

The role of electrochemistry and electrochemical technology in environmental protection

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Abstract

For decades electrochemical technology has contributed successfully to environmental protection. In addition, environmental electrochemistry is capable of giving a huge contribution to further reach this goal by (1) application and improvement of existing technology, and (2) research, development and implementation of new technology. There is a tendency in the metal finishing and metal processing industries to redesign processes as closed loop systems. Therefore, we think especially the purification of dilute heavy metal ion-containing process liquids needs much of our attention. Electrochemical processes relevant to this purpose are considered and examples of (possible) industrial applications are discussed. Moreover, a critical evaluation of the usefulness of different types of electrodes is given. Generally, the two-dimensional electrode is the most favourable electrode configuration: the static flat electrode at high flow rates and in combination with mass transfer promoters, and the rotating disc electrode at high peripheral velocity. In both cases turbulent flow condition at the electrode are preferred to enhance the mass transfer. For redox systems where both the reactant and the product are soluble, the porous electrode is favourable due to its high specific surface area. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

Electrochemical technology contributes in many ways to a cleaner environment and covers a very broad range of technology. Examples include generation of energy using (new) batteries [1] and fuel cells [2], selective synthesis of (organic) chemicals [3], removal of impurities from process liquids, air and soil, recycling of process streams [4] (e.g. from printed circuit industry) and sensors [5].

During the last two decades, a special research field, viz. environmental electrochemistry has been developed. Environmental electrochemistry [6–17] involves electrochemical techniques or methods to remove impurities from gases, liquids and soil to prevent or minimise environmental pollution.

In particular, emission to the atmosphere, discharges of pollutant into waters and disposal of solids to land sites have to be minimised. The best way to attack the problems is at their source, viz. mainly processes in the chemical and related industries. Environmental electrochemistry can contribute a great deal in reaching this goal. Especially, the purification of dilute heavy metal process liquids has been

exhaustively investigated, since many heavy metals are very toxic and cause great environmental damage. Moreover, the reuse of metals needs more attention to prevent the disposal of heavy metal solid compounds in land sites.

The removal of heavy metals especially from dilute liquids is extensively discussed in this paper. Some attention is also paid to the purification of dilute gases and the removal of organics.

Dilute solutions to be purified are characterised by the:

- Nature of polluting inorganics (heavy metal ions) and organics.
- Concentration range of polluting species; mostly lower than 1000 ppm.
- Nature and the concentration of supporting electrolyte mostly lower than 1000 ppm and in some cases the concentration is some orders of magnitude higher.
- Specific conductivity of solution; mostly lower than $1 \Omega^{-1} \text{m}^{-1}$.

Electrochemical removal of inorganics is obtained by direct electrolysis where only the reduction reaction is of interest, electrodialysis, and ion exchange assisted electrodialysis. To remove organics electrochemically from dilute solutions indirect electrochemical oxidation may be applied

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Nomenclature

a_e	specific electrode area (A/V) (m^{-1})
A	electrode area (m^2)
c_b	bulk concentration of selected species ($mol\ m^{-3}$)
c_i	inlet concentration of selected species ($mol\ m^{-3}$)
c_{min}	minimal concentration ($mol\ m^{-3}$)
c_o	outlet concentration of selected species ($mol\ m^{-3}$)
c_s	concentration of selected species at electrode surface ($mol\ m^{-3}$)
D	diffusion coefficient of selected species ($m^2\ s^{-1}$)
E	electrode potential (V)
f	rotation rate of the electrode (rps)
F	constant of Faraday ($96\ 485\ C\ mol^{-1}$)
i	current density ($A\ m^{-2}$)
$i_{eff, min}$	typical minimum effective current density ($A\ m^{-2}$)
i_L	limiting current density ($A\ m^{-2}$)
k_m	mass transfer coefficient ($m\ s^{-1}$)
k_s	standard reaction rate constant ($m\ s^{-1}$)
k_{app}	apparent reaction rate constant (-)
K	constant ($1\ mol^{1-\alpha_{app}}\ m^{3\alpha_{app}-3}$)
L_c	depth of a 3D-electrode (m)
M	molecular mass ($kg\ mol^{-1}$)
n	number of electrons in electrode reaction (-)
s_n	normalised space velocity (s^{-1})
$u_s = U_s$	superficial liquid velocity ($m\ s^{-1}$)
V	cell volume (m^3)
z_A	charge of cation (-)
z_B	charge of anion (-)
Greek letters	
α_{app}	apparent reaction order (-)
γ	enhancement factor of the mass transfer (-)
δ_N	thickness of Nernst diffusion layer (m)
μ	mobility of ion in the bulk solution ($m^2\ V^{-1}\ s^{-1}$)
ρ	spacetime yield ($kg\ m^{-3}\ s^{-1}$)
ϕ	current efficiency
ϕ_{an}	current efficiency for anion
ϕ_{cat}	current efficiency for cation

in some particular cases. Direct electrochemical oxidation methods are industrially of very little or no interest. The reasons for their uselessness can be:

- Oxidation of organics at an electrode to CO_2 and H_2O is mostly a very slow electrochemical process and practically impossible.

- No cheap and inert electrode material is available, e.g. Pb corrodes slowly, and then the water will be poisoned by Pb-ions. Recently, borium-doped diamond electrodes [18] have been used; it seems these are very inert, but expensive.
- Charge per molecule organic species is very high.
- Cheap alternatives are available, e.g. adsorption by active carbon and thereafter burning and oxidation by H_2O_2 or O_3 in or not in combination with UV.

Dilute gases contain small quantities of pollutants (500–5000 ppm). Moreover, many pollutants poisoning the air, for instance CO , NO_x , NH_3 and H_2S are very difficult to oxidise or reduce on an electrode.

The main purpose of this paper is a critical review of the real possibilities of electrochemistry and electrochemical technology to remove heavy metals from waste liquids, especially those from electroplating and surface finishing industry. First, direct electrolysis (Section 2) is extensively discussed with its relevant process parameters. In this section results from a theoretical one-dimensional reactor model are discussed (Section 2.3). In addition, a review is given of different three-dimensional and two-dimensional electrodes (Section 2.4). In the next sections the following interesting electrochemical processes are discussed: indirect electrolysis (Section 3), electro dialysis (Section 4), and ion exchange assisted electro dialysis: a hybrid process (Section 5).

2. Direct electrolysis

The key parameters for an electrolysis in the removal of impurities are the current density i , current efficiency ϕ , and spacetime yield (or normalised space velocity). The cell voltage is generally not a dominant parameter in environmental electrochemistry. To apply direct electrolysis in the industry, the effective current density i_{eff} must be higher than a fixed minimum, mainly determined by investment costs. A rough-and-ready i_{eff} will be larger than $10\ A\ m^{-2}$, where $i_{eff} = \phi i$ and i is based on the electrode surface area projected perpendicularly to the direction of the electrical current through the solution.

The effectiveness of electrolysis for dilute solutions is strongly determined by the mass transfer of the species to be removed, the effective electrode surface area and the occurrence of electrode side reactions.

2.1. Mass transfer

Liquid convection, diffusion and migration can determine mass transfer. The liquid convection directed parallel to the electrode surface determines the thickness of the Nernst diffusion layer δ_N ; outside this layer the concentrations of species can be assumed to be constant. A schematic representation of a concentration profile of a species reacting on the electrode surface is given in Fig. 1.

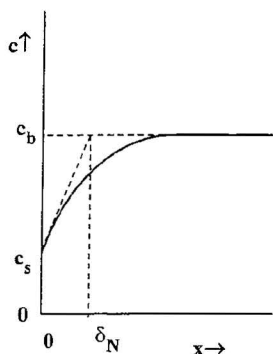


Fig. 1. A schematic representation of a concentration profile of a species reacting on the electrode surface.

If the concentration of the supporting electrolyte is a factor 10 higher than the concentration of the selected species to be oxidised or reduced, the migration of the selected species can be neglected. Its transport rate is then determined by diffusion and in stationary state given by Fick's first law:

$$i = nFD \left(\frac{dc}{dx} \right)_{x=0} \quad (1)$$

or

$$i = nFD \left(\frac{c_b - c_s}{\delta_N} \right) \quad (2)$$

or

$$i = nFDk_m(c_b - c_s) \quad (3)$$

where $k_m = D/\delta_N$.

The limiting diffusion current density is

$$i_L = nFD \frac{c_b}{\delta_N} = nFk_m c_b \quad (4)$$

In the absence of supporting electrolyte migration as well as diffusion determine the transport of selected species. For solutions containing exclusively a 1:1 valency electrolyte the mass transfer coefficient of the cation is given by $k_m =$

$2D/\delta_N$. Generally, $k_m = \gamma D/\delta_N$, where $\gamma \geq 1$ and γ depends on the composition of solution. For a $z_A:z_B$ electrolyte in the absence of supporting electrolyte for the migration of the cation the factor γ is given by [19]

$$\gamma = 1 + \left| \frac{z_A}{z_B} \right| \quad (5)$$

where z_A is the charge of the cation and z_B the charge of the anion as explained in Vetter [19]. For instance, assuming a dilute nickel sulphate solution contains NiOH^+ and HSO_4^- species only, it follows that $\gamma = 2$.

Very different configurations of electrodes are applied in environmental electrochemistry. They can be divided into two groups, viz. the two-dimensional (2D-electrode) and the three-dimensional (3D-electrode) electrode. These electrodes can be used under static as well as moving conditions. In addition, turbulence promoters are used, in particular at the static 2D-electrodes. The mass transfer rate constant k_m is also determined by the solution convection caused by, e.g. forced solution flow through or along the electrode, rotation of electrode and gas bubble evolution on electrode.

Interesting electrode configurations in the environmental electrochemistry are given in Table 1. To norm the mass transfer rate constant k_m , its value is given for a $1 \times 1 \times 0.01 \text{ m}^3$ cell with a projected electrode surface of $1 \times 1 \text{ m}^2$. The flat-plate electrodes are placed in the 1×1 planes at a distance of 0.01 m and the 3D-electrode fills the whole cell. Estimated k_m values [8,10,13,20–24] are given for workable high mass transfer rate conditions. Moreover, for each electrode configuration a minimum concentration, c_{\min} , where the electrolysis can be carried out on an industrial scale, is shown in Table 1. The minimum concentration c_{\min} is based on k_m given in this table, $i_{\text{eff},\min}$ is 10 A m^{-2} and $n = 2$. The current density $i_{\text{eff},\min}$ is a typical minimum effective value proposed to use in industry.

Mass transfer to a membrane is similar to mass transfer to an electrode. This situation occurs in conventional electrodialysis cells. This type of electrochemical technology often applied in industry and is well described in [8,10]. An electrodialysis stack containing a great number of anion

Table 1

Interesting electrode configurations and corresponding transfer coefficients and minimum concentrations at industrially accepted conditions [8,10,13,20–24]^a

Electrode	High mass transfer conditions (m s^{-1})	k_m (m s^{-1})	c_{\min} (mol m^{-3})
Flat-plate electrode	$u_s = 1$	1×10^{-5}	5
RCE ^b	$U_e = 10$	1×10^{-4}	5×10^{-1}
High-porosity 3D-electrode			
Porous electrode (RVC; 100 ppi)	$u_s = 0.1$	1×10^{-2}	5×10^{-3}
Low-porosity 3D-electrode			
Packed bed electrode (2 mm particles) ^c	$u_s = 0.1$	2×10^{-4}	5×10^{-4}
Fluidised bed electrode (0.5 mm beads)	$u_s = 0.01$	6×10^{-3}	1×10^{-2}

^a c_{\min} is based on k_m given. $i_{\text{eff},\min}$ is 10 A m^{-2} and $n = 2$.

^b Diameter and height 0.5 m.

^c Rods with 1 mm diameter and 1.8 mm length.

and cation membrane pairs is common. The concentration of supporting electrolyte must be low. This means that the solution practically contains only the cation to be removed and anions. The rate of mass transfer to a membrane is comparable to that of a flat-plate electrode.

2.2. Spacetime yield and normalised space velocity

An important process design parameter, correlated with the specific investment costs, is the spacetime yield ρ of an electrochemical cell [25]:

$$\rho = a_e \frac{i \phi M}{nF} \quad (6)$$

in which a_e is the specific electrode area (A/V), i the current density, ϕ the current efficiency, M the molecular mass, and n the number of electrons in electrode reaction. Combining Eq. (6) and the formula for the limiting current density, Eq. (4), yields an important formula for the design of an electrochemical reactor for the purification of wastewater:

$$\rho = a_e M \phi k_m c_b \quad (7)$$

This formula for electrochemical reactor design shows that for a certain metal concentration c_b the product of specific electrode area a_e and mass transfer coefficient k_m should be as high as possible. It should be noted, however, that the spacetime yield of a reactor is dependent of the wastewater properties. Therefore, Kreysa [26,27] introduced the normalised space velocity to characterise reactor performance:

$$s_n = \frac{I \phi}{(c_i - c_o) V n F} \log \left(\frac{c_i}{c_o} \right) \quad (8)$$

where c_i and c_o are the concentrations of the reactant at, respectively, the inlet and the outlet of the cell. This figure of merit means the volume of wastewater (m^3) for which the concentration of the key reactant can be reduced by a factor 10 ($c_o = 0.1c_i$) during 1 s in a reactor volume of $1 m^3$.

2.3. Potential and current density distribution

In cells with two flat-plate electrodes the electrodes are normally placed parallel to each other, while in cells containing a rotating electrode a static counter cylinder electrode is concentrically placed around the working electrode. This means that under industrial conditions, where the bulk of solution has a practically uniform composition, the potential and current distributions over each electrode are uniform.

For a 3D-electrode, the potential E and the current density i change continuously with increasing depth of electrode L_c . The potential and the current density are strongly related to each other. The $E - L_c$ and $i - L_c$ curves depend on many parameters.

Portegies Zwart [20] has calculated the potential and dimensionless current density profiles in a packed bed electrode for the Fe^{3+} reduction, where its rate is determined

by both mass transfer and kinetic parameters. He has used a theoretical one-dimensional reactor model. Moreover, he has calculated the total dimensionless cathodic current density as a function of a great number of parameters, viz. three-dimensional cathode thickness, standard electrochemical rate constant k_s , mass transfer coefficient, potential driving force, apparent exchange current density, and concentration levels of Fe^{2+} and Fe^{3+} . There are two extremes, viz. the one where potential and current density profiles are determined by the kinetic parameters as well as the specific resistance of solution, and the other by the local mass transfer as well as the specific resistance of solution. It has been found that the solution conductivity particularly plays a very important role and strongly determines the effective thickness of a three-dimensional roll if the electrochemical kinetic parameters are of interest.

Experiments were carried out to reduce ferric ions in a sulphuric acid solution using an undivided GBC-reactor (Gas diffusion electrode packed Bed electrode Cell) consisting of a gas diffusion anode fed by hydrogen and a packed bed cathode of small carbon rods [20,28] (see Fig. 2).

The reduction reaction of ferric at the packed bed electrode is



and the oxidation reaction of hydrogen at the hydrogen gas diffusion anode is



The macroscopic reduction rate in the GBC-reactor can be described using an empirical reaction rate equation with apparent reaction parameters:

$$r = K k_{app} c^{a_{app}} \quad (11)$$

This equation combines the microscopic effects of mass transfer and electrochemical kinetics on the reduction

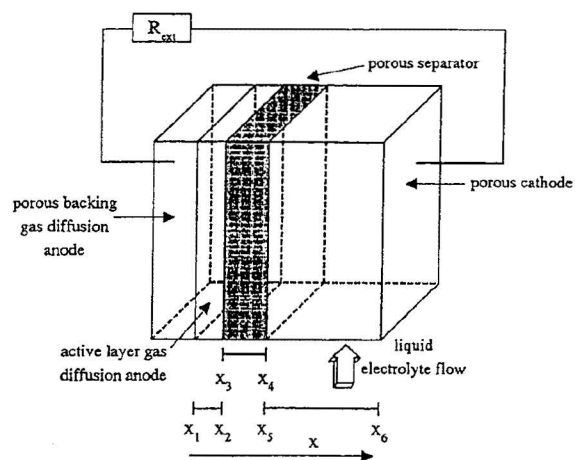


Fig. 2. Schematic presentation of the divided GBC-reactor configuration.

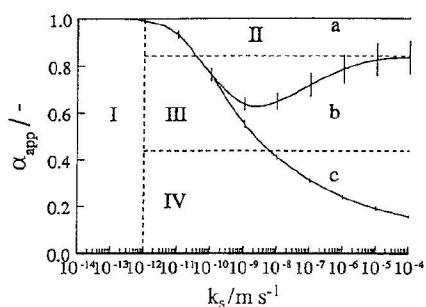


Fig. 3. Calculated apparent reaction order, α_{app} , as a function of the standard electrochemical reaction rate constant at different mass transfer rates. Roman numbers indicate different operating regimes (see text). k_m : 10^{-7} (a), 10^{-5} (b), 10^0 (c) m s^{-1} ($k_m = k_{mO} = k_{mR}$).

reaction into a macroscopic *apparent* reaction rate constant k_{app} and an *apparent* reaction order α_{app} . The parameter K is introduced as a constant, which has a value of 1 and a dimension of $\text{mol}^{1-\alpha_{app}} \text{m}^{3\alpha_{app}-3}$, so that k_{app} has the standard dimension of m s^{-1} . Thus K only maintains the dimensional integrity of Eq. (11).

Portegies Zwart [20] has linked the results for the one-dimensional reactor model with experimentally obtained parameters using the aforementioned empirical reactor rate equation. He distinguished four zones in the $\alpha_{app} - k_s$ figure (see Fig. 3) for α_{app} , viz. $\alpha_{app} = 1$ at $k_s < 10^{-13} \text{ m s}^{-1}$, where the reduction process is kinetically controlled (zone I), $0.85 < \alpha_{app} < 1$ at $k_s > 10^{-13} \text{ m s}^{-1}$, where the reduction process is mainly determined by mass transfer (zone II), $0.45 < \alpha_{app} < 0.85$ at $k_s > 10^{-13} \text{ m s}^{-1}$, where the reduction process is determined by kinetics, mass transfer and ohmic effects (zone III), where α_{app} shows a very complex behaviour, and $\alpha_{app} < 0.45$ at $k_s > 10^{-13} \text{ m s}^{-1}$ (zone IV), where very high mass transfer coefficient and standard electrochemical rate constant occur.

In zone IV, only the region of the 3D-electrode next to the gas diffusion anode is still active. It is very unlikely that this operating regime occurs in practice. For a kinetically limited process and a mass transfer limited process it is found that $\alpha_{app} = 1$, while k_{app} is, respectively, equal to the electrochemical rate constant for the reduction reaction or to the mass transfer coefficient. It has been concluded that the operating regime of the reactor can be identified using the values of α_{app} and k_{app} using the theoretical model. The model was used to optimise a GBC-reactor used for the regeneration of an electrochemical machining electrolyte [20]. Apart from its apparent practical usefulness, this work serves as an illustration of how mathematical modelling can be used in electrochemical technology in general.

The potential profile over a RVC-cathode (reticulated vitreous carbon) in a GBC-reactor at the reduction of a 1M H_2SO_4 solution containing small concentrations of ferric and ferrous was determined experimentally using a moving Luggin capillary. The potential profile was calculated using

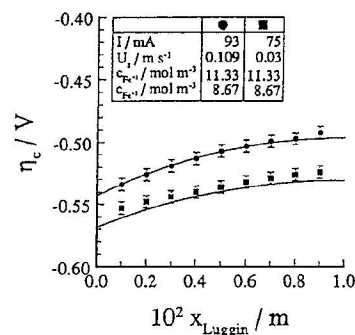


Fig. 4. Experimental cathode electrode potential profiles measured at different reactor current levels, superficial liquid velocities and concentrations of ferric and ferrous ions at $T = 313 \text{ K}$. Drawn lines show results of numerical model simulations [20].

the one-dimensional reactor model. The results are given in Fig. 4. The agreement between the experimental and theoretical potential profiles is reasonable [20].

2.4. Different electrode configurations

The industrially interesting electrode configurations, given in Table 1, are discussed: first 3D-electrodes and then 2D-electrodes. Their advantages, disadvantages, and possible applications are presented and some experimental results are given. The authors are limited by the scope of the article and, also, their knowledge about not all electrodes discussed is enough to be able to produce an elegant little essay on each. However, a critical review is given. For more detailed information and also for application in commercial reactors see for instance [7,8,10,25].

2.4.1. Fluidised bed electrode

The fluidised bed electrode is a dynamic, 3D-electrode. A schematic representation of a fluidised bed electrode reactor used in practice is given in [10]. AKZO Zout Chemie originally developed it and it was further developed by Billiton Research for the extraction and reclamation of metals.

Advantages are a high mass transfer coefficient and the possibility of continuous removal of metal deposit from the cell. Disadvantages are a non-uniform potential distribution over the bed; dissolution of metal deposit in the unprotected zones of the bed (where the electrode potential of the particles rises to the corrosion potential); particle-particle and particle current feeder agglomeration and formation of inactive zones; and preferential growth near and on the separating membrane. Also, metal concentrations below 2 mol m^{-3} are not effectively treated because dissolved oxygen will sharply decrease the effectiveness of metal removal.

An industrial application is removal of Cu^{2+} ions from high conductive process liquids [29]. Only metal-metal ion couples with $E_r \gg E_{r,\text{H}_2}$ can produce a successful process.

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