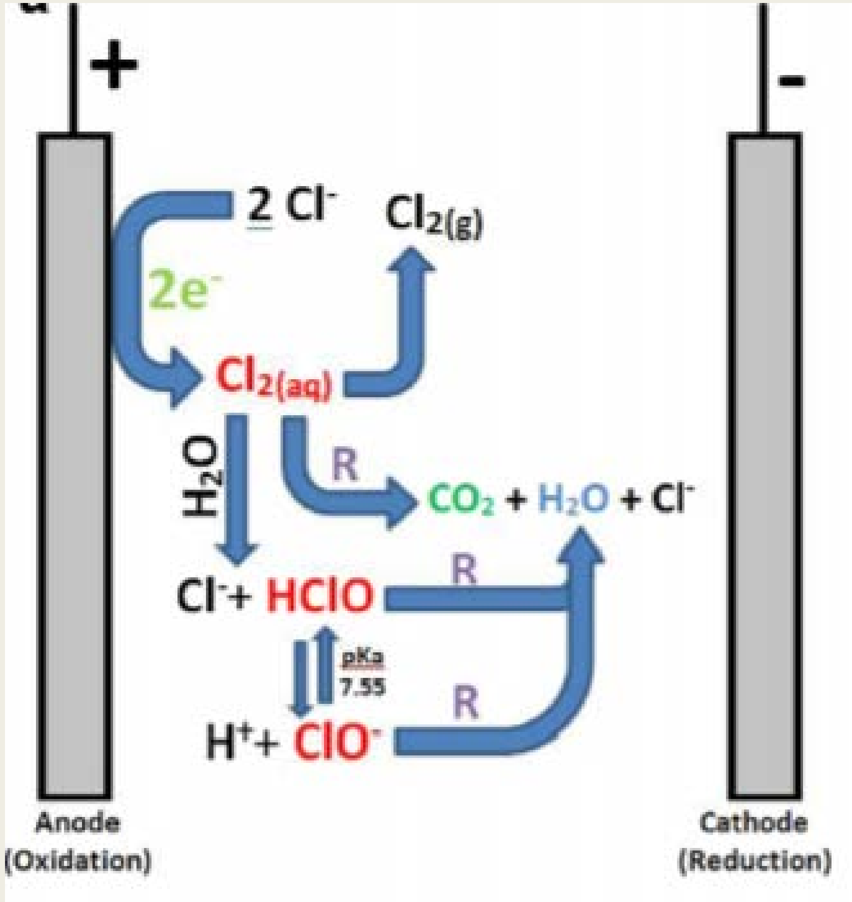
In the solution: $Cl_2(aq) + H_2O \rightarrow HClO + Cl^- + H^+$ (7)

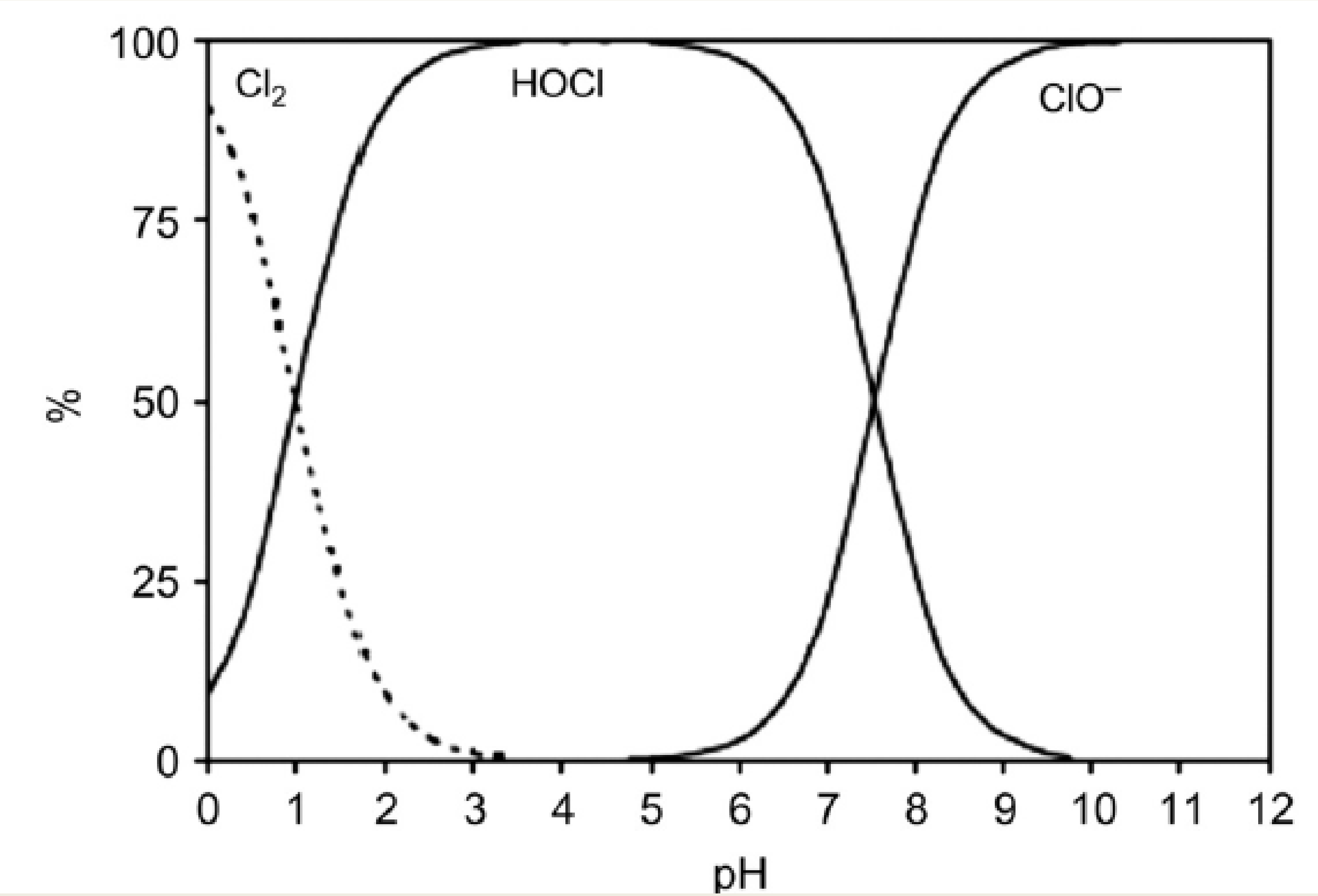
Hypochlorous acid is partly dissociated into hypochlorite ion and hydrogen ion

$$HClO \leftrightarrow H^+ + ClO^- \qquad (8)$$

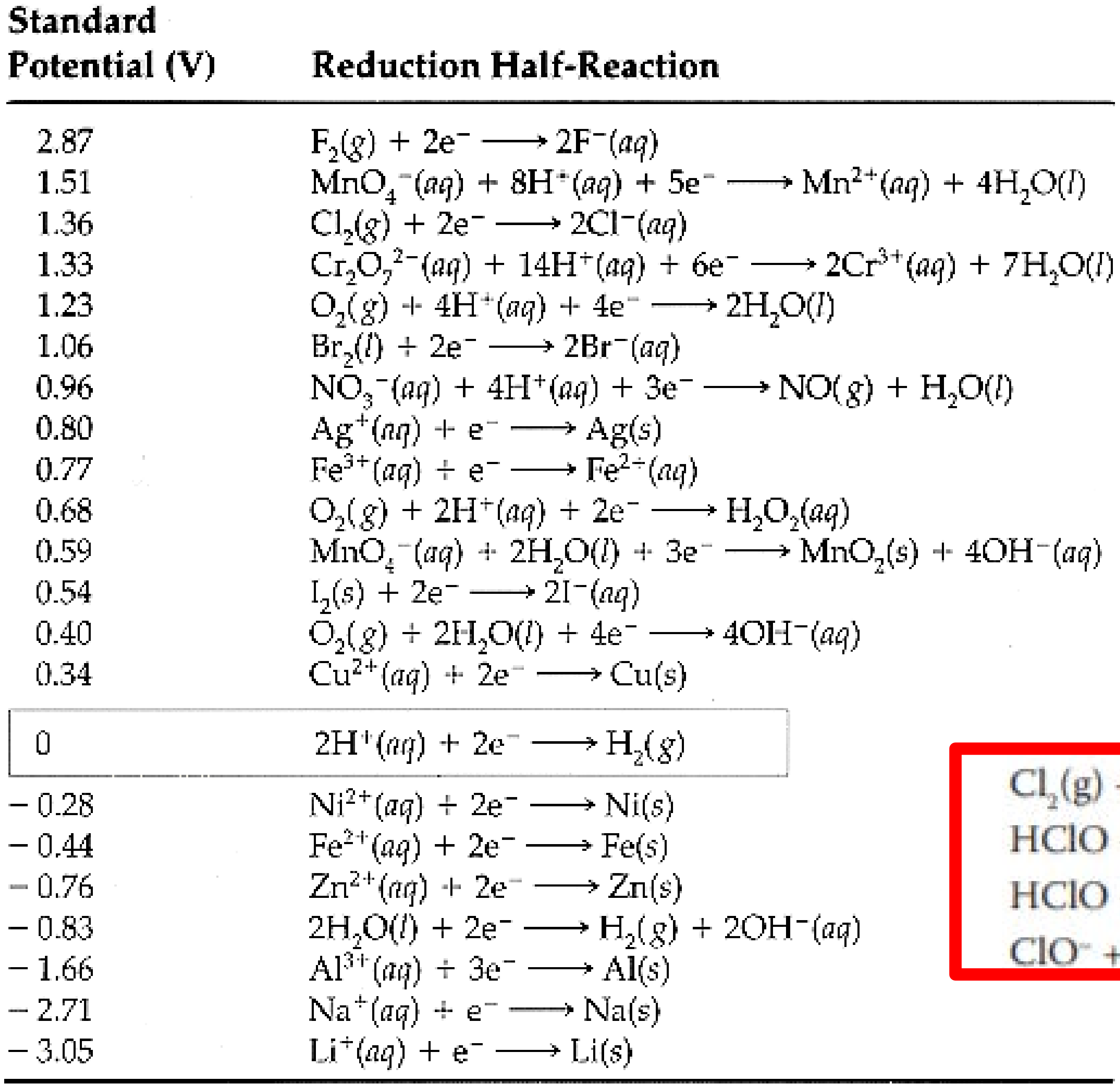
Hypochlorous acid Hypochlorite ion

- As a function of pH, chlorine remains in the solution as aqueous chlorine (pH<3) or disproportionates to hypochloric acid (pH<7.5) or hypochlorine ions (pH>7.5)





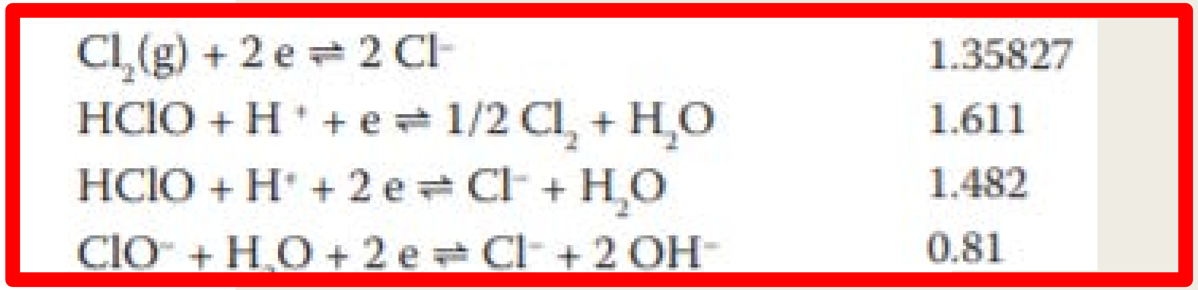
Relative distribution of the main aqueous chlorine species as a function of pH at 25 °C and for a chloride concentration of 5 × 10− 3 M.



Standard Potential (V)	Reduction Half-Reaction
2.87	$F_2(g) + 2e^- \longrightarrow 2F^-(aq)$
1.51	$MnO_4^-(aq) + 8H^+(aq) + 5e^- \longrightarrow Mn^{2+}(aq) + 4H_2O(l)$
1.36	$Cl_2(g) + 2e^- \longrightarrow 2Cl^-(aq)$
1.33	$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \longrightarrow 2Cr^{3+}(aq) + 7H_2O(l)$
1.23	$O_2(g) + 4H^+(aq) + 4e^- \longrightarrow 2H_2O(l)$
1.06	$Br_2(l) + 2e^- \longrightarrow 2Br^-(aq)$
0.96	$NO_3^-(aq) + 4H^+(aq) + 3e^- \longrightarrow NO(g) + H_2O(l)$
0.80	$Ag^+(aq) + e^- \longrightarrow Ag(s)$
0.77	$Fe^{3+}(aq) + e^- \longrightarrow Fe^{2+}(aq)$
0.68	$O_2(g) + 2H^+(aq) + 2e^- \longrightarrow H_2O_2(aq)$
0.59	$MnO_4^-(aq) + 2H_2O(l) + 3e^- \longrightarrow MnO_2(s) + 4OH^-(aq)$
0.54	$I_2(s) + 2e^- \longrightarrow 2I^-(aq)$
0.40	$O_2(g) + 2H_2O(l) + 4e^- \longrightarrow 4OH^-(aq)$
0.34	$Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)$
0	$2H^+(aq) + 2e^- \longrightarrow H_2(g)$
−0.28	$Ni^{2+}(aq) + 2e^- \longrightarrow Ni(s)$
−0.44	$Fe^{2+}(aq) + 2e^- \longrightarrow Fe(s)$
−0.76	$Zn^{2+}(aq) + 2e^- \longrightarrow Zn(s)$
−0.83	$2H_2O(l) + 2e^- \longrightarrow H_2(g) + 2OH^-(aq)$
−1.66	$Al^{3+}(aq) + 3e^- \longrightarrow Al(s)$
−2.71	$Na^+(aq) + e^- \longrightarrow Na(s)$
−3.05	$Li^+(aq) + e^- \longrightarrow Li(s)$

- The species near the top of the list prefer to be reduced (good oxidizing agents)
  while the species near the bottom prefer to be oxidized (good reducing agents.

- Note that the standard reduction potential of Cl_2(aq) (E◦ = 1.36 V/SHE) and HClO (E◦ = 1.49 V/SHE) are considerably higher than ClO^- (E◦ = 0.89 V/SHE), indicating that a faster oxidation of organics when mediated by chlorine active species is obtained under acidic pH conditions



$Cl_2(g) + 2\,e \rightleftharpoons 2\,Cl^-$	1.35827
$HClO + H^+ + e \rightleftharpoons 1/2\,Cl_2 + H_2O$	1.611
$HClO + H^+ + 2\,e \rightleftharpoons Cl^- + H_2O$	1.482
$ClO^- + H_2O + 2\,e \rightleftharpoons Cl^- + 2\,OH^-$	0.81

The formation of hypochlorite ions

- The formation of hypochlorite ions is dependent on many parameters such as

*concentration of chloride ions in the electrolyte solution,

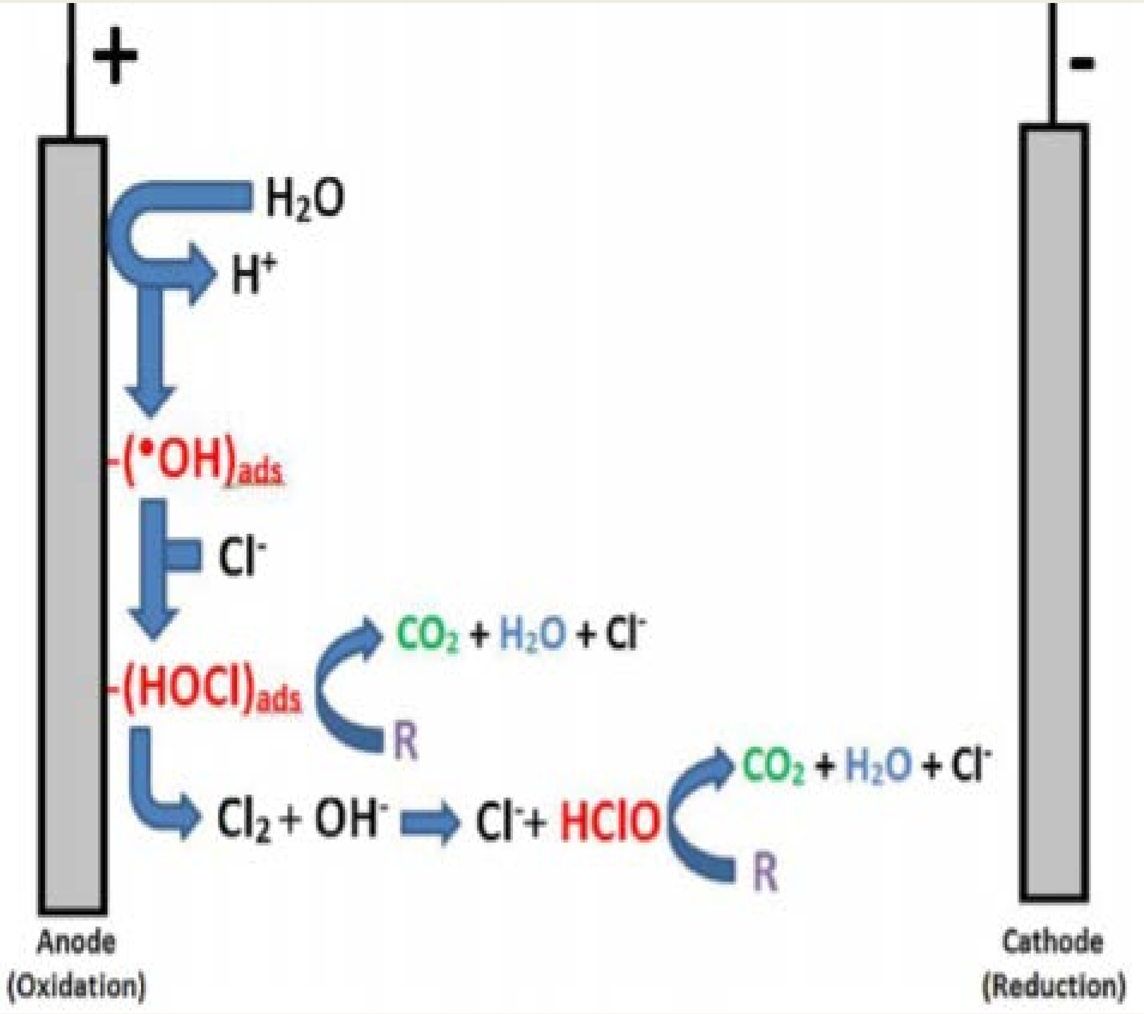
*the temperature of the electrolyte solution,

*applied current density,

*material of anode, and cathode.

- For example, higher concentration of chloride ions (usually higher than 3 g/L) in the electrolyte solution leads to the higher formation of hypochlorite ions; higher temperature of electrolyte solution leads to the higher evolution of oxygen, which is the waste reaction, and results to the lower formation of ClO^-.
- In this regard, the temperature control should be carried out during indirect EO and addition of sodium chloride salt can be required in the case of low chloride ions concentration in the treated wastewater. Anodic materials should have low overpotential toward chlorine evolution, which in turn leads to higher ClO^- production. Cathodic materials should have inert properties toward ClO^- ions reduction.

- The possible simultaneous electro-generation of chlorine active species mediated by the reactive oxygen species is such that the oxygen transfer reactions will be carried out by adsorbed oxychlorinated species generated by reaction (9) as intermediates of the chlorine evolution (10).
- $M(OH) + Cl^- \rightarrow M(HOCl)$ (9)
- $M(HOCl) \rightarrow \frac{1}{2}Cl_2 + OH^-$ (10)



- The active anode materials present better performances than the non-active anode materials in the electrochemical anodic oxidation mediated by chlorine active species are .
- The better electrocatalytic properties for chlorine evolution is described for active anodes (i.e., Pt, RuO_2, TiO_2 and IrO_2) where chloride is oxidized to chlorine active species
- Conversely, the non-active anodic materials result to the further oxidation of Cl_2 and $HClO/ClO^-$ to undesired <u>non-oxidising chlorine species</u>.
- The degradation of organic pollutants mediated by electrogenerated chlorine active species is a process of great industrial interest due to the ubiquitous presence of chlorine in mainstream water bodies and industrial effluents.
- Even though the oxidation of organic pollutants is considerably faster with homogeneous chlorine active species than the mediated ones by adsorbed hydroxyl radicals, they also could yield undesirable organo-chlorinated by-products (e.g. haloacetic acids, halomethanes, etc) and noxious ionic species, such as chlorate and perchlorate

Side reactions:

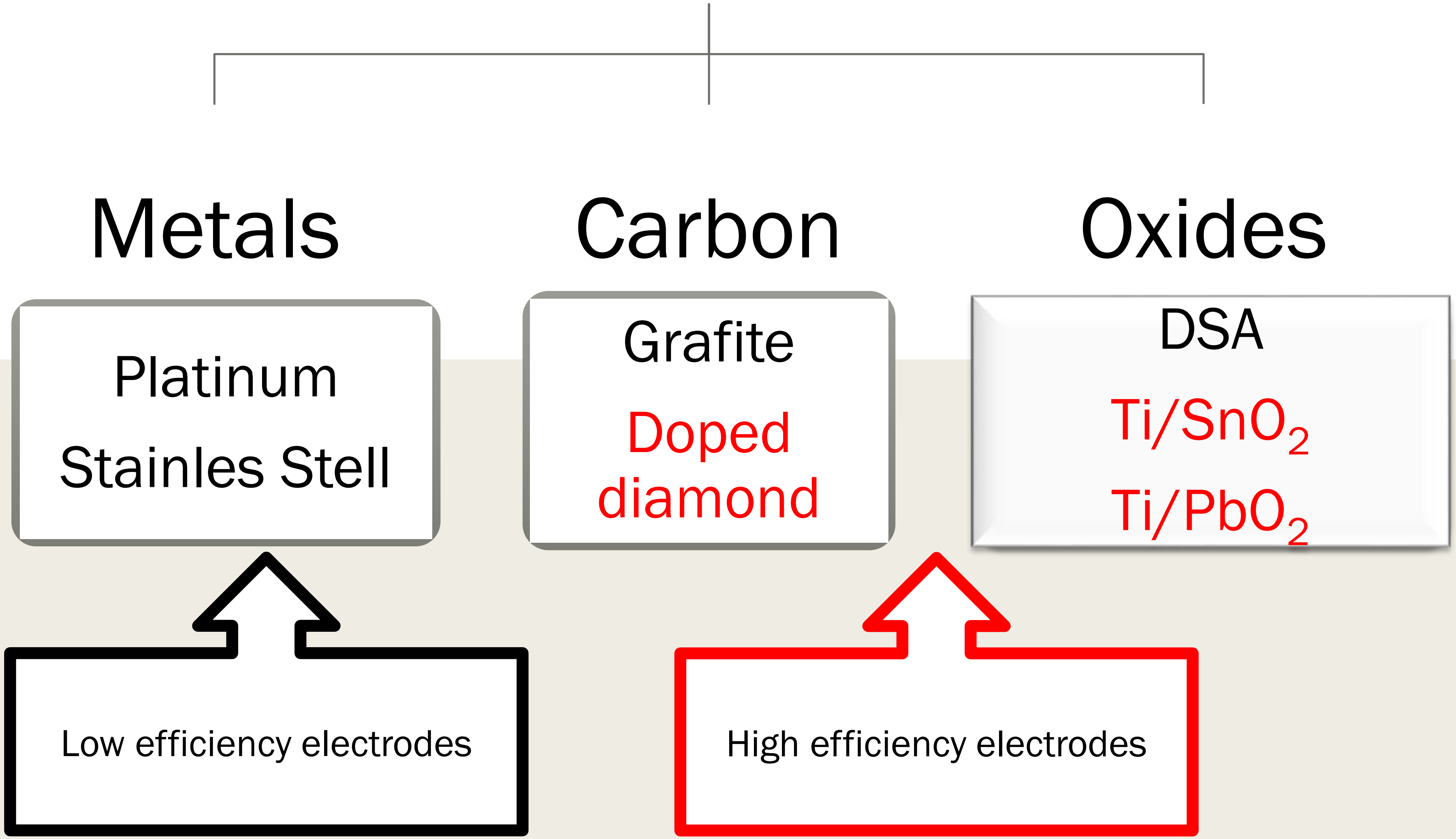
- The process of hypochlorite ions formation can be interrupted by side reactions. For example, ClO^- ions can be lost in anodic and cathodic transformation reactions with the formation of chlorate and chloride ions, respectively (R. 11-12).
- At anode: $12ClO^- + 6H_2O - 12e^- \rightarrow 4ClO_3^- + 8Cl^- + 3O_2 + 12H^+$ (11)
- At cathode: $ClO^- + H_2O + 2e^- \rightarrow Cl^- + 2OH^-$ (12)

Electrode Materials

Several electrodes have been used for water treatment by electrochemical oxidation.

- Mechanical stability
- Chemical stabiity
- Morphology
- Electrical Conductivity
- Catalytic properties
- Ratio price/lifetime
- For generating reactive oxygen species, a high oxygen overpotential is required; otherwise, a large portion of the applied current will be wasted to produce oxygen as a side reaction, thereby reducing the efficiency of the electrochemical process. Several electrode materials such as PbO_2, SnO_2-based DSA, and BDD have been reported to exhibit high oxygen overpotential. These electrode materials are able to hinder the thermodynamically favored oxygen evolution reaction, thus improving the ROS generation efficiency.

Material



Metals

Platinum

Stainles Stell

Carbon

Grafite

Doped diamond

Oxides

DSA

Ti/SnO_2

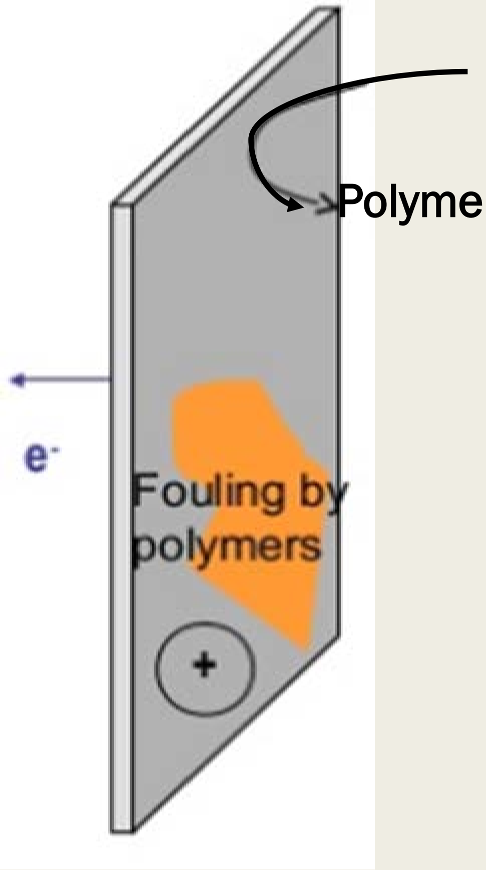
Ti/PbO_2

Low efficiency electrodes

High efficiency electrodes

Low oxidation power anodes:

Soft oxidation conditions
chacterized by a strong electrode-hydroxyl radical interaction resulting in a high electrochemical activity for the oxygen evolution reaction (low overvoltage anode) and to a low chemical reactivity for organics oxidation (low current efficiency for organics oxidation).

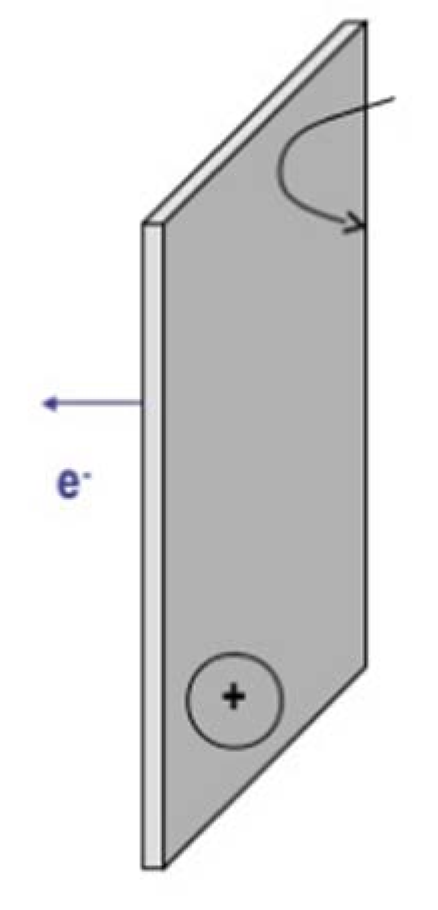


Phenol

Polymers, carboxylic acids, quinones

Many Intermediates
Slow oxidation rates
Small conversion to carbon dioxide
Small current efficiencies

High oxidation power anode: is characterized by a weak electrode-hydroxyl radical interaction resulting in a low electrochemical activity for the oxygen evolution reaction (high overvoltage anode) and to a high chemical reactivity for organics oxidation (high current efficiency for organics oxidation)



Phenol

Carbon dioxide

Large conversion to carbon dioxide
Few intermediates
Large current efficiency only limited by mass transfer

- **Active electrodes** (have low oxygen evolution overpotential and aconsequently are good electrocatalysts for the oxgen evolution reaction: only permit the partial oxidation of organics)

Carbon and Graphite

Pt based anodes

IrO_2 Iridium-based oxides

RuO_2 Ruthenium-based oxides

- **Non-active electrodes** (have high oxygen evolution overpotential and consequently are poor electrocatalysts for the oxygen evolution reaction and favor the complete oxidation of organics to CO_2 and so)

Ti/SnO_2 (Antimony-doped tin oxide)

Ti/PbO_2 (lead dioxide)

Boron-doped diamond (BDD)

- Drawbacks of non-active electrodes:

Conductive diamond: large price

PbO_2/SnO_2: Dissolution of toxic species

Carbon and Graphite

- Carbon and graphite electrodes are very cheap and have a large surface area.
- They have been used widely for the removal of organics with three-dimensional electrodes (e.g. Packed bed, fluidized bed, carbon particles, porous electrode, etc.)
- During the electrolysis there was a rapid decrease in the reaction rate due to the blocking of the anode surface with insoluble polymeric products that were slow to oxidize or desorb.

Platinum

- The platinum electrode is one of the most commonly used anodes in both preparative electrolysis and synthesis because of itsgood chemical resistance to corrosion even in strongly aggresive media.

[Platinum Mesh]

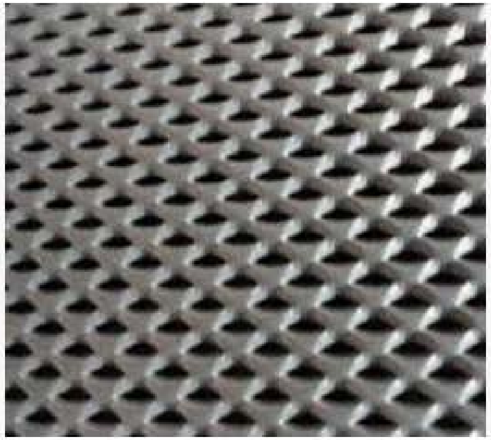
[Platinum Plated Titanium Anode]

Dimensionally Stable Anodes

- The dimensionally stable anodes (DSA) consists of a titanium base metal covered by a thin conducting layer of metal oxide or mixed metal-oxide oxides.
- The development of anodes coated with a layer of RuO_2 and TiO_2 brought about significant improvements in the chlor-alkali industry (DSA-Cl_2) while the anodes coated with IrO_2 have been commercially used for oxyygen evolution reaction (DSA-O_2) in acidic media is several electrochemical process.
- DSA-type anodes coated with a layer of RuO_2 or IrO_2 and other oxides can be used efficienctly for organic disposal by indirect electrolysis generating in situ active chlorine by the oxidation chloride ions presents in the solution.

DSA® anodes for chlorine evolutio...

DSA® anodes for chlorine evolution | De ...



MMO DSA Platinum Coated Titanium M...

Tin Dioxide

- The conductive Sb-doped SnO_2 anodes are highly effective for the electrooxidation of organics in wastewater treatment.
- It has an onset potential for O_2 evolution of about 1.9V vs.SHE.
- Anodic oxidation of a wide range of organic compounds at SnO_2 was very much unselective, which means that the electrode can be applied to a multitude of different wastewater compositions and proceeded with an average efficiency that was five times higher than with Pt anodes
- The SnO_2 anodes have the majör drawback of a short service life that limits their practical applications.

Tin Oxide Electrodes

Tin Oxide Electrodes

Lead Dioxide

- Lead dioxide have good conductivity and large overpotential for oxygen evolution in acidic media, enable the production of hydroxyl radicals during water discharge.
- The possible release of toxic ions, especially in basic solutions, is the main drawback of these electrodes.

Lead Dioxide Anode MMO pbo2 Titanium ...

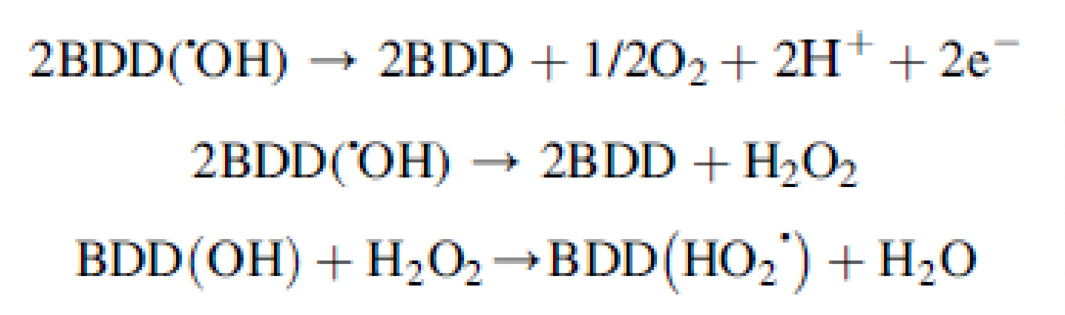
Lead Dioxide Anode ...

Boron-Doped Diamond

- High quality BDD electrodes possess several technologically important characteristics including an inert surface with low adsorption properties,remarkable corrosion stability even in strong acidic media, and extremely high oxygen evolution overpotential.
- During the electrolysis in the region of water discharge, a BDD anode produces a large quality of the $OH^{\cdot}$ that is weakly adsorbed on its surface, and consequently it has high reactivity for organic oxidation, providing the possibility of efficient application to water treatment.
- BDD anodes allow complete minerilization of several types of organic compounds.
- It has been shown that the oxidation is controlled by the diffusion of the pollutants toward the electrode surface, where the hydroxyl radicals are produced, and the current efficiency is favored by high mass-transport coefficient, high organic concentration, and low current density.
- Performing electrolysis under optimum conditions, without diffusion limitation, the current efficiency approaches 100%.

Boron-Doped Diamond(conc.)

- Howerver, despite the numerous advantages of diamond electrodes, their high cost and the difficulties in finding an appropriate substrate on which to deposit the thin diamond layer are their majör drawbacks.
- In fact, stable diamond films can really only be deposited on Silicon, Tantalum, Niobium and Tungusten, but these materials are not suitable for large-scale use. Tantalum, Niobium, and Tungsten are too expensive.



$$2BDD(^{\bullet}OH) \rightarrow 2BDD + 1/2O_2 + 2H^+ + 2e^-$$

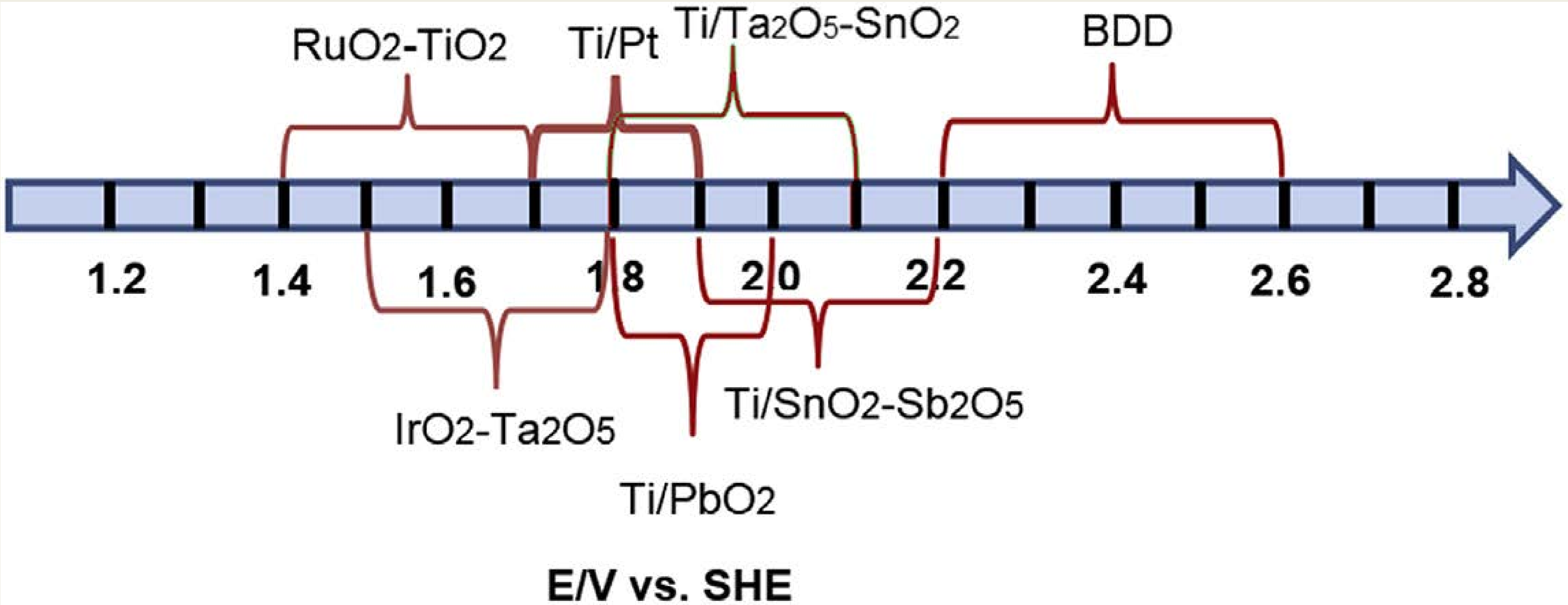
$$2BDD(^{\bullet}OH) \rightarrow 2BDD + H_2O_2$$

$$BDD(OH) + H_2O_2 \rightarrow BDD(HO_2^{\bullet}) + H_2O$$

Summary

- Anodes with low oxygen evolution overpotential, such as graphite, IrO_2, RuO_2, or Pt only permit the primary oxidation of organics, but not to complete mineralization, due to the accumulation of oxidation intermediates, mainly aliphatic acids, which are quite stable against further attack at these electrodes.
- The complete mineralization of the organics to CO_2 and good Faradic efficiency can be obtained using high oxygen overpotential anodes, such as SnO_2, PbO_2, and BDD, because these electrodes involve the production of oxygen evolution intermediates, mainly hydroxyl radicals, that nonselectively oxidize the organic pollutants and their intermediates.
- Despite their notable ability to remove organics, doped-SnO_2 anodes have the major drawback of a short service life that limits their practical applications.
- Even the application of Ti/PbO_2 anodes to wastewater treatment may be limited by the possible releaseof toxic lead ions, due to their dissolutions under specific anodic polarization and solution composition.
- On the contrary, conducting diamonds offer significant advantages over other electrodes in terms of current efficiency and stability. However, further improvements, such as finding an appropriate substrate on which to deposit the thin diamond layer and reduction of production costs, are required before their wide indutrial application.

The onset potential of oxygen evolution reactions for different anode materials in acidic media



- BDD anode along with Ti/SnO_2-Sb_2O_5 has the highest overpotential of OER followed by Ti/PbO_2 and Ti/Ta_2O_5-SnO_2 electrodes. This means that BDD and Ti/Ta_2O_5-SnO_2 anodes are the most efficient for complete mineralization of organic pollutants.
- Pt, IrO_2-Ta_2O_5, and RuO_2-TiO_2 anodes have the smallest overpotential toward OER, thus providing the low activity toward mineralization of organics.

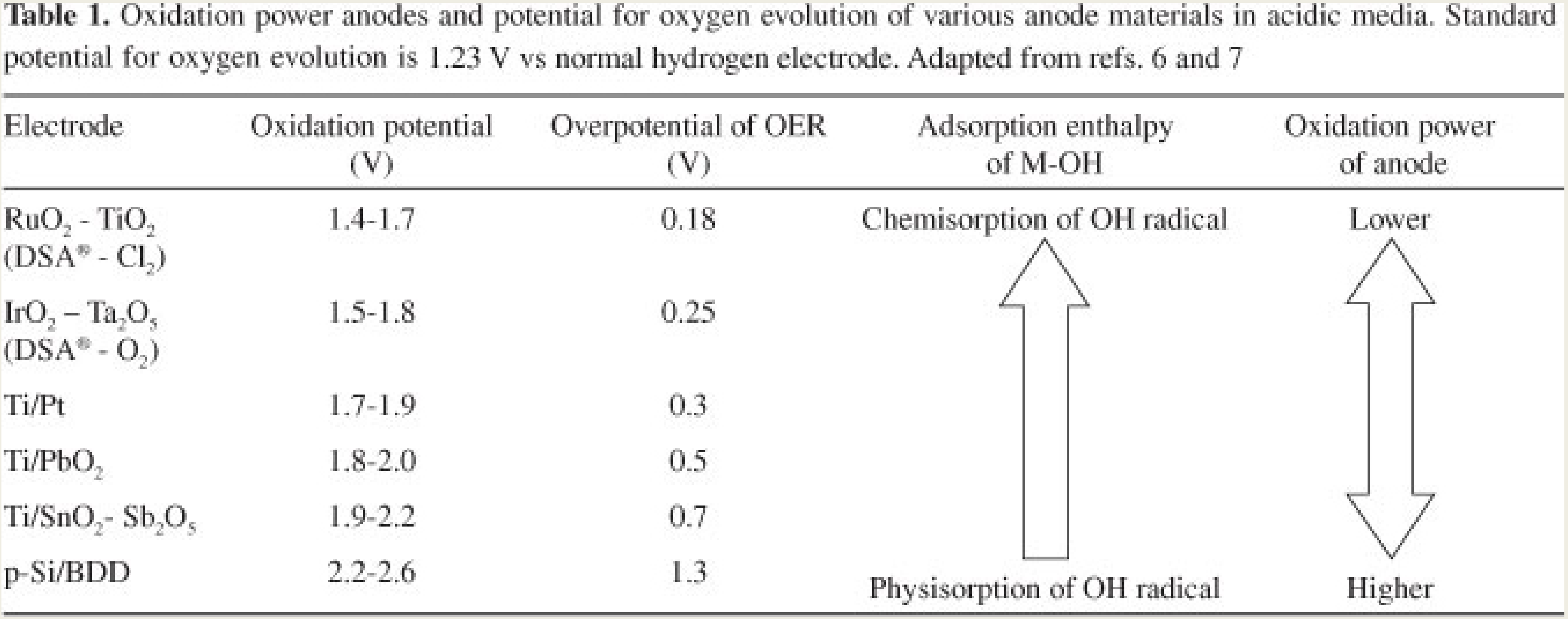
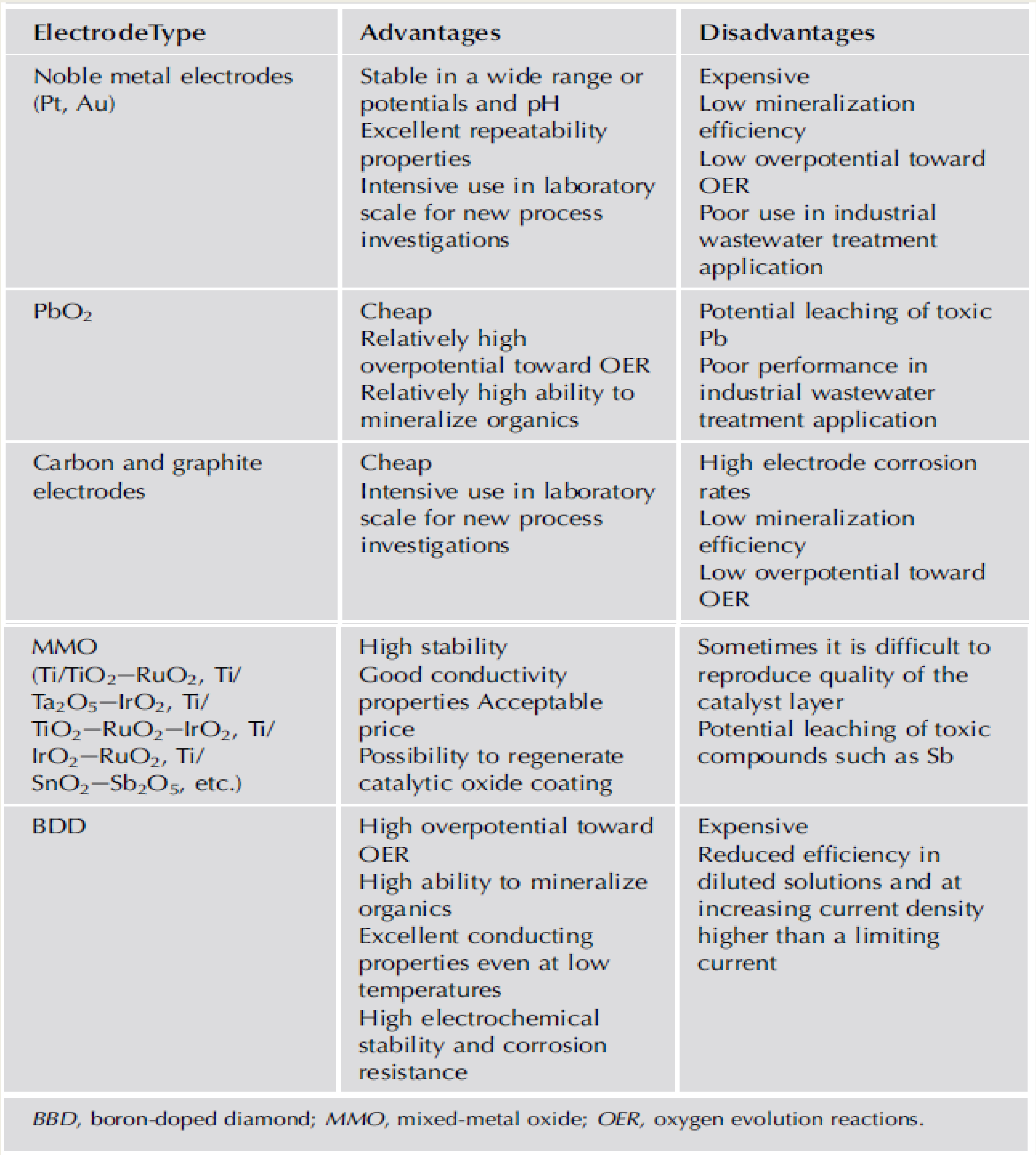


Table 1. Oxidation power anodes and potential for oxygen evolution of various anode materials in acidic media. Standard potential for oxygen evolution is 1.23 V vs normal hydrogen electrode. Adapted from refs. 6 and 7

Electrode	Oxidation potential (V)	Overpotential of OER (V)	Adsorption enthalpy of M-OH	Oxidation power of anode
RuO_2 - TiO_2 (DSA® - Cl_2)	1.4-1.7	0.18	Chemisorption of OH radical	Lower
IrO_2 – Ta_2O_5 (DSA® - O_2)	1.5-1.8	0.25		
Ti/Pt	1.7-1.9	0.3		
Ti/PbO_2	1.8-2.0	0.5		
Ti/SnO_2- Sb_2O_5	1.9-2.2	0.7		
p-Si/BDD	2.2-2.6	1.3	Physisorption of OH radical	Higher

Advantages and Disadvantages of Different Group Anodes Used in Electrochemical Oxidation Applications of Organic Compounds



ElectrodeType	Advantages	Disadvantages
Noble metal electrodes (Pt, Au)	Stable in a wide range or potentials and pH Excellent repeatability properties Intensive use in laboratory scale for new process investigations	Expensive Low mineralization efficiency Low overpotential toward OER Poor use in industrial wastewater treatment application
PbO_2	Cheap Relatively high overpotential toward OER Relatively high ability to mineralize organics	Potential leaching of toxic Pb Poor performance in industrial wastewater treatment application
Carbon and graphite electrodes	Cheap Intensive use in laboratory scale for new process investigations	High electrode corrosion rates Low mineralization efficiency Low overpotential toward OER
MMO (Ti/TiO_2-RuO_2, $Ti/Ta_2O_5-IrO_2$, $Ti/TiO_2-RuO_2-IrO_2$, Ti/IrO_2-RuO_2, $Ti/SnO_2-Sb_2O_5$, etc.)	High stability Good conductivity properties Acceptable price Possibility to regenerate catalytic oxide coating	Sometimes it is difficult to reproduce quality of the catalyst layer Potential leaching of toxic compounds such as Sb
BDD	High overpotential toward OER High ability to mineralize organics Excellent conducting properties even at low temperatures High electrochemical stability and corrosion resistance	Expensive Reduced efficiency in diluted solutions and at increasing current density higher than a limiting current

BBD, boron-doped diamond; *MMO*, mixed-metal oxide; *OER*, oxygen evolution reactions.

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