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REVIEWS OF ELECTROCHEMISTRY

Electrochemistry and the environment

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Advances in electrochemical methods for pollutant remediation, recycling and sensing are reviewed. Additionally, applications of these methods in the drinking water industry, and for disinfection scenarios are discussed. Lastly, new electrode materials for environmental applications are described. In a companion review, photoelectrochemical methods will be discussed.

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1. Introduction and scope of review

This review charts recent progress in the development of electrochemical methods for treating and, in many cases, recycling harmful chemicals. The viability of such methods for sterilization, disinfection, deodorization and similar microbiological applications is also considered. Environmental applications of electrochemistry have been the topic of several recent books and reviews [1–6]. Specific commercial processes and systems are not discussed; the interested reader may find such material elsewhere [2, 4, 6, 7] and in patent literature. Similarly, radioactive materials warrant special techniques for their handling and disposal, and are not discussed here. The literature cited is representative rather than comprehensive. Economic aspects, while undoubtedly important, are beyond the scope of this article.

A second area where electrochemistry is playing an increasingly key role is in sensor technology. Electrochemical sensors for environmental applications have been reviewed by previous authors [8–16]. Accordingly, only selected examples of, and approaches to, trace level detection of microorganisms and air, water, and soil-borne pollutants are given below. In both the instances involving treatment (or recycling) and sensing, we have adopted a (generic) concept-driven format for the review; case-by-case description of past and present work on the myriad of pollutant chemicals and microorganisms would have been prohibitive.

Finally, future opportunities and emerging materials in electrochemical environmental science and technology are discussed. A companion review [17] will treat the applicability of photoelectrochemical methods for pollutant sensing and treatment.

2. Electrochemical remediation and recycling

2.1. *General considerations*

Electrochemical processes offer several promising approaches for the prevention and remedy of pollution problems. Among the main characteristics that are attractive are (i) *versatility* – direct or indirect oxidations and reductions, phase separations, concentrations or dilutions, biocide functions, can deal with many pollutants: gases, liquids and solids, and can treat from microlitres to millions of litres, and (ii) *Energy efficiency* – electrochemical processes generally have lower temperature requirements than those of equivalent nonelectrochemical counterparts (e.g. thermal incineration). Potentials can be controlled and electrodes and cells can be designed to minimize power losses due to poor current distribution, voltage drops and side reactions.

Other characteristics include (iii) *amenability to automation* – the electrical variables used in electrochemical processes (I, E) are particularly suited for facilitating data acquisition, process automation and control, (iv) *environmental compatibility* – the main reagent here, the electron, is a 'clean reagent' and there often is no need for adding extra reagents. In addition, the high selectivity of many of these processes can be used to prevent the production of unwanted side-products, and (v) *cost effectiveness* – the required equipment and operations are generally simple and, if properly

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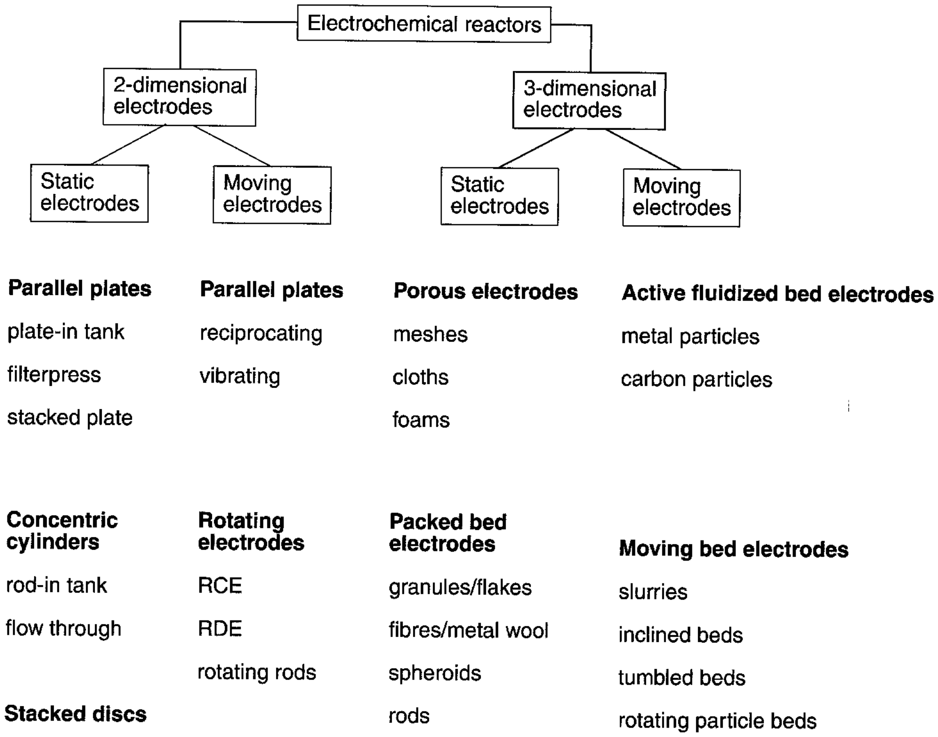

Fig. 1. Classification of electrochemical reactors according to electrode geometry and configuration. (Reprinted with permission from The Electrosynthesis Company Inc., East Amherst, New York.).

designed, are also inexpensive. Other attributes are discussed, for example, in [1–6].

'Zero effluent' technology necessitates the design of electrolytic cells to yield a high conversion of electroactive species. In this respect, it must be borne in mind that the pollutant species are seldom ever present in concentrations in excess of a few hundred or thousand parts per million at the upper limit, and thus the cell design considerations are very different from, for example, a metal electrowinning scenario [18]. Figure 1 contains a classification of electrochemical reactor designs [19]. Theoretical treatments are available for several of the electrode geometries indicated [2, 7, 20–26].

2.2. *Direct electrolysis*

Pollutants capable of undergoing direct electrochemical oxidation or reduction at an electrode can, in principle, be transformed and/or removed from water streams or reservoirs by the application of appropriate potentials in electrochemical reactors. Here, oxidation or reduction processes occur directly on inert electrodes without the involvement of other substances (e.g. electron mediators, biocidal species). Unfortunately, rather than the removal of unwanted material being the dominant electrode process, side reactions, particularly solvent breakdown, almost always occur, for example,

$$2H_2O \longrightarrow O_2 + 4H^+ + 4e^- \tag{1}$$

$$2H_2O + 2e^- \longrightarrow H_2 + 2OH^- \tag{2}$$

Although these reactions have a deleterious effect on the overall process efficiency, schemes have been devised to exploit the pH changes associated with Reactions 1 and 2 to bring about useful reaction chemistry. A case in point is the electrochemical reduction of the (very toxic) Cr(VI) to Cr(III) [27, 28]. The generation of hydroxyl ions at the cathode (Reaction 2) serves to immobilize the electrolytically generated Cr(III) as the insoluble hydroxide. Other examples are given below.

2.2.1. Anodic processes. Direct electrolytic oxidation has the capability of degrading many organic and inorganic compounds. Representative examples are listed in Table 1.

A good example of a direct process is the oxidation of Cr(III) to Cr(VI) [34].

$$2Cr^{3+} + 7H_2O \longrightarrow Cr_2O_7^{2-} + 14H^+ + 6e^- \tag{3}$$

An application of this reaction is the use of Cr(VI) as a regenerable oxidant in pharmaceutical, electronics, and aerospace industries. Oxidation of Cr(III) in the spent liquor streams may be carried out in a flow cell containing Nafion® as a separator membrane. Antimony-doped lead oxide or stainless steel anodes have been used although, for the more aggressive fluoride-containing etch media, PbO_2-modified ceramic electrodes based on Ebonex® (see below) are suitable. The Nafion® serves the important function of partitioning cationic impurities in the spent liquor (e.g. Al^{3+}, Cu^{2+}) into the cathode compartment wherein they may be reduced to the metal to regenerate value-added byproducts. The result is a cleaner etch solution which may be recycled back into the process. A recent paper [35] describes the innovative use of a Cr(VI)-strip phase containing Aliquat 336 which is immobilized in a solvent loaded polypropylene membrane. This facilitates the partitioning of

Table 1. Some examples of direct anodic processes

Pollutant	*Product*	*Remarks*	*Ref.*
Cyanide	NH_4^+, CO_3^{2-} or CO_2 and N_2	Product dependent on pH	[29]
	Cyanate	Product much less harmful. Current efficiencies for conversion up to 100% for cyanide concentration in the 0.25–1.00 M range.	[30, 31]
Dyestuffs	Colourless substances	Process used in conjunction with activated carbon. Decolorization of ~ 99.9%.	[32]
Aniline dyes	Colourless substances	Up to 97.5% conversion of which 72.5% comprises CO_2. Current efficiency ranges from 15% to 40%.	[33]
Cr(III)	Cr(IV)	Product more toxic although it is regenerated in a closed loop.	[34]

the electrogenerated Cr(VI) into the supported liquid membrane phase.

The ease of electrochemical oxidation of the organic species can be estimated by using the so-called electrochemical oxidability index (*EOI*), which gives an idea of the average current efficiency achieved during the process [36–39]. The larger this value, the more easily the species can be oxidized. Furthermore, by calculating the fraction of current that oxidizes the organic species (as opposed to the fraction that oxidizes water) and converting it to its equivalent in grams of oxygen per gram of the organic species, an electrochemical oxygen demand (*EOD*) has been defined as follows [36–38]:

$$EOD = w_{O_2}/w_{org} = (It/4F)(EOI)(32)/w_{org} \qquad (4)$$

where I is the electrolytic current, t is the time of electrolysis at which the (instantaneous) current efficiency is practically zero, w_{org} is the weight of organic species present and F is the Faraday constant.

2.2.2. Cathodic processes. The removal of toxic metal ions from water streams or reservoirs constitutes an important example of this category. The literature is extensive [24–26, 40–47]. Metal ion concentrations, $[M^{n+}]$, in effluents from chemical process industries can be as high as 10^5 ppm, whereas maximum permissible concentrations are typically in the range between 0.05 and 5 ppm. Electrochemical methods are most commonly used for reducing the metal ion to its elemental state, usually as a strippable and recoverable deposit [43]. As $[M^{n+}]$ gets smaller during this process, mass transport enhancement to the electrode becomes increasingly important. If $[M^{n+}]$ is relatively high, say of the order of 100 ppm, this effect can be achieved by the use of two-dimensional cells (e.g. enhanced flow plate cells or

Table 2. Some examples of the direct cathodic processes

*Electrode configuration**	*Metal ions*	*Remarks*	*Ref.*
(a) Porous			
Porous RVC	Cu(II)	Enhancement of current density of 100–250 fold compared to flat-plate.	[40, 41, 49]
Graphite felt	Hg(II), Cr(VI)	Charge efficiency of ~ 92%	[50–52]
Packed metal (Cu, Ag) wool	Cu(II)	–	[44]
Galvanized steel screens	Pb(II)	Level reduction to ~ 2.5 ppm	[53]
(b) Packed bed electrodes			
Graphite grains	Cu(II), Zn(II), Ag(I)	–	[43]
Graphite felt and pulverized graphite	Cu(II)	Chelating agents simultaneously treated at the anode.	[54]
Raschig rings, perforated plates etc.	Cu(II) etc.	Simultaneous destruction of cyanide achieved under certain conditions.	[42]
(c) Rotating cylinder electrode	Cu(II) etc.	For Cu(II) 100 ⟶ 10 ppm with 72% current efficiency.	[19]
(d) Moving bed electrode	Cu(II) etc.	1000 ⟶ 10–20 ppm with current efficiency up to ~ 85%.	[46]
(e) Fluidized bed electrode	Cu(II)	Typical conversion from 350 ⟶ 20 ppm.	[55]

* See Fig. 1.

Table 3. Some examples of indirect electrolytic processes

Reversible couple	*Pollutants*	*Remarks*	*Ref.*
Fe(II/III)	Carbonaceous waste	Reactor operated at 120–150 °C	[2]
	Cr(VI)	Reduction to Cr(III). Direct reduction kinetically sluggish.	[59]
Mn(II/III)	Cr(VI)	Milder operating conditions than for the Fe(II/III) case.	[2]
Ag(I/II)	Organics	More than 98% conversion of organic carbon to CO_2 claimed.	[60, 61]
Cl^-/ClO^-	Cyanide	A bipolar trickle-tower reactor used. The mediated oxidation was faster than direct oxidation (cf. Table 1).	[62]

rotating cylinder cells), whereas if $[M^{n+}]$ is below say 1 ppm, three-dimensional electrodes are more appropriate (cf. Fig. 1). A review of electrochemical reactor systems for the recovery of metals and for pollution control applications, including a comparative economic analysis is available [25].

Chlorinated organic compounds comprise another important category of pollutants that are amenable to cathodic reduction. These compounds can be reduced in acidic [30] or basic [48] solutions by a replacement mechanism to yield the (less toxic) aromatic parent compounds plus chloride ions. Some examples of cathodic processes are contained in Table 2.

2.3. *Indirect electrolysis*

The idea here is to use an electrochemically generated redox reagent as a chemical reactant (or catalyst) to convert pollutants to less harmful products. The redox reagent acts then as an intermediary for shuttling electrons between the pollutant substrate and the electrode [56]. Indirect electrolytic processes can be viewed as chemical on/off switches [57] since they stop when the current supply is discontinued. Among the principal requirements for obtaining high efficiencies in the indirect electrolytic processes are: (i) the potential at which the intermediate species is produced must not be near the potential for oxygen or hydrogen production, (ii) the rate of generation of the intermediate species must be large, (iii) the rate of reaction of the intermediate species with the pollutant must be higher than the rates of any competing reactions, and (iv) adsorption of the pollutant (or any other species) must be minimized [58].

2.3.1. Reversible processes. Here, the redox reagent can be electrochemically regenerated and recycled into the process. Table 3 provides representative examples.

The use of solution redox couples implies in some cases the need for a solution–solution separation step which may be undesirable. An alternative approach consists of the use of insoluble inorganic catalysts (BaO_2, MnO, CuO, NiO) capable of being suspended in the solution and of being oxidized to valence states that will in turn oxidize undesired pollutants [63, 64]. This approach requires a simple separation step. To avoid the need for separation, the redox couple (e.g. SnO_2, CrO_3, Sb_2O_3) can be immobilized on an electrode surface [30, 65, 66].

Many anodic O-transfer processes (such as those involved in the oxidative degradation of chemical wastes) occur with considerable overvoltage in the potential region for anodic discharge of H_2O leading to the production of oxygen gas. A strategy has been developed for the modification of metal oxide [e.g. Bi(V) doped-PbO_2] electrodes for maximizing the rate of O-transfer without excessive evolution of oxygen [67, 68].

2.3.2. Irreversible processes. The examples discussed above are catalytic in that these (reversible) redox reagents are turned several times over. However, indirect electrolysis can also be employed in electrochemically irreversible situations involving the generation of potent oxidizing species such as chlorine, hypochlorite, peroxide and ozone. The production and use of these species for the electrochemical disinfection of water will be discussed in a later section.

(a) *Electrochemical production of short-lived intermediates.* Short-lived intermediates that have been reported to be present in the electrochemical destruction of pollutants include e_{solv}, $OH^\cdot$, $O_2^{\cdot-}$ and $HO_2^\cdot$ [30, 56, 60, 69]. The production of intermediates can be crucial to the mechanism involved in a given reaction in such a way that undesirable byproducts can be eliminated [30].

The electrochemical oxidation of phenol to CO_2 for waste water treatment at SnO_2 anodes involves the production of the highly oxidizing $OH^\cdot$ radicals [35]. These radicals are known to be produced in the reduction of hydrogen peroxide with ferrous ion:

$$Fe^{2+} + H_2O_2 = OH^- + OH^\cdot + Fe^{3+} \qquad (5)$$

and can also be produced electrochemically in an indirect form by reducing oxygen (which produces H_2O_2) and simultaneously reducing the Fe^{3+} produced in the reaction just described [70]. These radicals are also used for the oxidation of other substituted benzene derivatives [69, 70], formaldehyde [71] and for the electrochemical oxidation of CN^- to CNO^- in alkaline solutions [72]. Photoelectrochemical methods for generating $OH^\cdot$ radicals are discussed in the companion article [17].

(b) *Electrochemical incineration of wastes.* Waste biomass has been electrolyzed indirectly in sulfuric acid and urine electrolytes, yielding results of up to 95% reduction in the concentration of organic carbon [73, 74] without producing CO, NO, NO_2, CH_4 nor NH_3. The mechanism in the urine electrolyte involves oxidation of the organic matter through the anodic generation of ClO^- from the Cl^- content of the urine.
(c) *pH manipulation.* The production of H^+ at an anode during the electrolysis of water can be used to acidify the anolyte. This effect has been used for example for promoting the controlled coagulation of proteins. Here strict control of acidity is required to avoid protein denaturation [75] and for the neutralization of alkaline water streams [76]. Likewise, the production of OH^- at a cathode has been used, for example, to precipitate metal hydroxides as mentioned above, as well as to shift the equilibrium towards the formation of CO_3^{2-} ions in hard waters in order to promote the coalescence and precipitation of $CaCO_3$ crystals [77].
(d) *Electroflotation-electrocoagulation.* Gases (e.g. O_2, H_2) produced during the electrolysis of aqueous solutions can be used to attach pollutants (e.g. fats and oils) to the gas bubbles and carry them out to the top of the solution where they can be more easily collected and removed. Pulsed electrogeneration of bubbles for electroflotation yields optimum-sized bubbles that are independent of solution conditions [78]. If hydrogen gas is produced at the cathode and Fe or Al are used as anodes [79], the Fe^{n+} or Al^{3+} ions resulting from the oxidation of the anode can react with the OH^- ions produced at the cathode and yield insoluble hydroxides that will precipitate adsorbing pollutants (e.g. Cr(VI) [79]) out of the solution and also will contribute to coagulation [80]. The solid sludge thus produced has been reported to be more compact than those obtained by chemical methods [79]. In addition, the presence of Fe^{2+} ions, for example in water/oil emulsions, promotes the coalescence-flocculation of colloidal particles due to the neutralization of the negative charge responsible for the repulsion between colloidal particles; this effect facilitates the breaking up of the emulsion. The electric field also facilitates the movement of the charged colloidal particles in the solution, increasing the probabilities for collisions [79]. Yields of up to 99% removal of suspended matter, 99% reduction of chemical oxygen demand (*COD*), 91% reduction of biological oxygen demand (*BOD*), 100% removal of PO_4^{3-} and 100% decoloration using electrocoagulation and electroflotation to treat waste waters of various industrial processes have been reported [79]. To decrease costs, iron scrap can be used as the anode. Electrocoagulation has also been used to achieve essentially complete (98–100%) removal of dye stuffs [81].

2.4. *Membrane-based approaches*

Membrane-based technologies have achieved commercial success in recent years especially in the separation of gaseous and liquid mixtures and purification of chemical and biological mixtures [82, 83]. Even with these commercial successes and the maturity of the technology, there are still many unresolved issues and significant opportunities remain for advancements in the development of new membranes and membrane process systems [82–85]. The sales of membrane technology for separation and filtration applications currently exceed $1B worldwide [84]. A study was recently published by the US Department of Energy (DoE) in which the ten highest ranked priority areas in membrane technology were given [85]. The basic interest of DoE in the use of membranes is to foster more energy-efficient technology. Two review articles discuss the current status of membrane technology and emphasize the enormous prospects for combining membrane science with electrochemistry [82, 83].

A major electrochemical, membrane-based separation process in commercial use today is electrodialysis. Electrodialysis involves the separation and concentration of electrolytes based on electromigration through ion exchange membranes. An array of alternating anion and cation exchange membranes is positioned between two electrodes separated by insulating screens. The alternating arrangement of the membranes allows ions to be passed by one membrane and blocked by the next. Solutions from the alternating compartments are collected and transported out of the membrane stack. Cellulose acetate is one of the more commonly used membranes along with Nafion® – a perfluorosulfonate polymer, polyacrylonitrile, and polysulfone. Electrodialysis is best known for its use for the desalination of brackish water. This separation results in two useful byproducts: potable water and natural salt deposits such as NaCl (table salt). Electrodialysis is also particularly useful for (i) removing ionized solutes from one solution and concentrating them in another and (ii) removing electrolytes from nonelectrolytes (e.g. organic process streams and mixed waste). The driving force for the latter process is migration of the charged electrolytes from the non-charged species. The fractionation, concentration and desalting of effluents from metal finishing processes represents an example of a technology which could benefit enormously from the congruence of membrane science and electrochemistry.

The use of ion-exchange and permselective membranes in separations and chemical processing is a rapidly growing field [82, 83]. Recent years have witnessed the development of ion exchange membranes with increased selectivity and chemical stability, and decreased mass transport resistance. Ion-selective membranes such as Nafion®, Flemion® and the Dow membranes are all perfluorinated polymers which were developed originally for the chlor–alkali industry. The development of these highly permeable, ion-selective membranes has revolutionized electrochemical processing technologies such as the production of caustic soda and chlorine via salt electrolysis [2, 7]. A major use for ion exchange membranes is in water softening. The ion exchange process is accomplished by passing water, successively, over a series of ion exchangers which replace the anions and cations in solution with hydrogen and hydroxide ions. The net result is that each equivalent of salt is replaced in solution with an equivalent of water. Deionization by this method generally produces water of very high quality. Certain organic compounds foul the ion exchangers and microbial growth also can reduce the efficiency of the process [2, 7].

The properties and uses of Nafion® have been reviewed [86]. These membranes must remain hydrated in order to retain their conductivity. Consequently, water and reactant mass transport through these membranes is an active area of research. Thus, the transport number of water in Nafion® membranes has been experimentally determined [87]. Hydrogen diffusion, hydrogen solubility and water uptake in Dow perfluorocarbon membranes have been measured [88]. The effect of temperature on the equilibrium and transport properties of water in Nafion® membranes has been studied [89–91]. Ion-transport in Nafion® and similar ionomers has also been intensively studied [92–97]. Luminescence spectroscopy has been useful for elucidating the structure of Nafion® and similar membranes [98–102]. These membranes can be pictured as having chemically stable fluorocarbon backbones organized so that the hydrophilic groups can aggregate together forming hydrated channels which the ions can migrate [103, 104].

The vast majority of examples of the use of Nafion® and other membranes in metal ion removal are found in the patent literature.

2.5. *Electroremediation of soils*

Electric fields have been used for the decontamination of soils containing unwanted organic or inorganic substances. Here, suitable anodes and cathodes are strategically placed in the ground and an electric field from a DC source is applied [105–107]. An electroosmotic effect produces a transport of the liquid phase pollutants across charged substrate pores or channels to wells, where they are collected and removed. This *in situ* transport promotes a high degree of flow direction control. In addition, an acid front is generally produced at the anode during the electrolysis of water and moves towards the cathode. This front can be used to inject acidity to soils, solubilize basic metal hydroxides, carbonates or adsorbed species, and protonate electron-rich organic functional groups in order to give molecules a more cationic character and promote their migration across the electric field thus facilitating their removal. Some of the aspects that will have to be addressed to make optimum use of this approach include: the complexity of the media, surface interactions, chemical and electrodic reactions and low solubilities of the target substances. The field of soil decontamination using electrokinetic processing has been recently reviewed [106, 107].

2.6. *Electrochemical conversion of gasous pollutants*

The increase in the CO_2 content of the atmosphere is a major factor in the 'greenhouse effect'. This problem coupled with the attractive possibility of converting a plentiful chemical to energy-rich products has prompted a number of investigations on the electrochemical reduction of CO_2. The advances in this area have been reviewed [108, 109]; therefore, only a brief discussion is given below.

Reduction in aqeous media suffers from problems due to the interference from proton reduction. Thus the best electrode materials are those with high hydrogen overpotential (e.g. Pb, Sn, In) [110, 111]. The main reduction product in aqueous solutions is formic acid or the formate ion, although faradaic efficiencies close to 100% have been reported also for methanol formation [110]. There are even reports of CO_2 reduction leading to methane as the product [112, 113]. The mechanistic and kinetics aspects of the electroreduction of CO_2 in aqueous solutions have been discussed for a wide variety of metals [114, 115]. These authors have also considered the effects of different factors such as CO_2 partial pressure, solution pH and buffer composition, electrode potential and solution hydrodynamics. Electrode materials other than metals have been used including TiO_2/RuO_2 and other oxides [116, 117]. In many cases, metal complexes are used as electrocatalysts and candidates in aqueous media include nickel cyclam (cyclam = 1,4,8,11-tetraazacyclotetradecane) and metallated porphyrins or phthalocyanines [118–121]. Catalysts such as $[Co(terpy)_2]^{2+}$ (terpy = $2,2':6',2''$-terpyridine) have also been immobilized in polymer coatings (e.g. Nafion®) on a support electrode [e.g. glassy carbon (GC)] surface [122].

A second electrochemical route to CO_2 reduction revolves around the use of nonaqueous solvents (e.g. CH_3CN, acetonitrile, dimethylsulfoxide). The first step in these cases has been determined to be the formation of the anion radical ($CO_2^{\bar{\cdot}}$) [123]. The major product on a preparative scale is the oxalate dianion although CO, CO_3^{2-}, $(COO)^{2-}$ and $HCOO^-$ may all be formed from $CO_2^{\bar{\cdot}}$ in follow-up reactions [109].

A third alternative route is the electrochemical fixation of CO_2 in organic compounds. Thus the electrolysis of 1,4-benzoquinone in the presence of CO_2 yields 2,5-dihydrobenzoic acid [124]. More recently, CO_2 has been fixed in oxoglutaric acid using an enzyme (isocitrate dehydrogenase) which is recycled using methyl viologen as a mediator [125]. Current efficiencies close to 100% were reported by these authors.

Photoelectrochemical and photocatalytic methods for the reduction of CO_2 are reviewed in the companion article [17]. The *electrooxidation* of CO on noble metals has been the topic of a recent review [126]. Much of the work cited therein has been motivated by applicability to fuel cells, rather than for environmental reasons.

Gases such as SO_x and NO_x are generally transferred by absorption or reaction to aqueous solutions prior to electrochemical oxidation or reduction. This conversion can be effected in two modes: (a) the gas is directly absorbed in an electrochemical cell for treatment (inner-cell process), or (b) the gas is absorbed in a separate reservoir and then transferred to the electrochemical cell (outer-cell process) [127]. In many cases, useful products may be generated as exemplified by the electrolytic production of sodium hydrosulfite (an important commodity chemical in the paper and textile industries):

$$4NaOH + 4SO_2 + 4e^- \longrightarrow 2Na_2S_2O_4 + 2H_2O + O_2 \tag{6}$$

Three-dimensional electrode structures (cf. Fig. 1) provide large surface areas for gas adsorption. For example, a packed bed of graphite spheres has been used for the electrochemical reduction of chlorine gas and for the oxidation of SO_2 [127]. Porous carbon electrodes have been used for the electrolysis of H_2S [80]. Molten salt electrolytes (e.g. molten sulfides) have been employed for similar applications [128, 129]. Electrode technology borrowed from developments in the fuel cell field has been used for the treatment of NO_x [130, 131].

3. Electrochemical disinfection of water

Disinfection and odour removal are important problems that impact on the quality of our everyday life in a technology-intensive world. The new regulations likely to be promulgated by the US Environmental Protection Agency and the amendments to the Safe Drinking Water Act (1986) will necessitate the evaluation of new technologies for the disinfection and treatment of water in the United States. A similar scenario may be envisioned in other countries. Specifically, the use of free chlorine as a disinfectant will have to be limited to high-quality ground water in order to meet the disinfection byproduct (DBP) regulations [132]. Chlorination of ground waters high in total organic carbon would produce unacceptable levels of trihalomethanes and other (carcinogenic) DBPs. Some alternative technologies to chlorination include the use of chlorine dioxide, ozone, u.v. radiation and advanced filtration processes.

Electrochemical methods for generating disinfection chemicals in-situ have been described by a number of authors [133–140]. The approaches based on the generation of species such as chlorine and ozone suffer from several drawbacks. First, they are rather energy-intensive. Second, it is not clear to what extent these alternative approaches are immune from the drawbacks associated with DNPs. Bactericidal agents such as H_2O_2 clearly are attractive in this regard and they can be electrolytically generated under rather mild conditions. Thus a recent report has described the electrochemical deactivation of marine bacteria (*Vibrio anguillarum*) using *in situ* electrochemical generation of H_2O_2 [141].

A variety of other microorganisms varying in size from viruses through bacteria and algae to relatively large species such as *Euglena* appear to have been successfully deactivated by electrochemical methods [136]. The types of electrodes used have ranged from graphite or graphite fibres [136, 142], metals including titanium [134, 137] and stainless-steel [134] to materials such as porous carbon [143, 144], carbon cloth [143] and SnO_2 [141].

Contrasting with the approach based on the in situ electrochemical generation of lethal species is the one based on the electrosorption of microorganisms [134, 144], and the direct anodic oxidation of intracellular components such as coenzyme A [143, 144]. The applicability of these alternative electrochemical approaches to *nonbacterial* pathogens (e.g. viruses, protozoan cysts), however, remains to be established.

4. Electrochemical sensing of pollutants

Electrochemical methods for sensing pollutants may be categorized as (i) potentiometric, (ii) amperometric/coulometric, (iii) voltammetric (incorporating preconcentration and stripping steps), and (iv) conductometric. Each of these approaches is discussed below. A further point of distinction pertains to whether the pollutant is gaseous (e.g. ozone, H_2S, CO, O_2, NO_x, SO_x) or whether it is confined to the solution phase. However, in many instances, it is beneficial to bring out a phase change or a phase transfer prior to detection. A case in point is a moisture detection scheme wherein the water molecules are electrothermally vaporized prior to the (amperometric) detection stage [145]. Electrochemical detectors are also often a component of a larger (chromatographic) system having the important function of separating the constituents of a complex mixture. Two such classes of 'composite instrumental systems', namely capillary electrophoresis and ion chromatography, have made spectacular advances in recent years. These are only peripherally addressed in this review, although their importance to environmental sensing applications cannot be overemphasized. While ion selective electrode (ISE) potentiometry and conductometry are briefly discussed below, *dynamic* electroanalytical measurements, such as categories (ii) and (iii) above, fall more directly within the purview of this article.

4.1. *Potentiometric sensors*

The field of ISEs has grown voluminously over the past few years and the number of studies recently published are too numerous to cite here.A comprehensive review of this field is available [10]. Well-known strategies for the determination of hydrogen ion (pH), fluoride, cyanide, ammonia,

Table 4. Representative examples of studies of potentiometric ion sensors based on chemically-modified electrode surfaces

Membrane/coating	*Analyte ion(s)*	*Ref.*
Graphite modified with poly(pyrenamine)	H^+	[146]
Metal (Ir, Pb, Pd) oxides	H^+	[147]
Polyaniline or polyphenol	H^+	[148]
Poly(vinyl chloride) (PVC) modified with a calixarene ionophore and a polypyrrole solid contact	Na^+	[149]
PVC modified for improved adhesion	NH_4^+, K^+	[150]
PVC modified with Sn(IV) and Mn(III) porphyrins	ClO_4^-, IO_4^-, SCN^-, I^- etc.	[151]
Glassy carbon modified with electro-polymerized Co(III) porphyrin	SCN^-, ClO_4^-, I^-, NO_3^- etc.	[152]

magnesium, calcium, etc. exist using ISEs. These electrodes also now possess many applications in water and environmental analysis. The selective and sensitive potentiometric determination of an ion of interest depends on the measurement of a potential difference established across a membrane between the solution of interest and a reference solution. Ultimately, the utility of an electrode depends on the properties of the membrane used. The membrane-electrode should equilibrate rapidly, should change only in response to an ion of interest and should preferably change linearly with the concentration of this species. The origins of the membrane potential are not fully understood but are believed to be related to Donnan equilibria (ion partitioning) on both sides of the membrane as well as diffusion through the membrane. Understanding transport phenomena in polymer/membrane systems remains an area of active research [82, 83]. Several types of membranes are used to fabricate ISEs, including (i) glasses, (ii) solid-state membranes, (iii) heterogeneous membranes, and (iv) liquid membranes. Potentiometric sensors can be categorized into those utilizing an internal reference solution and solid-state sensors [16] requiring no internal solution. Much work has been devoted in recent years to the development of the latter due to the ease with which these sensors can be miniaturized [16].

The selectivity of glass membranes made of $Na_2O-Al_2O_3-SiO_2$ mixtures depends on the composition of the glass and they are used for the determination of hydrogen ion (pH). Some compositions are more selective to the alkali metal ions than towards hydrogen ion and vice versa. At low pH the electrodes are primarily sensitive to only hydrogen ion while at higher pH values responses of the alkali metal ions, sodium, lithium and potassium become more influential. The most advanced solid-state membrane perhaps is the lanthanum fluoride crystal doped with EuF_2 for the determination of fluoride. These electrodes exhibit a stable and reproducible response selective for fluoride provided the solution pH remains neutral or lower. Heterogeneous membranes are formed by incorporating an active component within the pores of an inert high surface area support such as silicone rubber. Liquid membrane electrodes involve the incorporation of large, charged organic molecules capable of a specific interaction with a cation or anion in solution. The active organic molecule is adsorbed into a porous inert support. Some of the organic molecules used include transition metal complexes and neutral macrocycle crown ethers. The deployment of novel organic molecules in these types of ISEs is currently a highly active area of research. A list of the commercially available ISEs along with the in useful concentration range and the primary interferences is given by Pletcher and Walsh [7].

Two areas not covered in this review are organic ISEs and solid-state ion selective field effect transistors (ISFETS). The reader is referred to the aforementioned reviews for further information on these topics [10, 16].

Table 4 contains some examples of potentiometric sensors for cations and anions. This tabulation also illustrates the virtues of chemical modification schemes for rendering ion selectivity to the parent electrode surface.

There has been an intensive effort in recent years to develop gas sensors given the recent concern over environmental pollution. Nafion® and poly(ethylene oxide) are commonly used as gas permeable membranes which separate the analyte solution from an internal reference solution. The gas diffuses through the membrane into the internal reference solution which is in contact with an ISE. The electrolyte and ISE are chosen to introduce selectivity into the assay. A thin, semi-permeable membrane along with a thin layer of the internal reference solution insures fast equilibration times. The development of novel organic molecules for use in membranes coated on quartz crystals for piezoelectric monitoring of vapours and in ISE membranes, has been reviewed [153].

The preceding discussion hopefully shows that in addition to the important role that membranes play in pollutant remediation (separation) strategies, they are also exceedingly versatile for sensing applications.

An important class of potentiometric gas sensors involves solid electrolytes such as fast or superior conductors (e.g. NASICON). The selectivity in these all-solid-state devices is built-in using a suitable sensing layer comprised of, for example, carbonates (for CO_2), sulfates (for SO_x), nitrates (for NO_x) and oxides (for O_2). Problems with suitable reference electrodes in these systems have been recognized and discussed [154]. Ceramic, particularly zirconia-based, sensors have also been developed, for example, for O_2 [155–158], CO_2 [159–162], CO [163], and SO_x [164–166]. These solid-state sensors are robust and have the miniaturization advantage because they do not require water, and can be operated at high temperatures in corrosive environments. Solid-state gas sensors utilizing ceramic and semiconductor films have recently been reviewed [16].

4.2. *Amperometric and coulometric sensors*

In an amperometric sensor, the potential is controlled at a convenient location (usually at the mass-transfer controlled plateau region of the current-potential curve), and the current is measured and related to the concentration of the (electroactive) analyte. Amperometric sensors have come into prominence for use with liquid chromatography (LC) and flow-injection analysis (FIA) systems [167, 168]. Coulometric detectors operate in an exhaustive electrolysis made unlike their amperometric counterparts wherein the fraction of electroactive species electrolysed is usually much less than unity. However the methodology of applying the perturbation signal and measuring the response is identical in both approaches such that, in principle, the same cell could be operated in either mode. Both types of detectors have been discussed by several authors [169–172], and the reader is also referred to a recent book on electrochemical detection in flowing streams [173].

A prototype amperometric sensor is the Clark electrode in which the measuring cathode is separated from the O_2-containing gas phase by a gas permeable membrane or porous barrier. These sensors are commercially available, and their use has also been extended to other gases including CO and SO_x. The cathodic detection of CO_2 is beset by interference problems from hydrogen evolution (as noted earlier). An amperometric device has been developed for use in aqueous media based on a complexation scheme involving copper(II) bis(1,3-propanediamine) [174]. The sensor operates at a potential higher than the oxygen reduction regime precluding interference from this species, although other acidic gases would interfere. Complexation chemistry with Cu(II) was also utilized for the development of an amperometric sensor for CO [175]. Negligible cross sensitivity was noted to oxygen, hydrogen, methane, ethanol or acetone.

The utility of membranes in amperometric sensors was mentioned earlier within the context of oxygen detection. Similar approaches have also been effective for ozone detection. A polarographic technique incorporating a gas-permeable membrane is reported to have a detection limit of 67 ppb [176]. A polytetrafluoroethylene membrane has been used in conjunction with a porous carbon felt electrode for the determination of residual ozone in water [177]. Sensors incorporating perfluorosulfonate ionomers have been developed for the amperometric determination of moisture [145, 178]. Amperometric moisture sensors based on P_2O_5 have a long history and a number of commercial units are available.

Anions in aqueous media have been detected amperometrically. For example, FIA has been coupled with amperometric detection for the phosphate and nitrite assay of water samples [179]. (These authors use the term 'voltammetric determination' although no potential scanning is involved.) The same group has also developed a method for the online reduction of nitrate to nitrite prior to amperometric assay [180].

In general, any electroactive species (organic, inorganic or biological) are amenable to amperometric (or coulometric) detection. Nonetheless, the real challenge in the sensor design rests largely on the ingenuity with which problems with electrode fouling, electrochemical reversibility and cross-sensitivity to interfering species can be circumvented.

4.3. *Voltammetric sensors*

Cathodic and anodic stripping voltammetry are widely used methods for the determination of organic and inorganic ions is environmental samples [181, 182]. Cathodic stripping voltammetry involves the application of a relatively positive deposition potential in the presence of anions which can be oxidized to form insoluble salts with metal constituents on the electrode surface (e.g. mercury and silver). The applied potential is then linearly swept from the deposition potential in the cathodic direction resulting in the selective reductive desorption of the anionic species according to the respective formal potential value. Anodic stripping voltammetry follows a similar sequence of events except that cationic species are reduced during the application of a negative deposition potential where, for mercury, amalgams form. The potential is then swept linearly in the anodic direction resulting in the selective oxidative desorption of the cationic species. Improved sensitivities can be achieved using pulsed waveforms to eliminate the charging current from small faradaic currents [181, 182]. Major problems with these methods, however, are (i) the toxicity of mercury, which makes the analysis less attractive from an environmental standpoint, and (ii) the surface fouling, which commonly occurs during analysis of a complex solution matrix, thus reducing the efficiency of the assay. The use of membrane-modified electrodes can circumvent these problems.

The controlled physical adsorption, or accumulation, of redox analytes on the electrode surface can improve the selectivity and sensitivity of the stripping voltammetric measurement [8, 181, 182]. Several reactions between a surface modifier (e.g. covalent binding or ion exchange polymer) and an analyte have been exploited to assist in the preconcentration step. The preconcentration of analyte is strongly influenced by

Table 5. Representative examples of trace analyses using stripping voltammetry

Electrode details	*Analyte(s)/matrix*	*Ref.*
Glassy carbon surface modified with Hg-coated Nafion	Trace metals in urine samples	[183]
Quinolin-8-ol silica gel membrane layer	Trace metals in sea water	[184]
Pt modified with poly(vinylpyridine)	Cr(VI)	[185]
Nafion modified with 1,10-phenanthroline and 2,2′-bipyridyl	Fe(II) and Co(II)	[186]
Carbon paste modified with polysaccharides	Cu(II) and Pb(II)	[187]

solvent, electrode material, membrane characteristics, pH, electrode potential, temperature, etc. The adsorptive accumulation of the analyte (i) improves the sensitivity of the measurement (10 to 100-fold over solution phase voltammetry), an especially useful attribute when low concentrations of analyte must be detected, (ii) renders the analysis less prone to mass-transfer limitations, (iii) improves the selectivity of the measurement in complex matrices, and (iv) reduces interference from organic constituents of the sample matrix which can interfere with the mass transport to the electrode surface and the electron transfer between the analyte and the electrode surface.

Representative examples of trace analyses using stripping voltammetry appear in Table 5.

Potentiometric stripping analysis has been used for trace analyses of heavy metals [188, 189]. As with the anodic stripping technique discussed earlier, the first step is the formation of a mercury amalgam. After this preconcentration step, the metals are stripped by chemical oxidation and the potential-time profile at the working electrode is recorded. The metals are identified by their stripping potentials and are quantified by measuring the stripping time for each metal. This method has been employed for several matrices including sea water [190], ground water [191], and sediments/sludge [192]. A variety of metals including Hg [193], Cu and Pb [190–192], and Pb, Tl, Cd, Bi, and Sn [191] have been quantitated. The method has also been combined with FIA [191].

Charging currents have a deleterious influence on the detection limits of conventional stripping voltammetry techniques. A way around this is stripping voltammetry combined with collection. This is done either with a rotating ring-disc assembly [194] or with two tubular electrodes in series in a flow system [195]. A variety of flow systems with large surface-area electrodes have been described [196]. Even non-metals such as phosphate and silicate have been determined by flow coulometry [197].

There is another important analytical advantage with the above approach. If *complete* electrochemical deposition of the trace metals has been achieved, then the method could operate as an *absolute* analytical procedure not demanding the need for calibration and standards. This has been discussed in a recent paper [198].

4.3.1. Metal speciation. The toxicity of many metals depends on their oxidation state and chemical form [199]. For example, inorganic mercury is much more toxic than the organoderivatives. Arsenic(V) is about 50 times less toxic than As(III). Similarly, Cr(VI) is much more toxic than Cr(III). Finally, like mercury, organolead compounds are much more toxic than the inorganic derivatives. Electro- analytical chemistry offers a convenient route to metal speciation and selective assay. Let us consider arsenic as a model system.

Arsenic in the higher oxidation state [As(V)] is not electroactive under normal conditions. However, the electroactivity is much better defined in the presence of catechol [200, 201], pyrogallol [200, 202], and D-mannitol [203] for reasons still not well understood. Three well-defined waves are now seen corresponding to the stepwise scheme: As(V) $\longrightarrow$ AS(III) $\longrightarrow$ AS(O) $\longrightarrow$ As(−III). Comparison of the corresponding half-wave potential values to those obtained for As(III) shows that the reduction of the As(V)-polyhydroxyalcohol complex (initially formed) proceeds to *uncomplexed* As(III).

The above findings suggest a scheme for incorporating speciation into the electrochemical assay. Thus, As(III) can be initially determined in a medium such as 1 M HCl, wherein As(V) is electroinactive. Then a complexing agent can be added and the total arsenic determined. An assay as As(V) is then obtained as a difference.

Chemical methods have also been employed [203–205] as a prelude to the electrochemical (stripping voltammetry) assay for reducing As(V) to As(III).

The organic arsenic derivatives (monomethylarsonic acid or MMA and dimethyl arsinic acid or DMA) have been determined by pulse voltammetry or polarography [206, 207].

4.4. *Conductometric sensors*

Conductance-based sensing strategies have recently found prominence following their use in ion chromatography (IC) [208] and capillary electrophoresis [209]. Electrodialytic membranes have been recently used as a suppressor for IC applications [210–212]. These membranes have also been used as generators to afford a combination which is claimed to eliminate conductivity contributions from chemical regenerant penetration in the suppressor column [212]. However, amperometric detectors with reportedly better detection limits (than conductometry) for anions such as sulfate, have been described for use with an IC system [213]. A flow-through detection system comprising a d.c. potential applied between two narrow gauge hypodermic needles has been described for IC applications [214]. Although the authors use the term "d.c. conductivity detection" to describe their system, electrolysis is actually involved here, and as the authors themselves point out, their terminology is not synonymous with the ionic conductance of solutions as usually measured by a.c. techniques.

Commercial detectors based on a.c. conductometric methodology have been described [215–217]. A novel IC system comprising sequential suppressed and single column detectors has been described, wherein an upstream detector uses a conventional suppressed NaOH eluent followed by a second detector employing a low concentration (0.1 mM) of NaOH eluent [218]. A wide range of analyte pK_as up to ~ 9.5 are reported to be accessible using this approach, permitting the assay of anions such as arsenate.

5. New electrode materials and electrolytes for environmental applications

An integral part of any new technology concerns materials and environmental electrochemical systems are no exception. In this section, we review some important developments in new electrode materials and electrolyte compositions; again the listing below is representative rather than comprehensive. A review of new electrode materials, is found in [219].

5.1. *Electronically conductive polymers*

These materials have recently attracted interest for a wide range of applications including batteries, electrochromic displays, anti-static and radar absorption coatings, corrosion protection etc. From an environmental perspective, one of the authors of this review has used polypyrrole for Cr(VI) remediation [220]. The use of polyaniline and polyphenol as pH sensors [148] has already been mentioned earlier in this review. Polypyrrole has also been used in amperometric sensors for the detection of anions such as chloride, carbonate, nitrite, phosphate and sulfate [221, 222], and a variety of cations [223–225]. Polyaniline or polyaniline-Nafion® composites [226–228] have been utilized for a similar purpose, and in some instances in combined FIA and IC systems. Polyaniline composites have also been examined for gas sensing applications [229]. Finally voltammetric measurements based on poly(3-methylthiophene)-coated glassy carbon electrodes have been described for the determination of phenolic compounds [230].

5.2. *Novel carbon-based electrodes*

Carbon aerogel composite electrodes have been prepared by the sol–gel condensation or resorcinol and formaldehyde in a basic medium followed by drying and pyrolysis [231]. The electrodes possess a high porosity, a surface area between 400–1000 $m^2 g^{-1}$, a nominal pore size of less than 50 nm and a solid matrix composed of interconnected colloidal-like particles or fibrous chains with characteristic diameters of 10 nm. The porosity and particle size can be varied over a wide range given the flexibility in the fabrication procedure. The authors are currently exploring the utility of these structures in a variety of electroanalytical applications. They describe the stripping voltammetric analysis of trace metals at a mercury-coated composite electrode. Detection limits in the ppm range were obtained with short deposition times.

Composite metal-carbon electrodes have been recently described [232, 233]. Stainless steel fibres (2 μm diam.) and carbon fibre bundles (20 μm diam.) are combined with cellulose fibres, used as a binder, into a continuous interwoven paper preform. The composite paper preform is then cut into electrodes with desired dimensions and geometry and sintered to a stainless steel foil substrate. These electrodes possess surface areas, as measured by the BET technique, of ca. 750 $m^2 g^{-1}$. The resultant high surface area allows high accessibility to gases and electrolytes while providing adjustable porosities and void volumes. The electrodes can be prepared with other metal fibres such as nickel.

Other novel carbon-based electrodes beginning to emerge include carbon foam composites [234], epoxy-impregnated reticulated vitreous carbon [235], doped carbon thin films and doped glassy carbon [236, 237].

5.3. *Ebonex® ceramic electrodes*

A new chemically inert conductive ceramic electrode based on the Magneli phase suboxides of titania has been developed [238]. The electrode is corrosion resistant in a variety of harsh chemical environments such as fluoride and chloride-containing media and can be operated as either the cathode or the anode. In the bulk ceramic form, the Magneli phases of the electrode exhibit a conductivity comparable to that of graphite. The high conductivity combined with the high level of chemical stability, make this electrode of great interest to researchers both as a direct electrode material and as a support for electrocatalysis. The electrode material has a wide potential window in aqueous electrolytes exhibiting large overpotentials for the oxygen and hydrogen evolution reactions. The electrode also possesses excellent permeability to liquids rendering it quite useful in flow-through waste recovery and waste management processes. Further work continues on this material for modifying the electrode microstructure and for surface modification with electrocatalytic coatings [239, 240] (also see above).

5.4. *Diamond electrodes*

Diamond offers exciting new possibilities as an electrode material for electrochemical systems. The unique properties of this material which include (i) extreme hardness, (ii) corrosion resistance, (iii) optical transparency, (iv) heat and radiation resistance, and (v) high thermal conductivity make this an attractive electrode material. Normally the insulating character of virgin diamond ($> 10^{12}\ \Omega$ cm) would preclude the use of this material in electrochemical cells. However, the resistivity of chemical vapour deposited diamond thin films can be made as low as $0.01\ \Omega$ cm by doping with boron. One of the authors of this review has made some initial observations regarding the behaviour of boron-doped diamond electrodes in contact with aqueous solutions [241]. The diamond electrodes have been observed to be chemically inert and microstructurally stable in a variety of acidic and alkaline electrolytes containing fluoride and chloride ions during hydrogen and oxygen evolution. A recent paper on the electrochemical reduction of nitrate to ammonia using conductive diamond film electrodes [242] exemplifies the promise of this material for environmental applications. However, much fundamental research remains to be done on how the electrochemical reaction kinetics are influenced by the structural and electronic properties of this material.

5.5. *Novel membranes and coatings*

We have seen the pivotal role that membranes play in environmental electrochemical science and technology. New membranes will undoubtedly continue to evolve for environmental applications. Electrode modifiers for selective partitioning and sensing of targeted species as well as new separator membranes will emerge. An example of the first sort is a recent report on ultra low-level ($< 10^{-12}$M) detection of mercury using 4,7,13,16,21,24-hexaoxa-1,10-diazobicyclo[8.8.8]hexacosane (Kryptofix 22) modified glassy carbon electrodes [243].

5.6. *Novel electrolytes for environmental applications*

The use of surfactants is a key aspect in many direct or indirect electrolysis systems for the removal of pollutants (cf. Section 2). The use of surfactant (e.g. cethylmethylammonium bromide and CTAB) micelles in water combined with catalysts such as metallated phthalocyanines has been proposed as a low cost, safer alternative to (toxic) organic solvents for reductive dechlorination of pollutants such as PCBs [244]. Limited solubilities in these media have prompted these authors to recently explore the applicability of bicontinuous microemulsions for this purpose [245].

Other (less conventional) alternatives to aqueous media include molten salts (see above), but, more intriguingly, supercritical fluids (e.g. CO_2). Preliminary reports of electrochemistry in such media have appeared [246] albeit from a nonenvironmental perspective.

6. Concluding remarks

This review has identified some of the many opportunities that exist for electrochemical techniques in environmental science and technology. It is appropriate to finish with a reflection on how industry has adopted these techniques on a routine basis for pollutant cleanup/recycling and sensing. It seems safe to conclude that there are many more examples for the use of electrochemical methodology in applications related to cleanup/recycling than in the analytical (sensing) area. Even within the latter category, routine use of dynamic electroanalytical techniques appears to be lagging behind other approaches (e.g. ISEs, conductance-based sensors) for pollutant sensing and quantitation. These general trends underline the 'cultural' barriers that impede the adoption by end-users of any new technology. It is easier to work with power supplies and voltmeters than to understand the intricacies of a potentiostat/galvanostat. To make matters worse, chemical modification or optimization of a working-electrode surface is often an art rather than a science. Nonetheless, the advent of 'smart' and user-friendly electrochemical instrumentation [248] augers well for the future.

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References

[1] J. O'M. Bockris (Ed.), 'Electrochemistry of Cleaner Environments' (Plenum, New York, 1975).
[2] J. D. Genders and N. Weinberg (Eds), 'Electrochemistry for a Cleaner Environment', Electrosynthesis Co., East Amherst, New York (1992).
[3] C. A. C. Sequeira (Ed.) 'Environmental Oriented Electrochemistry' (Elsevier, Amsterdam, in press).
[4] Proceedings of the Sixth International Forum on Electrolysis, 'Environmental Applications of Electrochemical Technology,' Electrosynthesis Co., East Amherst, New York (1992).
[5] D. Pletcher and N. L. Weinberg, *Chem. Eng.*, Aug. (1992) 98.
[6] D. Pletcher and N. L. Weinberg, *ibid.*, Nov. (1992) 132.
[7] D. Pletcher and F. C. Walsh, 'Industrial Electrochemistry', Chapman & Hall, London (1990).
[8] J. Wang, *Anal. Proc.* **24** (1987) 325.
[9] D. Pletcher, *in* [4].
[10] B. Fleet, *Talanta* **39** (1992) 1449.
[11] J. Janata, *Anal. Chem.* **64** (1992) 196R.
[12] M. D. Ryan and J. Q. Chambers, *ibid.* **64** (1992) 79R.
[13] F. Scholz and B. Lange, *Tr. Anal. Chem.* **11** (1992) 359.
[14] J. M. Skeaff and A. A. Dubreuil, *Sensors and Actuators* **B10** (1993) 161.

[15] E. M. Logathetis, 'Chemical Sensor Technology', Kodansa Ltd (1991).
[16] M. J. Madou and S. R. Morrison, 'Chemical Sensing with Solid State Devices', Academic Press, New York (1989).
[17] K. Rajeshwar, *J. Appl. Electrochem.*, to be published.
[18] D. Pletcher and F. C. Walsh, *in* [2].
[19] F. C. Walsh, *in* [2].
[20] J. A. Trainham and J. Newman, *J. Appl. Electrochem.* **7** (1977) 287; *J. Electrochem. Soc.* **124** (1977) 1528.
[21] R. Alkue and P. K. Ng, *J. Electrochem. Soc.* **121** (1974) 95.
[22] G. Kreysa and C. Reynvaan, *J. Appl. Electrochem.* **12** (1982) 241.
[23] S. Ehdaie, M. Fleischmann and R. E. W. Jansson, *ibid.* **12** (1982) 59.
[24] J. S. Newman and W. Tideman, *Adv. Electrochem. Electrochem. Eng.* **11** (1978) 353.
[25] B. Fleet, *Coll. Czech. Chem. Comm.* **53** (1988) 1107.
[26] R. E. Sorda and K. B. Keating, *Electroanal. Chem.* **12** (1982) 1.
[27] D. Golub and Y. Oren, *J. Appl. Electrochem.* **19** (1989) 311.
[28] M. Abda, Z. Gavra and Y. Oren, *ibid.* **21** (1991) 734.
[29] U. Ogutveren, E. Toru, S. Koparal and Z. Poyraz, 44th meeting of the international Society for Electrochemistry, Berlin, Germany, 5–10 Sept. (1993).
[30] N. L. Weinberg, *in* [4].
[31] F. Hine, M. Yasuda, T. Iida and Y. Ogata, *Electrochim. Acta* **31** (1986) 1389.
[32] P. M. Bersier *in* [4].
[33] D. W. Kirk, H. Sharifian and F. R. Foulkes, *J. Appl. Electrochem.* **15** (1985) 285.
[34] A. Kuhn and R. Clarke, *J. Appl. Chem. Biotechnol.* **26** (1976) 407.
[35] K. Scott and A. O. Ibhadon, *Electrochim. Acta* **38** (1993) 847.
[36] Ch. Comninellis and E. Plattner, *Chimia* **42**(7, 8) (1988) 250.
[37] Ch. Comninellis and C. Pulgarin, *J. Appl. Electrochem.* **21** **(1991) 703.**
[38] *Idem, ibid.* **23** (1993) 108.
[39] S. Stucki, R. Kotz, B. Carcer and W. Suter, *J. Appl. Electrochem.* **21** (1991) 99.
[40] D. Pletcher, I. Whyte, F. C. Walsh and J. P. Millington, *ibid.* **21** (1991) 659 and references therein.
[41] *Idem, ibid.* **23** (1993) 82.
[42] Y. Bingkun, *ibid.* **20** (1990) 974.
[43] D. Simonsson, *ibid.* **14** (1984) 595.
[44] B. G. Ateya, A. A. Ateya and M. E. El-Shakre, *ibid.* **14** (1984) 357.
[45] E. Avci, *ibid.* **18** (1988) 288.
[46] K. Scott, *ibid.* **18** (1988) 504.
[47] *Idem, ibid.* **11** (1981) 339.
[48] D. Schmal, P. J. van Duin and A. M. C. P. deJong, 'Electrochemical Dehalogenation of Toxic Organic Compounds in Industrial Waste Water,' Dechema Monogr. Band 124, VCH Weinheim (1991) pp. 241–247.
[49] D. Pletcher, I. Whyte, F. C. Walsh and J. P. Millington, *J. Appl. Electrochem.* **21** (1991) 667.
[50] V. Tricoli, N. Vatistas and P. F. Marconi, *ibid.* **23** (1993) 390.
[51] M. Abda, Y. Oren and A. Soffer, *Electrochim. Acta* **32** (1987) 1113.
[52] D. Golub and Y. Oren, *J. Appl. Electrochem.* **19** (1989) 311.
[53] R. Spotnitz, G. Ambrose-Ritchey, D. S. McFarland, R. Wormsbecher, H. Zerhusen and J. T. Lundquist, *in* [2].
[54] K. Kusakabe, H. Nishida, S. Morooka and Y. Kato, *J. Appl. Electrochem.* **16** (1986) 121.
[55] S. C. Yen and C. Y. Yao, 179th Meeting of the Electrochemical Society, Washington, DC, May 1991 (Extended Abstract No. 532).
[56] R. L. Clarke, A. T. Kuhn and E. Okoh, *Chem. Brit.* (1975) 59.
[57] R. G. Hickman, J. C. Farmer and Z. Chiba, *in* [4].
[58] T. M. Mill, C. C. D. Yao, S. Smedley, B. Dougherty and P. Cox, *in* [4].
[59] A. T. Kuhn, *Chem. Ind.* (1971) 946.
[60] D. E. Kurath, L. A. Bray and J. L. Ryan, *in* [4]
[61] C. Zawadzinski, W. Smith and K. Martinez, *in* [4].
[62] E. A. El-Ghaoui, R.-E. W. Jansson and C. Moreland, *J. Electrochem. Soc.* **12** (1982) 69.
[63] T. C. Franklin, G. Oliver, R. Nnodimele and K. Couch, *ibid.* **139** (1992) 2192.
[64] T. C. Franklin, J. Darlington, T. Soulouki and N. Tran, *ibid.* **138** (1991) 2285.
[65] F. Beck and H. Schulz, *J. Appl. Electrochem.* **17** (1987) 914.
[66] *Idem, Electrochim. Acta* **29** (1984) 1569.
[67] J. Feng and D. C. Johnson, *J. Electrochem. Soc.* **137** (1990) 507 and references therein.
[68] D. C. Johnson, *in* [2].
[69] R. Tomat and A. Rigo, *J. Appl. Electrochem.* **14** (1984) 1.
[70] T. Matsue, M. Fujihara and T. Osa, *J. Electrochem. Soc.* **128** (1981) 2565.
[71] J. S. Do and C. P. Chen, *ibid.* **140** (1993) 1632.
[72] B. Wells and D. C. Johnson, *ibid.* **137** (1990) 2791.
[73] L. Kaba, G. D. Hitchens and J. O'M. Bockris, *ibid.* **137** (1990) 1341.
[74] J. O'M. Bockris, R. C. Bhardwaj and C. L. L. Tennakoon, *in* [4].
[75] R. Labrecque, A. Theoret, F. Lamarche and M. Boulet, *in* [2].
[76] V. A. Kolesnikov, E. A. Shalyt and P. K. Aarinola, 181st meeting of the Electrochemical Society, St. Louis, Missouri, May 1992 (Extended Abstract No. 394).
[77] J. Nanzer and F. Coeuret, *J. Appl. Electrochem.* **22** (1992) 364.
[78] N. K. Khosla, S. Venkatachalam and P. Somasundaran, *ibid.* **21** (1991) 986.
[79] F. Persin and M. Rumeau, *Trib. Eau (France)* **82** (1989) 45.
[80] R. Kalvoda, *in* 'Electrochemistry in Research and Development' (edited by R. Kalvoda and R. Parsons), Plenum, New York (1985).
[81] M. R. Matsumoto, J. N. Jensen, P. M. McGinley and B. E. Reed, *Water Environ. Res.* **65** (1993) 309.
[82] A. S. Michaels, *Desalination* **77** (1990) 5.
[83] A. S. Michaels, *Chemtech*, March (1989) 162.
[84] J. Haggin, *Chem. & Eng. News*, 1 Oct. (1989) 22.
[85] R. W. Baker, E. L. Cussler, W. Eykamp, W. J. Koros, R. L. Riley and H. Strathmann, 'Membrane Separation Systems – A. Research and Development Needs Assessment,' Report DE-90-011770, Vols. 1, 2, US Department of Energy, Washington, DC (1990).
[86] A. Eisenberg and H. L. Yeager (Eds.), 'Perfluorinated Ionomer Membranes', ACS Symposium Series 180, American Chemical Society, Washington, DC (1982) p. 79.
[87] T. F. Fuller and J. Newman, *J. Electrochem. Soc.* **139** (1992) 1332.
[88] Y. Tsou, M. C. Kimble and R. E. White, *ibid.* **139** (1992) 1913.
[89] M. W. Verbrugge, E. W. Schneider, R. S. Connell and R. F. Hill, *ibid.* **139** (1992) 3421.
[90] T. A. Zawodzinski, C. Derouin, S. Radzinski, R. J. Sherman, V. T. Smith, T. E. Springer and S. Gottesfeld, *ibid.* **140** (1993) 1041.
[91] R. Liu, W. Her and P. S. Fedkiw, *ibid.* **139** (1992) 15.
[92] H. S. White, J. Leddy and A. J. Bard, *J. Am. Chem. Soc.* **104** (1982) 4811.
[93] D. A. Buttry and F. C. Anson, *ibid.* **105** (1983) 685.
[94] C. R. Martin and K. A. Dollard, *J. Electroanal. Chem.* **159** (1983) 127.
[95] C. R. Martin, I. Rubinstein and A. J. Bard, *J. Am. Chem. Soc.* **104** (1982) 4817.
[96] G. Nagy, G. A. Gerhardt, A. Oke, M. E. Rice, R. N. Adams, R. B. Moore, M. N. Szentirmay and C. R. Martin, *J. Electroanal. Chem.* **188** (1985) 85.
[97] L. D. Whiteley and C. R. Martin, *J. Phys. Chem.* **93** (1989) 4650.
[98] N. Prieto and C. R. Martin, *J. Electrochem. Soc.* **131** (1984) 751.
[99] Y. Kurimura, H. Yokota, K. Shigehara and E. Tsuchida, *Bull. Chem. Soc. Jpn* **55** (1982) 55.
[100] D. Meisel and M. S. Matheson, *J. Am. Chem. Soc.* **99** (1977) 6577.
[101] P. C. Lee and D. Meisel, *ibid.* **102** (1980) 5477.
[102] E. Blatt, A. Launikonis, A. W. -H. Mau and W. H. F. Sasse, *Aust. J. Chem.* **40** (1987) 1.
[103] Z. Porat, I. Rubinstein and B. Zinger, *J. Electrochem. Soc.* **140** (1993) 2501.
[104] H. L. Yeager and A. Steck, *ibid.* **128** (1981) 1880.
[105] R. F. Probstein and R. E. Hicks, *Science* **260** (1993) 498.
[106] D. Cabrera-Guzmán, J. T. Swartzbaugh and A. W. Weisman, *J. Air Waste Manag. Assoc.* **40** (1990) 1670.
[107] R. J. Gale, H. Li and Y. B. Acar, *in* [3].
[108] I. Taniguchi in J. O'M. Bockris, R. E. White and B. E. Conway (Eds.), 'Modern Aspects of Electrochemistry', Vol. 20, Plenum Press, New York (1989) p. 327.

[109] H. L. Chum and M. M. Baizer (Eds.), 'The Electrochemistry of Biomass and Derived Materials', American Chemical Society, Washington, DC (1985) Chapter 3, p. 141.
[110] P. G. Russell, N. Kovac, S. Srinivasan and M. Steinberg, *J. Electrochem. Soc.* **124** (1977) 1329.
[111] S. Kapusta and N. Hackerman, *ibid.* **130** (1983) 607.
[112] R. L. Cook, R. C. MacDuff and A. F. Sammells, *ibid.* **135** (1988) 1470.
[113] D. P. Summers and K. W. Frese, Jr., *ibid.* **135** (1988) 264.
[114] Yu. B. Vassiliev, V. S. Bagotzky, N. V. Osetrova, O. A. Khazova and N. A. Mayorova, *J. Electroanal. Chem.* **189** (1985) 271.
[115] Yu. B. Vassiliev, V. S. Bagotzky, N. V. Osetrova and A. A. Mikhailova, *ibid.* **189** (1985) 311.
[116] A. H. A. Tinnemans, T. P. M. Koster, D. H. M. W. Thewissen, C. W. de Kreuk and A. Mackor, *ibid.* **145** (1983) 457.
[117] J. Augustynski, *ibid.* **145** (1983) 457.
[118] M. Beley, J. P. Collin, R. Ruppert and J. P. Sauvage, *J. Am. Chem. Soc.* **108** (1986) 7461.
[119] C. M. Lieber and N. S. Lewis, *ibid.* **106** (1984) 5033.
[120] S. Kapusta and N. Hackerman, *J. Electrochem. Soc.* **131** (1984) 1511.
[121] T. Atoguchi, A. Aramata, A. Kazusaka and M. Enyo, *J. Electroanal. Chem.* **318** (1991) 309.
[122] T. Yoshida, T. Iida, T. Shirasagi, R-J. Lin and M. Kaneko, *ibid.* **344** (1993) 355.
[123] Yu. B. Vassiliev, V. S. Bagotzky, O. A. Khazova and N. A. Mayorova, *ibid.* **189** (1985) 295 and references therein.
[124] L. O. Bulhoes and A. Zara, *ibid.* 248 (1988) 159.
[125] K. Sugimura, S. Kuwabata and H. Yoneyama, *J. Am. Chem. Soc.* **111** (1989) 2361.
[126] B. Beden, C. Lamy, N. R. de Tacconi and A. J. Arvia, *Electrochim. Acta* **35** (1990) 691.
[127] D. Van Velzen, *in* [2].
[128] D. S. Schmidt and J. Winnick, 183rd meeting of the Electrochemical Society, Honolulu, Hawaii, May 1993 (Extended Abstract No. 965).
[129] S. R. Alexander and J. Winnick, 179th meeting of the Electrochemical Society, Washington, DC May 1991 (Extended Abstract No. 535).
[130] N. Furuya and T. Okada, 179th meeting of the Electrochemical Society, Washington, DC May 1991 (Extended Abstract No. 728).
[131] N. Furuya and K. Murase, 183rd meeting of the Electrochemical Society, Honolulu, Hawaii, May 1993 (Extended Abstract No. 953).
[132] R. L. Wolfe, *Environ. Sci. Technol.* **24** (1990) 768.
[133] M. Rumeav and A. Garmerone, *French Patent 2 470 097* (1979).
[134] A. Porta and A. Kulhanek, *US Patent 4 619 745* (1986).
[135] C. E. Smith, *in* Progress in Water Technology (edited by W. W. Eckenfelder and L. K. Cecil), Pergamon, New York (1972) pp 325–334.
[136] G. E. Stoner and G. L. Cahen, *Bioelectrochem. Bioenerg.* **9** (1982) 229.
[137] G. Patermarakis and E. Fountonkidis, *Water Res.* **24** (1990) 1491.
[138] A. Pareilleux and N. Sicard, *Appl. Microbiol.* **19** (1970) 421.
[139] B. Rosenberg, L. Van Camp and T. Krigas, *Nature* **205** (1965) 698.
[140] K. Shimada and K. Shimahara, *Agric. Biol. Chem.* **46** (1982) 1329.
[141] H. P. Dhar, J. O'M. Bockris and D. H. Lewis, *J. Electrochem. Soc.* **128** (1981) 229.
[142] Y. Oren, H. Tobias and A. Soffer, *ibid.* **11** (1983) 347.
[143] T. Matsunaga, Y. Namba and T. Nakajima, *Bioelectrochem. Bioenerg.* **13** (1985) 393.
[144] T. Matsunaga, S. Nakasono, T. Takamuku, J. G. Burgess, N. Nakamura and K. Sode, *Appl. Environ. Microbiol.* **58** (1992) 686.
[145] H. Huang and P. K. Dasgupta, *Anal. Chem.* **62** (1990) 1935.
[146] N. Oyama, T. Hirokawa, S. Yamaguchi, N. Ushizwa and T. Shimomura, *ibid.* **59** (1987) 258.
[147] M. L. Hitchman and S. Ramanathan, *Analyst* **116** (1991) 1131.
[148] T. Wickstroem, W. Lund and S. Buoeen, *Anal. Chim. Acta* **219** (1989) 141.
[149] A. Cadogan, Z. Gao, A. Lewenstam, A. Ivaska and D. Diamond, *Anal. Chem.* **64** (1992) 2496.
[150] G. Cha, D. Liu, M. E. Meyerhoff, H. C. Cantor, A. R. Midgley, H. D. Goldberg and R. B. Brown, *ibid.* **63** (1991) 1666.
[151] N. A. Chaniotakis, S. B. Park and M. E. Meyerhoff, *ibid.* **61** (1989) 566.
[152] S. Daunert, S. Wallace, A. Florido and L. G. Bachas, *Anal. Chem.* **63** (1991) 1676.
[153] J. D. R. Thomas, *Intl. J. Environ. Anal. Chem.* **38** (1990) 157.
[154] H. Schettler, J. Jui, W. Weppner and R. A. Huggins, *Appl. Phys.* **A57** (1993) 31.
[155] W. F. Chu, V. Leonhard, H. Erdmann and M. Illgenstein, *Sensors and Actuators* **B4** (1991) 321.
[156] E. Haefele, K. Kaltenmaier and U. Schoenauer, *ibid.* **B4** (1991) 525.
[157] T. Usui, A. Asada, M. Nakazawa and H. Osanai, *J. Electrochem. Soc.* **136** (1989) 534.
[158] F. Allegretti, N. Buttá, L. Cinquegrani and S. Pizzini, *Sensors and Actuators* **B10** (1993) 191.
[159] R. Cote, C. W. Bale and M. Gauthier, *J. Electrochem. Soc.* **131** (1984) 63.
[160] S. Yao, S. Hosohara, Y. Shimizu. N. Miura, H. Futata and N. Yamazoe, *Chem. Lett.* (1991) 2069.
[161] Q. Liu, X. Sun and W. Wu, *Solid State Ionics* **40–41** (1990) 456.
[162] C. M. Mari, M. Beghi, S. Pizzini and J. Faltemier, *Sensors and Actuators* **B2** (1990) 51.
[163] S. Yao, Y. Shimizu, N. Miura and N. Yamazoe, *Chem. Lett.* **11** (1990) 2033.
[164] H. Pink, L. Trietinger and L. Vite, *Jap. J. Appl. Phys.* **19** (1980) 513.
[165] M. Akiyama, J. Tamaki, N. Miura and N. Yamazoe, *Chem. Lett.* (1991) 1610.
[166] Y. Yan, Y. Shimizu, N. Miura and N. Yamazoe, *Sensors and Actuators* **B12** (1993) 77.
[167] K. Štulik and V. Pacáková, *Crit. Rev. Anal. Chem.* **14** (1984) 297.
[168] J. Ruzicka and E. H. Hansen, 'Flow Injection Analysis,' John Wiley, New York (1981).
[169] K. Štulik and V. Pacáková, *J. Electroanal. Chem.* **129** (1981) 1.
[170] H. B. Hanekamp, P. Bose and R. W. Frei, *Trends Anal. Chem.* **1** (1982) 135.
[171] D. Mackoul, D. C. Johnson and K. G. Schick, *ibid.* **56** (1984) 436.
[172] D. J. Curran and T. P. Tonyas, *ibid.* **56** (1984) 672.
[173] K.Štulik and V. Pacáková, 'Electroanalytical Measurements in Flowing Liquids', John Wiley, New York (1987).
[174] J. Evans, D. Pletcher, P. R. G. Warburton and T. K. Gibbs, *Anal. Chem.* **61** (1989) 577.
[175] P. R. G. Warburton, W. Wu, T. Kuwana and D. H. Busch, *ibid.* **63** (1991) 2772.
[176] J. H. Stanley and J. D. Johnson, *ibid.* **51** (1979) 2144.
[177] S. Uchiyama, T. Ikarugi, M. Mori, K. Kasama, Y. Ishikawa, M. Kaneko and A. Usmezawa, *Electroanalysis* **5** (1993) 121.
[178] H. Huang, P. K. Dasgupta and S. Ronchinsky, *Anal. Chem.* **63** (1991) 1570.
[179] A. G. Fogg and N. K. Bsebsu, *Analyst* **109** (1984) 19.
[180] A. G. Fogg, A. Y. Chamsi and M. A. Abdalla, *ibid.* **108** (1983) 464.
[181] B. Kalvoda and M. Kopanica, *Pure Appl. Chem.* **61** (1989) 92.
[182] J. Wang, 'Stripping Analysis: Principles, Instrumentation and Applications,' VCH, Deerfield Beach, FL (1985).
[183] B. Hoyer, T. M. Florence and G. E. Battey, *Anal. Chem.* **59** (1987) 1608.
[184] J. Wang and L. D. Hutchins-Kumar, *ibid.* **58** (1986) 402.
[185] B. Daih and H. Huang, *Anal. Chim. Acta* **258** (1992) 245.
[186] Z. Gao, G. Wang, P. Li and Z. Zhao, *Anal. Chem.* **63** (1991) 953.
[187] J. Wang and Z. Taha, *Talanta* **38** (1991) 81.
[188] D. Jagner and A. Granelli, *Anal. Chim. Acta* **83** (1976) 19.
[189] D. Jagner, *Anal. Chem.* **50** (1978) 1924.
[190] D. Jagner and K. Årén, *Anal. Chim. Acta* **107** (1979) 29.
[191] A. Hu, R. E. Dessy and A. Granéli, *Anal. Chem.* **55** (1983) 320.
[192] P. P. Madsen, I. Draback and J. Sorensen, *Anal. Chim. Acta* **151** (1983) 479.
[193] J. Wang and B. Tian, *ibid.* **274** (1993) 1.
[194] D. C. Johnson and R. E. Allen, *Talanta* **20** (1973) 305.
[195] G. W. Schieffer and W. J. Blaedel, *Anal. Chem.* **49** (1977) 49.

[196] T. Fujinaga and S. Kihara, *Crit. Ref. Anal. Chem.* **6** (1977) 223.
[197] T. Hori and T. Fujinaga, *Talanta* **30** (1983) 925.
[198] E. Beinrohr, M. Németh, P. Tschöpell and G. Tölg, *Fresenius J. Anal. Chem.* **344** (1992) 93.
[199] G. M. P. Morrison, G. E. Battey and T. M. Florence, *Chem. Br.* Aug. (1989) 791.
[200] T. Ferri, R. Morabito, B. M. Petronio and E. Pitti, *Talanta* **36** (1989) 1259.
[201] C. McCrory-Joy and J. M. Rosamilia, *Anal. Chim. Acta* **142** (1982) 231.
[202] S. M. C. White and A. J. Bard, *Anal. Chem.* **38** (1966) 61.
[203] D. Chakraborti, R. L. Nichols and K. J. Irgolic, *Z. Anal. Chem.* **319** (1984) 248.
[204] R. S. Sadana, *Anal. Chem.* **55** (1983) 304.
[205] F. T. Henry and T. M. Thorp, *ibid.* **52** (1980) 80.
[206] R. K. Elton and W. E. Geiger, Jr., *ibid.* **50** (1978) 712.
[207] G. Spini, A. Profumo and T. Soldi, *Anal. Chim. Acta* **176** (1985) 291.
[208] H. Small, T. S. Stevens and W. C. Bauman, *Anal. Chem.* **47** (1975) 1801.
[209] W. G. Kuhr, *ibid.* **62** (1990) 403R.
[210] D. L. Strong and P. K. Dasgupta, *ibid.* **61** (1989) 939.
[211] D. L. Strong, P. K. Dasgupta, K. Friedman and J. R. Stillman, *ibid.* **63** (1991) 480.
[212] D. L. Strong, C. U. Joung and P. K. Dasgupta, *J. Chromatogr.* **546** (1991) 159.
[213] J. G. Tarter, *Anal. Chem.* **56** (1984) 1264.
[214] D. Qi, T. Okada and P. K. Dasgupta, *ibid.* **61** (1989) 1383.
[215] K. J. Caserta, F. J. Holler, S. R. Crouch and C. G. Euke, *ibid.* **50** (1978) 1534.
[216] C. R. Pauley, R. F. Geiger, Jr. and T. A. Neiman, *ibid.* **52** (1980) 705.
[217] J. M. Keller, *ibid.* **53** (1981) 344.
[218] I. Berglund, P. K. Dasgupta, J. L. Lopez and O. Nara, *ibid.* **65** (1993) 1192.
[219] A. M. Couper, D. Pletcher and F. C. Walsh, *Chem. Rev.* **90** (1990) 837.
[220] C. Wei, S. German, S. Basak and K. Rajeshwar, *J. Electro-Chem. Soc.* **140** (1993) L60.
[221] Y. Ikariyama and W. Heineman, *Anal. Chem.* **58** (1986) 1803.
[222] P. Ward and M. R. Smyth, *Talanta* **40** (1993) 1131.
[223] C. G. Wallace and Y. P. Lin, *J. Electroanal. Chem.* **247** (1988) 145.
[224] M. D. Imisides and G. G. Wallace, *ibid.* **246** (1988) 181.
[225] D. M. T. O'Riordan and G. G. Wallace, *Anal. Chem.* **58** (1986) 126.
[226] J. Ye and R. P. Baldwin, *ibid.* **60** (1988) 1979.
[227] E. Wang and A. Liu, *Anal. Chim. Acta* **252** (1991) 53.
[228] J-Y. Suang and H. J. Huang, *ibid.* **246** (1991) 275.
[229] S. Dogan, U. Akbulut, T. Yalcin, S. Suzer and L. Toppare, *Synth. Met.* **60** (1993) 27 and references therein.
[230] J. Wang and R. Li, *ibid.* **61** (1989) 2809.
[231] J. Wang, L. Angnes, H. Tobias, R. A. Roesner, K. C. Hong, R. S. Glass, F. Kong and R. W. Pekala, *ibid.* **65** (1993) 2300.
[232] D. Kohler, J. Zabasajja, A. Krishnagopalan and B.J. Tatarchuk, *J. Electrochem. Soc.* **137** (1990) 136.
[233] D. Kohler, J. Zabasajja, F. Rose and B. J. Tatarchuk, *ibid.* **137** (1990) 1750.
[234] J. Wang, A. Brennsteiner and A. Sylwester, *Anal. Chem.* **62** (1990) 1002.
[235] N. Sleszynski, J. Osteryoung and M. Carter, *ibid.* **56** (1984) 130.
[236] M. R. Callstrom, T. X. Neenan, R. L. McCreery and D. C. Alsmeyer, *J. Am. Chem. Soc.* **112** (1990) 4954.
[237] D. Ingersoll and D. H. Huskisson, *J. Electroanal. Chem.* **307** (1991) 281.
[238] P. C. S. Hayfield, *US Patent 4 422 917* (1983).
[239] R. Clarke and R. Pardoe, *in* [2].
[240] V. B. Baez, J. E. Graves and D. Pletcher, *J. Electroanal. Chem.* **340** (1992) 273.
[241] G. M. Swain and R. Ramesham, *Anal. Chem.* **65** (1993) 345.
[242] R. Tenne, K. Patel, K. Hashimoto and A. Fujishima, *J. Electroanal. Chem.* **347** (1993) 409.
[243] I. Turyan and D. Mandler, *Nature* **362** (1993) 703.
[244] J. F. Rusling, *Acc. Chem. Res.* **24** (1991) 75.
[245] S. Zhang and J. F. Rusling, *Environ. Sci. Technol.* **27** (1993) 1375.
[246] D. E. Tallman and S. A. Olsen, 184th meeting of the Electrochemical Society, New Orleans, Louisiana, Oct. 1993 (Abstract No. 599).
[247] J. Osteryoung, *Acc. Chem. Res.* **26** (1993) 77.
[248] J. Wang, *Analyst* **119** (1994) 763.