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Electrochemical Water Disinfection: A Short Review

ELECTRODES USING PLATINUM GROUP METAL OXIDES

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Electrochemical water disinfection is a rarely used but convenient and highly efficient way to produce germ-free water. The technique works without the addition of chemical compounds to the water to be treated, but is nevertheless based on the biocidal action of various chemical substances. Electrodes with platinum group metals (pgms) or their oxides as active coatings are generally the best suited to electrochemical water disinfection. In special cases, novel doped diamond electrodes can be applied. A short historical and technical overview of the process is given, augmented by some application examples.

1. Background

Electrochemical water disinfection can be defined as the eradication of microorganisms by using an electric current passed through the water under treatment by means of suitable electrodes. At the phase boundary between the electrodes and the water, the electric current leads to the electrochemical production of disinfecting species from the water itself (for example, ozone), or from species dissolved in the water (for example, chloride is oxidised to free chlorine).

Attempts to clean or disinfect water by direct electrolysis had been reported as early as the nineteenth century (see, for example, Reference (1)). It has even been speculated that the electrical elements (the so-called 'Baghdad battery'), which were discovered in 1936 in the ruins of a Parthian city (inhabited from about 300 BC to 300 AD) near Baghdad in Iraq, were in use for the electrochemical preparation of germ-free water (2). Since the end of the nineteenth century there have been frequent attempts to use electrochemical disinfection (for example, References (3–6)). Until recently none have been successful, at least not for long-term practical use.

Different terms are or have been in use to describe this type of water treatment process or the water produced by this process, such as 'electrolytic disinfection', 'electrochemical disinfection', 'anodic oxidation', 'functional water' and 'electrochemically activated water' among others.

There are three reasons why electrochemical water disinfection has arrived at technical maturity only recently, rather than earlier in the (possibly) 2000 years since its discovery:

(a) Sufficiently stable and efficient electrode materials for electrochemical water disinfection have been developed and optimised only in the last forty years. These are titanium electrodes with mixed oxide coatings based on iridium and/or ruthenium oxide (7–9), and doped diamond electrodes (10).

(b) The functional interrelationships between chloride concentration in the water, current, current density, electrode material, water quality, electrochemical production of free chlorine and disinfecting action have been investigated in detail only recently (11–15).

(c) Development work on electrochemical water disinfection has often been undertaken by amateurs in both electrochemistry and water chemistry, and this remains somewhat true today. Only a few electrochemists have been interested in this topic, mostly only for a short period in their career. This has resulted in mistakes in device dimensioning and in unscientific explanations of the mechanism of the process.

2. General Processes for Water Disinfection

Conventional disinfection methods may be divided between chemical and physical processes. In chemical processes, disinfecting substances such as ozone, chlorine, sodium hypochlorite or chlorine dioxide are added to the water to be treated. These processes are reliable, and have proven their efficiency over many decades. They not only kill microorganisms, but also provide a disinfection reservoir which protects the water against recontamination for a certain time. A frequent drawback of the chemical processes is unwanted side reactions of the disinfectants with substances present in the water. These reactions lead to disinfection byproducts, some of which are considered dangerous. There are also hazards in producing, transporting and handling large amounts of such substances as chlorine and ozone.

In physical disinfection processes the microorganisms are removed or killed by means of irradiation with ultraviolet or ionising radiation, heating to elevated temperatures, ultrasound, or separation through membrane filtration. The main drawback of the physical disinfection methods is the lack of a reservoir effect. These processes are only effective in the immediate surroundings of their operating devices.

As compared with other chemical disinfection methods, the advantages of electrochemical water disinfection are obvious: no transport, storage and dosage of disinfectants are required. The disinfecting effect can be adjusted according to the on-site demand. Electrochemical water disinfection shows a reservoir effect and is often more cost-effective and requires less maintenance than other disinfection methods. Photovoltaic power supply makes it possible to use electrochemical water disinfection far from the electrical supply grid. This may be important for its application to drinking water in developing countries. Electrochemical water disinfection can also be used in conjunction with other disinfection methods.

In electrochemical water disinfection, electrodes (at least one cathode and one anode) are inserted either directly into the volume of water to be disinfected, or into a bypass pipe. A DC voltage is applied between the electrodes, leading to the electrolysis of the water. At the anode the main product is oxygen (Equation (i)):

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^- \quad \text{(i)}$$

accompanied by an acidification of the water in the vicinity of the anode. At the cathode, hydrogen is formed (Equation (ii)):

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^- \quad \text{(ii)}$$

and the water near the cathode becomes alkaline. Since the evolved hydrogen is generally unwanted, it must be separated from the water stream. Because only small amounts are formed at normal currents (about 0.4 litres of hydrogen is produced per amp-hour), this is possible without problems in most cases.

In most practical applications, simple undivided electrochemical reactors employing parallel-plate, monopolar electrode stacks are inserted into the reactor pipe. The electrode plates may be configured as unperforated or perforated plates, or as expanded metal.

Recently, an electrochemical disinfection process which completely avoids hydrogen production has been developed. Atmospheric oxygen is reduced to hydroxyl ions at a gas diffusion cathode (16) (Equation (iii)):

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \quad \text{(iii)}$$

Here the cathodic reaction (Equation (iii)) replaces the hydrogen producing reaction (Equation (ii)). The gas diffusion electrodes are composed of a porous graphite-polytetrafluoroethylene (PTFE) layer, in contact with a metal mesh as current collector, and backed by an oxygen-permeable PTFE layer to prevent water leakage. The graphite carries a manganese oxide catalyst which eliminates unwanted hydrogen peroxide.

3. Production of Free Chlorine from the Chloride Content of the Water

If electrochemical disinfection is applied to drinking water, industrial water, seawater or other solute-containing water, its effect is mainly based on the electrochemical production of hypochlorite

and/or hypochlorous acid from the chloride content of the water. The effectiveness of this method has always been accepted for water which contains higher concentrations of chloride ions (17), such as seawater with about 19 g l^{-1} chloride (18), or where large amounts of sodium chloride have been added, for instance to swimming pool water (chloride concentrations here are usually about 2–5 g l^{-1}). For the disinfection of drinking water and other waters with much lower chloride content, the effectiveness of the method was not clear for a long time (19). It was eventually demonstrated that even at very low chloride concentrations (less than 100 mg l^{-1}) sufficient free chlorine can be produced to efficiently disinfect water (11–15).

The disinfectant hypochlorous acid/hypochlorite is produced at the anode in a side reaction to oxygen evolution. The following simplified reaction mechanism is proposed. First, chlorine is produced electrochemically from chloride ions dissolved in the water (Equation (iv)):

$$2Cl^- \rightarrow Cl_2 + 2e^- \quad \text{(iv)}$$

Chlorine hydrolyses in water and hypochlorous acid (HClO) is formed (Equation (v)):

$$Cl_2 + H_2O \rightarrow HClO + HCl \quad \text{(v)}$$

Hypochlorous acid and the hypochlorite anion form a pH-dependent equilibrium (Equation (vi)):

$$HClO \leftrightarrows ClO^- + H^+ \quad \text{(vi)}$$

In the nomenclature of water disinfection, the sum of hypochlorous acid and hypochlorite concentrations is usually termed 'free chlorine' or 'active chlorine'. The disinfecting effect of free chlorine is based on the release of atomic oxygen according to Equations (vii) and (viii):

$$HClO \rightarrow O + Cl^- + H^+ \quad \text{(vii)}$$

$$ClO^- \rightarrow O + Cl^- \quad \text{(viii)}$$

During the disinfection, chloride ions which have been consumed by electrochemical free chlorine production are reformed. Thus there is no overall change in the chemical composition of the water during electrochemical water disinfection.

Where there is a low chloride concentration in the water to be treated (as in drinking water) the current efficiency of the electrode material for the production of free chlorine is crucial; it should be as high as possible. Very great differences have been found in the efficiency of free chlorine production between different electrode materials at low chloride concentrations (11–13, 15). Figure 1 shows the dependence of the free chlorine production efficiency on chloride concentration for two dimensionally stable anode (DSA®) type electrodes (using active coatings of IrO_2 or IrO_2/RuO_2), platinum and boron-doped diamond electrodes. It can be seen that DSA® type electrode materials clearly outperform diamond and Pt electrodes, which are therefore not generally applicable as anodes for water disinfection based on the electrochemical

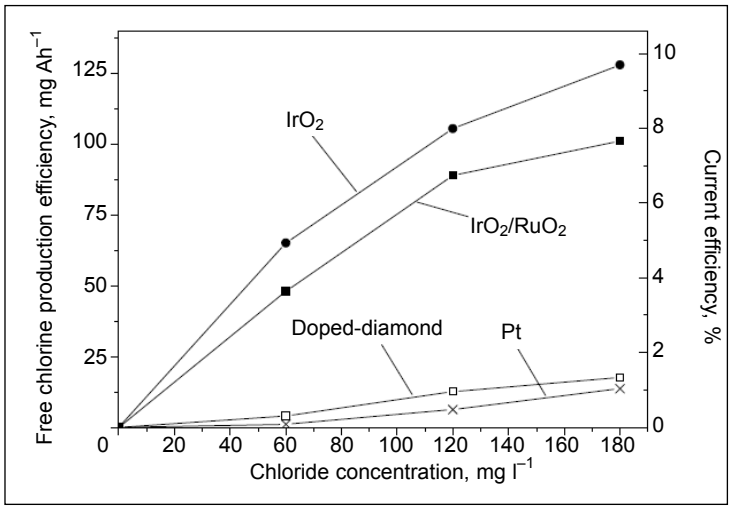

Fig. 1 Dependence of the electrochemical free chlorine production efficiency on the chloride content of the electrolysed water under standard conditions using four different anode materials (iridium oxide, mixed iridium/ruthenium oxides, platinum, doped-diamond)

production of free chlorine. Diamond electrodes have another disadvantage in this application area. Because of their high overvoltage for both oxygen and chlorine evolution, they may further oxidise hypochlorite to chlorate and perchlorate (20). Only very low levels of these disinfection byproducts are permissible in potable water. Chlorate and perchlorate are not formed at DSA® type and Pt electrodes (11, 13). Earlier devices for electrochemical water disinfection employed anode materials such as carbon (1) or Pt (3, 4) with very low production efficiency for free chlorine.

Another important aspect in choosing the appropriate electrode material is electrode lifetime. Although electrode lifetime has been improved where electrode polarity remains constant, frequent polarity change between anode and cathode is still problematic in this regard. Because of the formation of calcareous deposits at the cathode during electrolysis in water containing calcium and magnesium ions, polarity reversal is necessary to clean the cathode surface of these deposits at regular intervals (12, 13). The alkaline pH in the vicinity of the cathode (see Equation (ii)) leads to the precipitation of calcium carbonate ($CaCO_3$) and magnesium hydroxide ($Mg(OH)_2$). On reversing the polarity, the former cathode acts as an anode and the scaling is removed due to the acidic anodic pH (see Equation (i)). But polarity reversal reduces electrode lifetime. This is especially true for IrO_2 or mixed IrO_2/RuO_2 electrodes (12, 13). Figure 2 shows the results of a long-term experiment (still running) on the lifetime of electrodes of various materials under periodic reversal of polarity. A steep rise in cell voltage indicates the total stripping of the active coating at the end of the electrode lifetime. The shortest lifetime of the electrodes tested was observed for the RuO_2-coated Ti electrodes, followed by IrO_2-coated electrodes with a lifetime of about three months. Mixed IrO_2/RuO_2-coated electrodes had a lifetime of nearly one year under our experimental conditions. These materials are all clearly outperformed by platinised Ti electrodes, which are still running seemingly unaffected after nearly eight years.

Other means for cathode cleaning have been investigated, such as ultrasonication (21), and continuously rotating brushes (22) or vanes (23) which move over the cathode surface. Another method is the imposition of a current pulse, which increases the formation of gas bubbles (24). None of these techniques have been successful in long-term operation, so that polarity reversal remains the best automatic cathode cleaning technique to date.

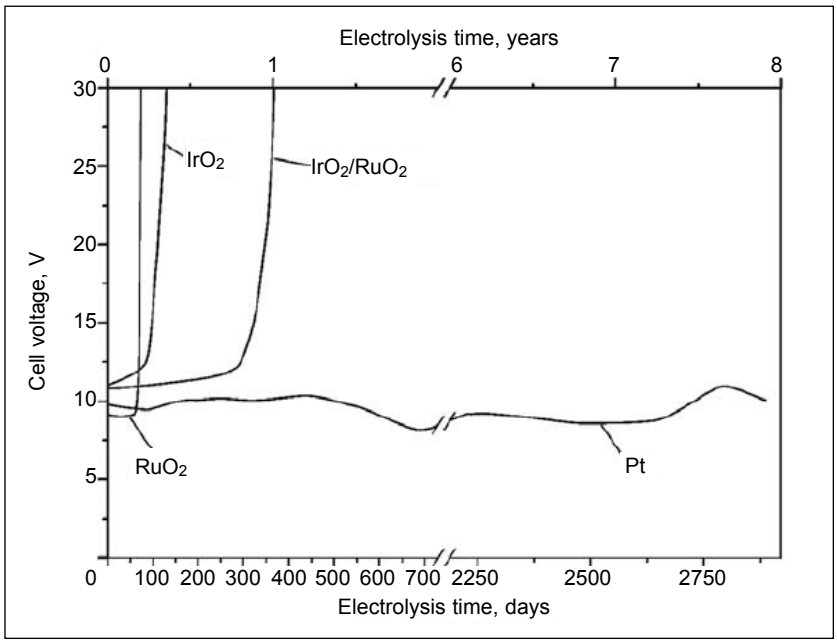

Fig. 2 Cell voltage versus electrolysis time in Berlin tap water (conductivity about 0.8 mS cm^{-1}) for titanium electrodes coated with different active electrode materials (ruthenium oxide, iridium oxide, mixed iridium/ruthenium oxides, platinum): polarity reversal every 30 minutes, current density 20 mA cm^{-2}, electrode distance 4 mm

An example of an application of electrochemical water disinfection based on free chlorine production is the 'AQUADES-EL' device. This is optimised for the cyclic operation of hot water recirculating systems in larger residential and commercial buildings. Potable water, especially in such systems, is especially prone to microbial contamination. This is due to high water temperatures which favour the growth of microorganisms such as *Legionella*. From time to time the media report on legionellosis outbreaks due to contaminated drinking water systems in hotels, hospitals etc. However, *Legionella* is only the most notorious genus of germs. Others are also dangerous, such as *Pseudomonas aeruginosa*, *Escherichia coli* and *Staphylococcus aureus*, to name but a few.

The AQUADES-EL system has been produced and distributed since 1998 by the German companies AquaRotter GmbH and G.E.R.U.S mbH. More than 400 systems have been sold and installed in hotels, hospitals, barracks, retirement homes and other buildings. Figure 3 shows the AQUADES-EL device, which is usually located in a bypass to the water recirculation system. It employs Ti electrodes coated with mixed IrO_2/RuO_2. An advanced control system measures the free chlorine concentration in the water at several locations in the distribution system at regular time intervals by amperometric detection.

In many industrial areas, large amounts of water are used for cooling purposes, as evidenced by the cooling towers dominating the landscape. Microbial contamination of cooling water, whether in cooling towers or air conditioning systems, currently poses a major problem. Large concentrations of disinfectant are usually added to

Fig. 3 Electrochemical disinfection device AQUADES-EL (AquaRotter GmbH and G.E.R.U.S mbH, Germany) equipped with mixed iridium/ruthenium oxide-coated titanium electrodes: right-hand side: reactor pipe with inserted electrode stack; upper middle: power supply and control unit; upper left: amperometric free chlorine sensor equipment

the cooling water. The two commonest biocides for cooling towers are free chlorine and quartenary ammonium compounds. New biocides continue to be developed, but electrochemical water disinfection is a promising alternative for this application.

Electrochemical disinfection has been successfully implemented in the cooling water recirculation system of a German paper mill (Figure 4). The 'Hypocell® B4' device from G.E.R.U.S mbH employs four parallel reactor pipes. The titanium electrodes carry a mixed IrO_2/RuO_2 coating. About 130 m^3 of water is treated. The water has a typical pH of 8.3, a conductivity of 1.9 mS cm^{-1} and a chloride concentration of about 280 mg l^{-1}. The flow rate in the treatment bypass is 1000 l h^{-1}.

4. Ozone Production

If water with low or zero chloride concentration is required, the addition of sodium chloride is not acceptable and free chlorine cannot be produced *in situ*. Disinfection must therefore be based on other electrogenerated species. By using anodes with a high oxygen overvoltage, a high current density and a low water temperature it is possible to produce ozone directly from the water according to Equation (ix):

$$3H_2O \rightarrow O_3 + 6e^- + 6H^+ \quad \text{(ix)}$$

Fig. 4 Hypocell® B4 electrochemical disinfection device (G.E.R.U.S. mbH, Germany), with four pipe reactors equipped with mixed iridium/ruthenium oxide-coated titanium electrodes in a cooling water system, installed at a German paper mill

Electrochemical ozone production has been known since the nineteenth century (25). Electrolysis was the first production method for ozone (25), but for most applications ozone is now produced by corona discharge. The disadvantages of electrolytic production include too low a current efficiency, complicated production systems, unstable electrode materials (such as lead oxide (PbO_2) anodes) and/or difficult-to-handle electrolytes. Electrolytic production may become more attractive using a new simple electrode assembly (26) of a 'sandwich' configuration: diamond anode/solid polymer electrolyte (SPE)/cathode sandwich.

By using such a diamond-SPE sandwich or similar device in deionised water, ozone can be produced with a high current efficiency (up to 47%) (27, 28). These devices can easily be inserted into water pipes or reservoirs to produce the required quantity of ozone directly from the water to be treated. The Nafion® ion exchange membrane may be employed as the SPE material. If the doped diamond anode is replaced by a Pt- or IrO_2-coated anode, a much lower ozone production rate is measured. On the other hand, if Pt is used as the cathode material, the overvoltage for hydrogen production can be lowered, minimising the cell voltage.

For the electrochemical disinfection of ultrapure water, or other waters with very low conductivity (such as rain water), electrochemical ozone production with diamond-SPE sandwich electrodes is the method of choice. Figure 5 shows a small stack of two diamond electrode/SPE/diamond electrode sandwiches. With this technology, water volume rates from 60 l h^{-1} up to 5 m^3 h^{-1} can be treated using different sized electrode stacks. In recent years several pilot projects have been equipped with this technology. An improved ozone generating device is in development. This produces no hydrogen, and the cathode consumes oxygen.

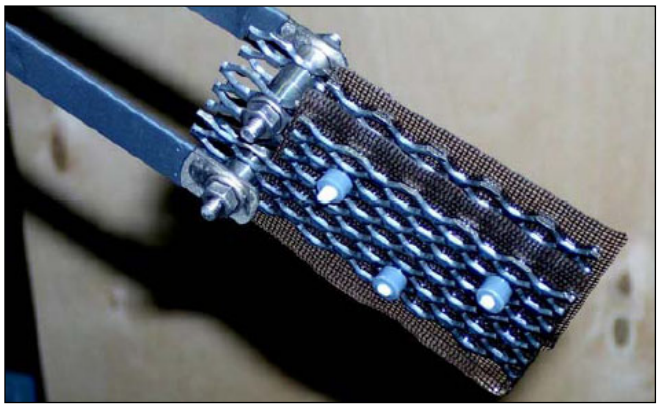

Fig. 5 Electrode stack with two diamond-SPE-electrode sandwiches for ozone production in deionised water (Gerozon device by G.E.R.U.S. mbH, Germany)

5. Disinfection or Germ Minimisation by Electrochemically Produced Oxygen

In some applications, electrolytically produced oxygen, the main anodic reaction product, shows some germicidal activity. This is especially true if anaerobic bacteria are the disinfection target.

An example of this type of application is the wash water cycle of car wash stations. Here, the formation of anaerobic digestion products often leads to bad odours. Anaerobic conditions are eliminated *via* the fine dispersion of bubbles of electrolytically produced oxygen in the water. This is a highly effective mode of dissolution. For this application, Pt-coated electrodes are the most suitable anodes, because the main germicidal effect is based on electrolytically produced oxygen and not on free chlorine. Figure 6 shows the Hypocell® B4 device for germ minimisation in car wash stations, based on this technology. About twenty-five systems have been successfully installed.

6. Disinfection by Cathodically Produced Hydrogen Peroxide

While most of the possible disinfectants in electrochemical water treatment are produced at the anode, hydrogen peroxide may also be produced at the cathode. This process has been used by Dhar *et al.* (29) and Drogui *et al.* (30, 31) for water disinfection (Equation (x)):

$$O_2 + 2H_2O + 2e^- \rightarrow H_2O_2 + 2OH^- \qquad (x)$$

Oxygen dissolved in the water may serve as the reactant in Equation (x). The maximum concentration of oxygen in water which is in equilibrium with air at 25°C is about 10 mg l^{-1} (0.3 mmol l^{-1}). The oxygen produced by the anodic half reaction according to Equation (i) can also be used for the cathodic production of hydrogen peroxide. In this case, higher concentrations of dissolved oxygen are possible, because the water is in contact with pure oxygen, and not merely with air. It is also possible to use a gas diffusion cathode on which the oxygen from the surrounding air is reduced to H_2O_2. In terms of energy efficiency, the electrode material best suited to H_2O_2 production is graphite. This material (without additional catalysts) is also the core component in gas diffusion electrodes for H_2O_2 production.

Because of its lower oxidation potential, H_2O_2 is a less effective disinfectant than free chlorine or ozone. Therefore, higher concentrations and/or longer disinfection times are necessary, limiting its applicability. Hydrogen peroxide has the advantage that its disinfectant action produces neither byproducts nor residues.

7. Conclusion

Electrochemical water disinfection has many advantages compared with conventional disinfection technologies. It has proven its reliability in several practical applications, mainly for the disinfection of drinking water, swimming pool water and industrial cooling water. Electrochemical water disinfection has also been used or tested for the reduction of bacterial contamination in dental water supplies (32), and for the disinfection of contact lenses (33) and ion exchange

Fig. 6 Hypocell® B4 electrochemical disinfection device (G.E.R.U.S. mbH, Germany) equipped with platinised titanium electrodes, mounted in a car wash station

resins (34) etc. However, only a few electrochemical water disinfection products are currently available on the market. This is due to the relative unfamiliarity of the technology, and to fierce market competition with other technologies. Eventually, the cost and performance advantages of electrochemical technology should lead to its wider use.

RuO_2 and/or IrO_2-coated electrodes are the best suited to disinfection based on hypochlorite generation. This is due to their high production efficiency for hypochlorite from water with a very low chloride content. Pt is the favoured electrode material for oxygen production from natural waters. Pt electrodes are also the most stable.

For the production of ozone and hydrogen peroxide, pgm electrodes are not the first choice, being outperformed by carbon electrodes, i.e. doped diamond for ozone, and graphite for hydrogen peroxide production.

This article is a translated and revised version of Reference (35).

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