CHEMICAL SOCIETY REVIEWS

Electrochemistry for a cleaner environment

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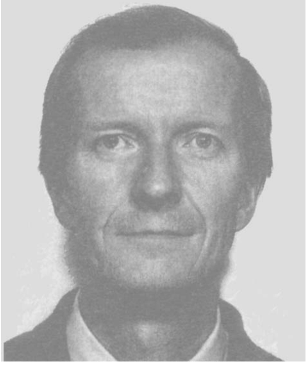
This article reviews electrochemical processes and devices that can contribute to a cleaner environment. Electrochemical processes for treatment of waste water solutions, flue gases and contaminated groundwater and soil are described, as well as improvements of existing electrochemical processes or products in order to minimize their environmental impact. Electrochemical power sources for cleaner generation of electricity in fuel cell power stations and for electrically driven vehicles are also discussed. Finally, the important role of electrochemical sensors for monitoring toxic substances is stressed.

1 Introduction

With a rapidly growing world population and an increasing number of reports on detrimental effects on the environment, its protection has become a major issue and a crucial factor for future technological progress, which will have to meet the requirements for sustainable development. The strategies for environmental protection in industry generally include processes for waste treatment as well as development of new processes or products which have no or less harmful effects on the environment. Electrochemistry has important roles to play in both types of strategies. Electrochemical processes can be used for recovery or treatment of effluents from industrial or municipal plants. Industrial electrochemistry has undergone a development towards cleaner processes and more environmentally friendly products. Electrochemical sensors are effective and inexpensive devices for environmental monitoring of an increasing range of toxic substances. A big and important class of environmental problems can be found in the energy and transportation sectors. Electrochemistry offers unique ways to generate pure electric power at high effeciency in fuel cells or to store it in batteries. These power sources may be used in stationary power systems or in electrically driven vehicles.

The potential of electrochemistry for environmental protection has been reviewed in many journal articles and monographs (see *e.g.* ref. 1,2) since the first book devoted to the topic appeared a quarter of a century ago.[3] Many of the concepts discussed in that early publication are still of interest today, but progress in materials science (new electrode materials and membranes) and electrochemical engineering (new and more effective cell designs) have offered new and more effective solutions. This review aims to provide the same broad perspective on the possible electrochemical future as in ref. 3 by describing electrochemistry being used both in the electrolytic mode (electrolytic processes for purification and recovery) and in the galvanic mode (for electrical energy production and storage in fuel cells and batteries, respectively) but focuses mainly on recent developments.



Daniel Simonsson was born in Arboga, Sweden, in 1943. He received his Master of Science degree and his PhD from the Royal Institute of Technology (KTH) in 1968 and in 1973, respectively. Since 1989, he has been professor of Applied Electrochemistry at KTH. His research interests include batteries, fuel cells, electrolytic processes and electrochemical environmental engineering.

2 Electrochemical processes for waste treatment

Electrochemistry, with its unique ability to oxidize or reduce compounds at a well-controlled electrode potential and by just adding (at the anode) or withdrawing (at the cathode) electrons, offers many interesting possibilities in environmental engineering. Anodic processes can be used to oxidize organic pollutants to harmless products and to remove toxic compounds from flue gases. Cathodic processes using effective cell designs can remove heavy metal ions from waste water solutions down to very low outlet concentrations. In both types of electrode processes, the operating conditions must be carefully controlled in order to avoid side reactions. In aqueous solutions, which are most often used, the side reactions are mainly oxygen evolution at the anode and hydrogen evolution at the cathode. These side reactions lower the current efficiency (*i.e.* the proportion of the total current used in the required rather than loss reactions), thereby increasing the operating costs, and may disturb the process because of vigorous gas evolution or pH changes at the electrodes.

Not only can the two electrodes of the electrochemical cell be used in purification processes, but the ion-selective membrane(s) that are often placed between the electrodes to have a selective transfer of only anions or cations can also. New electrodialytic processes using such membranes have been developed, which can solve a variety of environmental problems.

2.1 Anodic oxidation of toxic species

High electrode potentials can conveniently be set for oxidation of toxic compounds at the anode of an electrochemical cell. The upper limit is set by the stability of the anode material and the onset of side reactions such as oxygen evolution and, in chloride solutions, chlorine evolution, which lower the current efficiency. Therefore, the anode material must have a high overpotential for the oxygen evolution reaction. Lead dioxide is well known to possess this property and has been extensively used in oxidations at high potentials. Dimensionally stable anodes of the types used in chlor-alkali and water electrolysis processes do not give high oxygen overpotentials. Platinized titanium is better in this respect but is expensive. On the other hand, doped SnO_2-coated titanium electrodes have been developed[4] that give significantly higher oxygen overpotentials than both lead dioxide and platinum. Using the oxidation of phenol as a test case showed that the rate of phenol removal was much higher for SnO_2 than for PbO_2 and Pt. Similar results have been obtained for the oxidative treatment of biologically refractory waste water.[5] The efficiency (typically between

30–40%) was about five times higher than on a platinum anode. In chloride containing media, less chlorine was produced than with platinum anodes. No interference with the cathode was found, which indicates irreversible oxidation to reaction products that cannot be reduced at the cathode. The energy requirement of electrochemical oxidation of organics in waste water could thus be reduced to 30–50 kW h kg^{-1} of COD (Chemical Oxygen Demand) removed.

2.1.1 Direct anodic oxidation

Within the electroplating and surface finishing industry, large amounts of cyanides are still used to obtain very finely grained metal deposits. The waste water must be purified with respect to its cyanide content. The conventional chemical method is to oxidize the cyanide to the less harmful cyanate using hypochlorite as an oxidizing agent. An electrochemical process, in which the cyanide is oxidized anodically, is economically more feasible at higher concentrations of cyanide (>1 g dm^{-3}). At the cathode, the main part of the metal ions may simultaneously be deposited, with hydrogen evolution as a side reaction. The overall reaction at the anode, which is generally made from graphite or stainless steel, is in a first step [eqn. (1)]. The

$$CN^- + 2OH^- \rightarrow CNO^- + H_2O + 2e^- \quad (1)$$

cyanate then reacts further in the alkaline solution to Na_2CO_3, N_2, NH_3 *etc.* Oxygen is evolved in a side reaction. The temperature is *ca.* 50–90 °C, and the current density *ca.* 500 A m^{-2}. The energy demand is 10–40 kW h kg^{-1} cyanide.

The remaining cyanide in the outlet stream is at low concentration and has to be oxidized by hypochlorite. In order to achieve lower residual concentrations and also a better process economy, sodium chloride may be added to the electrolyte so that chlorine is formed at the anode. Hypochlorite, which is formed in the solution, can then react with cyanide ions homogeneously in the solution. This is an example of indirect or mediated electrochemical oxidation. Further examples of this principle will be shown below. Alternatively, the efficiency of the direct electrooxidation process can be improved by using three-dimensional electrodes of the type that will be discussed later.

The treatment of phenol has already been mentioned above with respect to the choice of anode material. Comninellis and Pulgarin[6] have studied this process using Pt and SnO_2 anodes and proposed a reaction scheme that involves the initial formation of hydroxyl radicals by the electrooxidation of water. These radicals are adsorbed on the electrode surface and react on an SnO_2 anode with phenol to carbon dioxide, or react to oxygen in a side reaction. On this anode material aromatic intermediates were formed only in very small concentrations, while they were formed in large concentrations on Pt. The rate of phenol removal is almost the same for both anodes, while the Ti/SnO_2 anode gives a much higher rate of total organic carbon (TOC) removal.

Chlorinated hydrocarbons are used as solvents and disinfectants. They may also appear as products in chemical reactions between chlorine and dissolved hydrocarbons in various waste streams, *e.g.* chlorinated phenols from bleaching in the pulp and paper industry. Combustion is a frequently used destruction method but is not suitable for the treatment of diluted waste waters, because of the high cost of transportation, the high consumption of fuel and, in some cases, corrosion problems. Other treatment options could involve membrane separation, adsorption on activated carbon and stripping, chemical oxidation with air, ozone or other oxidants. Chemical reduction techniques, such as catalytic dehalogenation with hydrogen or other reducing agents, are also used. Biological techniques using special microorganisms or enzymes are under development. Electrochemical dechlorination is an alternative that can be employed either anodically or cathodically.

Wabner *et al.*[7] have shown that *p*-chlorophenol and pentachlorophenol can be destroyed anodically on lead dioxide anodes. The decomposition of *p*-chlorophenol follow concentration–time curves that are similar to those of phenol. Therefore, the mechanism seems to be similar in the two cases involving hydroxyl radicals formed from water. In the first step chlorine is substituted by these radicals. In subsequent steps further oxidation yields quinone, which decomposes into maleic acid, oxalic acid (primarily) and carbon dioxide. Oxygen and significant amounts of ozone were formed as by-products at the anode. There is a risk that the chloride ions formed may be oxidized to hypochlorite, which can then form chlorinated organic compounds with low molecular mass species formed in the reaction sequence. An interesting alternative is to use the dechlorination step only and decompose the less toxic phenolic substances biologically.

The electrochemical treatment may also be used for dechlorination of other chlorinated aromatic compounds in aqueous solutions, such as hexachlorobenzene, PCB[8] and tetrachlorodibenzodioxin.

2.1.2 Mediated electrochemical oxidation

It has already been noted that dilute alkaline cyanide solutions can be oxidized homogeneously by anodically formed ClO^-. While ClO^- is an efficient oxidant, it has the disadvantage that it forms toxic chlorinated compounds. Other examples of mediators are Ag^{II}, Co^{III} and Fe^{III} for oxidation of organic compounds. The standard potentials *vs.* SHE are 1.987, 1.842 and 0.77 V, respectively. The higher the redox potential, the higher is the coulombic efficiency.

A process using Ag^{II} has been developed by AEA Technology in Dounreay, Scotland[9]. Ag^{I} is oxidized anodically to Ag^{II} on platinized titanium in concentrated nitric acid in a membrane-divided cell. Some Ag^{II} may oxidize the organic compounds directly in the anolyte, but the main route is believed to be the reaction of Ag^{II} with water to form radicals, which then react with organics. Ag^{II} is probably stabilised in the solution as a nitrate complex, $AgNO_3^+$.

In the cathode chamber, which is separated from the anode chamber by means of a cation selective membrane, nitric acid is reduced to nitrous acid, which is reoxidized to nitric acid by air in a separate reactor. Water is recycled to the anode chamber to replace water lost due to electroosmosis through the membrane. The overall effect is that dissolved organics are converted to CO_2 and H_2O by oxidation with air. The process has been shown to successfully destroy a variety of organic compounds, including benzene, phenols, oils and chlorinated organic compounds.

2.2 Cathodic processes

2.2.1 Cathodic Electrochemical Dechlorination

Dechlorination of organic toxicants can occur not only anodically, as discussed above, but also cathodically, according to the overall reaction in eqn. (2). Hydrogen evolution is a

$$RCl + H^+ + 2e^- \rightarrow RH + Cl^- \quad (2)$$

competing reaction which decreases the current efficiency. Schmal *et al.*[10] have evaluated the feasibility of electrochemical reduction of waste waters containing halogenated organic compounds. As electrode material, they used thin graphite/carbon fibres which give a high specific surface area and have a reasonably high overpotential for the competing hydrogen evolution reaction. Their experiments showed that it was possible to remove all chlorine atoms from the organic molecules in aqueous solution. The current efficiency was low, of the order of 1%. As the organic substrate concentration was low (*ca.* 100 ppm), the energy consumption per cubic metre was still acceptable (*ca.* 10–100 kW h m^{-3}).The dehalogenation results in a decreased toxicity and an increased biodegradability, thus enabling further biological treatment. They concluded that energy consumption and conversion rates are such that a technically and economically viable method for the detoxification of waste waters can be developed.

The total cost was estimated to be of the same order of magnitude as that of adsorption on carbon. In contrast to the latter method, electrochemical reduction can be used with polar compounds and does not give a concentrated toxic waste that has to be treated further or dumped in special depots.

Cathodic destruction of monochloroethane, trichloroethane, epichlorhydrin[11] and of aromatic halides (models of dioxin)[12] has also been demonstrated.

2.2.2 Removal of heavy metal ions

Waste waters containing heavy metal ions are generated in metallurgical and electroplating industries and in the manufacture of printed circuit boards. The conventional purification of these streams uses hydroxide precipitation, which gives a voluminous metal hydroxide sludge that has to be disposed of in an environmentally acceptable way. With complexed metal ions in alkaline solutions, hydroxide precipitation is not a viable method.

Cathodic removal of heavy metal ions from different waste waters is an attractive alternative process, since the metal can be recovered in its pure metallic form or as a concentrated solution that can be recycled or allow the extraction of the pure metal in an electrowinning process. The basic problem is that the mass transport controlled limiting current density for cathodic metal deposition from dilute solutions is so low that the conventional use of planar electrodes would require too large a surface, unless the mass transfer rate could be substantially improved. This might be achieved in various ways, *e.g.* with a rotating cylinder cathode or using expanded metal mesh electrodes immersed in a fluidized bed of small glass beads. The more efficient electrochemical engineering solution is the packed bed electrode, or, more generally, three-dimensional electrodes, Fig. 1.

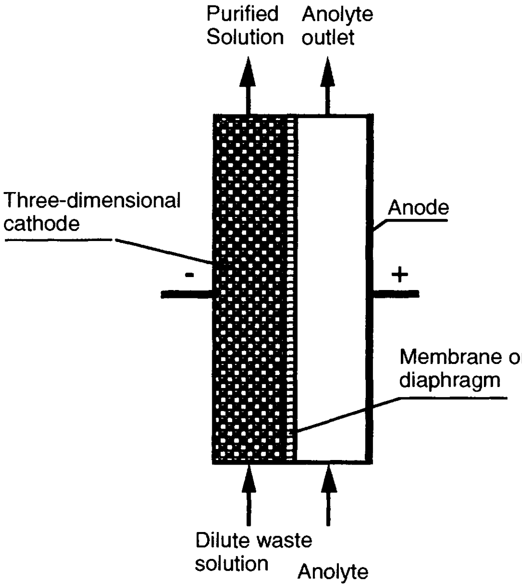


Fig. 1 Cell with three-dimensional cathode for heavy metal removal

This wider concept also includes fluidized bed and circulating particulate-bed electrodes. However, most three-dimensional electrodes being used for metal removal are of the fixed bed type. The anode may also be a three-dimensional electrode or just a planar electrode for *e.g.* oxygen evolution. As cathode material, graphite particles, expanded metal, graphite felt, metal wool, graphite fibres and reticulated vitreous carbon have been examined.

The engineering design has to consider the potential drop in the dilute electrolyte along the depth of the electrode in the direction of current flow, since this determines the extent of the side reaction, hydrogen evolution.[13] If the bed is too thick, operation at the limiting current density across the whole depth of the electrode would give too a high hydrogen evolution rate in the part of the bed facing the membrane or diaphragm, which separates the cathode from the anode.

Three-dimensional electrodes are effective in the treatment of dilute solutions since they offer both a high specific surface area and high mass transport rate conditions. In electrodes of this type the metal concentration can be reduced from, say, 100 to 0.1 ppm at a residence time of a few minutes.[14] Operational costs are favourable compared with classical waste water treatment systems. In some cases the removal efficiency is higher, and the space required by the process is low.

The deposited metal in the cathode may be recovered as a concentrated solution by chemical dissolution with *e.g.* an acidified solution of hydrogen peroxide, or by switching the polarity of the cell. In the latter case, the cell will function as a concentrator. At the anode, the metal deposited during the preceding cathodic phase is dissolved into a concentrated solution. This method requires robust anion-selective membranes to prevent leakage of metal ions from the concentrated anolyte solution to the dilute catholyte solution. In the best case, the concentrated metal ion solution can be recycled to the process which generated the waste solution. An alternative regeneration procedure is to use three-dimensional electrodes made of *e.g.* foamed graphite or carbon felt as cartridges that may be removed to recover the deposited metal in an external procedure, for example, according to the principles of electrorefining.

Processes utilizing packed-bed electrodes have been applied in the chemical industry mainly to waste solutions containing Cu and Hg.[11] Outlet concentrations of less than 1 ppm can generally be achieved. The energy consumption is of the order of 1 kW h m^{-3}. For less noble metals, such as Zn and Cd, the side reaction of hydrogen evolution increases and the current efficiency is low, especially at lower concentrations. Therefore, it is not possible to decrease the concentration of these species below 1 ppm at an acceptable overall current efficiency. A further complication is that excessive cathodic hydrogen evolution may increase pH, so that the metal precipitates as hydroxide. This phenomenon can be used to advantage to remove Cr^{VI} as $Cr(OH)_3$.

2.3 Electrodialytic processes

Cation exchange membranes, introduced commercially in the membrane cells for chlor-alkali production, can also be used in electrochemical processes for environmental protection. Anion selective membranes, which allow only anions to pass, can be used in cells with three-dimensional electrodes for metal deposition as described above. Acid can be recovered from spent pickling baths by using anion-selective membranes with oxygen evolution at a suitable anode. In electrodialytic processes the membranes themselves do the main part of the work by splitting the inlet flow into one more concentrated and one more dilute stream. Electrodialysis has long since been used for salt or brine production and in desalination processes for obtaining fresh water. It can also be used in combination with electrolysis for desalinating waste streams.

Aqueous streams containing *e.g.* NaCl and Na_2SO_4 are generated in many chemical processing operations such as flue gas scrubbing, metal pickling, fermentation and rayon manufacture. One important example is splitting of sodium sulfate solutions into sodium hydroxide and sulfuric acid solutions. The simplest design for this is to use a three-compartment cell with cationic and anionic selective membranes, as shown in Fig. 2. In such a cell hydroxide concentrations of *ca.* 10 mass% can be achieved. The cell voltage and thus the energy demand is to a great extent determined by the anode and cathode potentials. The energy requirement can be reduced by using, instead of the oxygen evolving anode, a hydrogen gas diffusion electrode of the type used in fuel cells on the anode side and utilizing the hydrogen evolved at the cathode. This concept can also be used in a two-chamber process,[15] as shown schematically in Fig. 3.

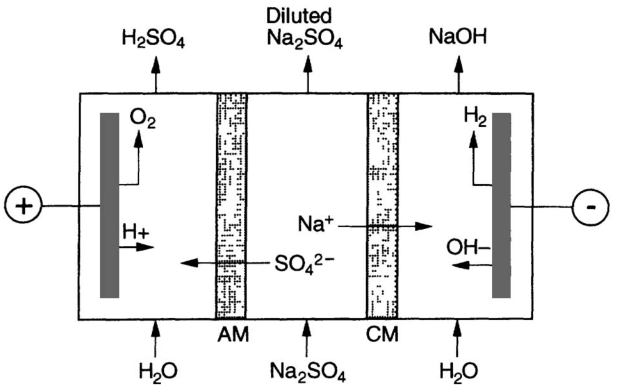


Fig. 2 Three-compartment cell for splitting of sodium sulfate into sodium hydroxide and sulfuric acid solutions. AM = anion selective membrane, CM = cation selective membrane.

However, in this case a pure sulfuric acid solution is not obtained as in the three-compartment cell. The energy consumption is 1600–1800 kW h tonne^{-1} caustic at a concentration of 13–18%.

Energy savings may also be achieved by using bipolar ion exchange membranes, which consist of threee parts: a cation selective region, an anion selective region and the interface between the two regions. When a direct current is passed through the bipolar membrane with the cation selective side toward the cathode, electrical conduction is achieved by the transport of H^+ and OH^- ions which are obtained from the dissociation of water. A high efficiency requires that the membrane has a high water permeability to provide water from the external solutions to the interface, and a very thin interface between anion and cation regions to allow efficient transport of H^+ and OH^-. Such a membrane can be combined with anion and cation selective membranes into three-compartment units, which can be repeated a large number of times into a compact stack.

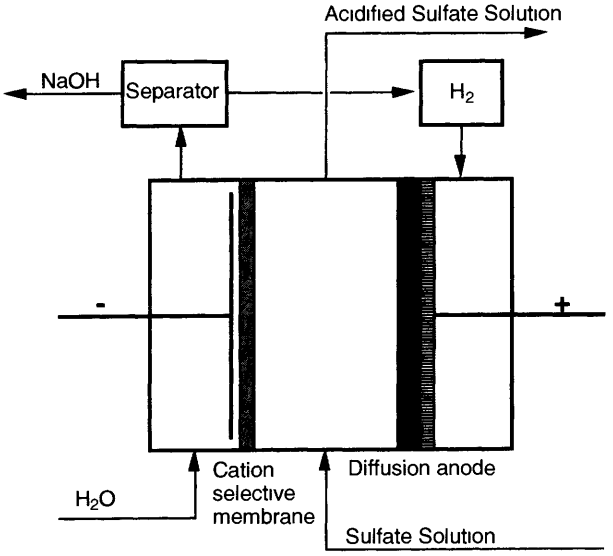


Fig. 3 Two-chamber cell with gas diffusion anode in which the hydrogen gas evolved at the cathode is oxidized The gas diffusion anode consists of a porous sheet containing a catalytic layer, which is pressed against a cation-exchange membrane on the electrolyte side and a suitable porous current collector on the gas side The electrochemical reaction occurs at the membrane/catalytic layer interface, where hydrogen gas, electrolyte and active electrode material can form three-phase contact zones After ref 15.

The energy requirement for producing sodium hydroxide is in the range 1300–2000 kW h tonne^{-1} at 1000 A m^{-2} and a current efficiency of 80%. This energy demand is lower than that for the conventional chlor-alkali processes. Therefore this technique may also be used to produce sodium hydroxide without the simultaneous generation of chlorine.

2.4 Electrochemical remediation of soils

There is a great need for cost-effective methods for restoration of contaminated soils. The use of electrochemistry for this purpose simply means putting electrodes in the soil and applying a voltage over them, as shown schematically in Fig. 4. The groundwater or an externally supplied fluid is used as electrolyte. This technique has been reviewed by Acar and Alshawabkeh[16] and Probstein and Hicks.[17]

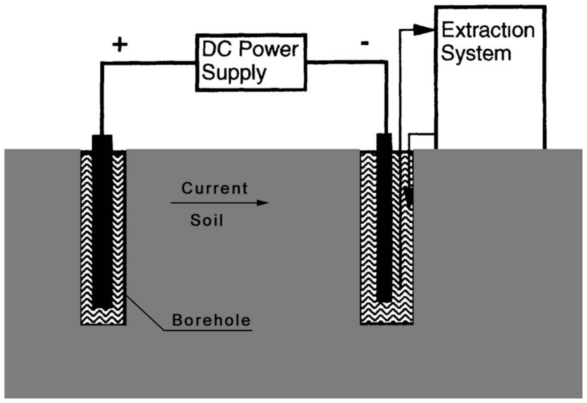


Fig. 4 Schematic illustration of electrochemical soil remediation

The main electrode reactions are generally oxygen evolution at the anode and hydrogen evolution at the cathode, eqn. (3) and (4).

$$H_2O \rightarrow 1/2\ O_2 + 2H^+ + 2e^- \qquad (3)$$

$$H_2O + 2e^- \rightarrow H_2 + 2OH^- \qquad (4)$$

As in ordinary electrolysis, ions will move through the soil due to migration, diffusion and convection. If heavy metal ions are present in the ground water they will move to the cathode and become electrodeposited on its surface. The method is not restricted to ionic contaminants but can also be used to extract organic compounds by means of the electroosmotic flow that is generated by the electric field in fine-grained soils with pores that are of micrometre-size or smaller. Thus, in contrast to forced convection by means of pumping, which will make the pore liquid flow preferentially through the larger pores, electroosmotic flow will be effective in smaller pores. For ions, mass transfer by migration will generally be much higher than that by electroosmosis.

The technique can be applied *in situ*, on-site and off-site. The flow around the electrodes and through the soil can be controlled so that the contaminating species in the fluid may be removed either at the electrodes or in an external extraction system (*e.g* by ion exchange or chemical precipitation). This also allows for a control of the chemical conditions. Without external control of the chemistry of the system, the electrode reactions are generally oxygen evolution at the anode and hydrogen evolution at the cathode according to eqns. (3) and (4). These reactions will make the anode region acidic and the cathode region basic. An acid front will thus move from the anode towards the cathode, while an alkaline front moves in the opposite direction. The penetrating acid solution will release heavy metals and other cations that are sorbed on negatively charged clay surfaces, the cations migrating towards the cathode. The alkaline front causes precipitation of most heavy metals and radionuclides, unless they form negatively charged complexes. These complexes migrate towards the anode and will form free metal ions again, when they meet the acid front. In this way species are concentrated in the region where the two pH-fronts meet and pH changes abruptly. The above problems may be solved by means of purging solutions. For example, the hydroxide precipitation at some distance from the cathode may be avoided by adding an acid solution to the cathode region.

Electrokinetic remediation has been tested successfully in field studies in The Netherlands and in the USA. Estimated costs for the technique[17] indicate that they may be several times lower than for conventional methods.

2.5 Electrochemical gas purification

The processes discussed above all deal with pollutions present in aqueous solutions. Gaseous pollutants may also be removed electrochemically, provided that they are first dissolved into an electrolyte. The overall process will then generally consist of at least two steps: absorption of the gaseous species in a liquid and the subsequent electrochemical conversion of them to less harmful products. The two steps can be integrated into one device or are separated in two different devices,[18] as shown schematically in Fig. 5. The rate and capacity of absorption will be increased, since the physical absorption process will not be limited by the equilibrium solubility of the absorbed gaseous pollutant. Examples include reduction of chlorine to chloride, oxidation of nitrous oxides to nitric acid and of sulfur dioxide to sulfuric acid. The reduction or oxidation may occur directly at the electrode or indirectly *via* a redox mediator. In the latter case, the mediator has to be regenerated electrochemically.

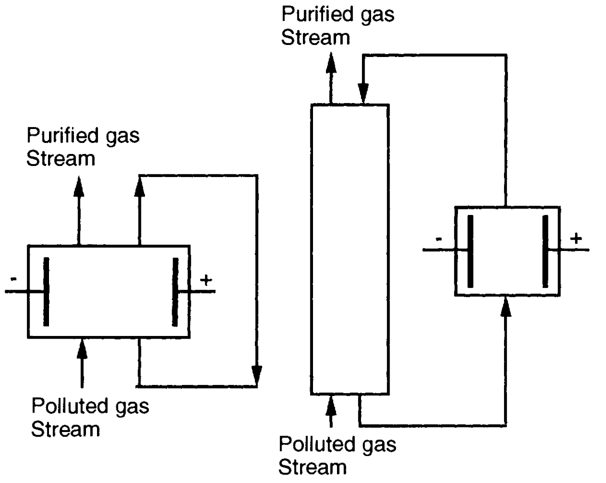


Fig. 5 Electrochemical gas purification using integrated absorber/electrochemical cell (left) or separate absorption column and electrochemical cell (right). After ref. 18.

The modified Mark 13A process[19] is an example of an indirect electrochemical process, which uses bromine as a mediator to oxidize SO_2 chemically, eqn. (5).

$$SO_2 + Br_2 + 2H_2O \rightarrow H_2SO_4 + 2HBr \qquad (5)$$

The hydrogen bromide formed is transferred to an electrochemical cell in which bromine is regenerated electrochemically according to the overall reaction (6).

$$2\,HBr \rightarrow Br_2 + H_2 \qquad (6)$$

Sulfur dioxide can also be removed electrochemically at higher temperatures in a cell with a molten electrolyte, which essentially concentrates the sulfur dioxide for further treatment.[20] At the cathode SO_2 is reacted with oxygen to sulfate ion, which migrates to the anode, where it is oxidized to SO_3 and O_2.

In a similar way hydrogen sulfide, which is hazardous to plant and animal life even at the ppm level, can be removed as elemental sulfur according to the overall reaction[20] in eqn. (7).

$$H_2S \rightarrow H_2 + 1/2\,S_2 \qquad (7)$$

3 Improved electrochemical processes and products

Electrochemical technology has traditionally relied to a significant extent on heavy metals. The electrochemist is aware of the great importance of mercury in both fundamental and industrial electrochemistry. From a technical point of view, mercury with its high overvoltage for the hydrogen evolution reaction has offered practical solutions both for the production of chlor-alkali and against self discharge and gassing of primary batteries. The most widely used battery, the lead–acid battery is the main consumer of lead. Similarily, poisonous cadmium is used in nickel–cadmium batteries.

Previous efforts to avoid or minimize the environmental impact of heavy metals and to meet the increasingly strict environmental regulations have been successful in many cases. Not so many years ago, alkaline batteries were a problem due to their mercury content, present to prevent the hydrogen evolving during self discharge of the zinc anode. However, fairly soon 'green' batteries were on the market with no or very little mercury thanks to the rational application of well known principles for corrosion inhibition, including very pure electrodes and electrolyte solutions.

Unfortunately, the situation is not that simple for lead–acid batteries, of which more than 100 million per year are sold. Most of them are used in cars, an application in which they are difficult to replace. The key word is recycling. Batteries are collected and the lead is recovered. Similarly nickel–cadmium batteries are collected and the cadmium recovered. In this case an alternative is available, which is more environmentally compatible: the nickel–metal hydride battery. This is being used to an increasing extent in new high tech products requiring cordless power, *e.g.* cellular phones, camcorders and notebook computers. The present status of aqueous rechargeable batteries has been reviewed in ref. 21. Rechargeable lithium batteries represent a further improvement for these applications, both with respect to energy density and environmental impact.[22]

In the electrolytic industries the losses of mercury from the mercury process for production of chlor-alkali have been reduced significantly during the last few decades, but new processes of this type will generally not be allowed in Western countries. Diaphragm processes are not a viable alternative, since the the state-of-the-art diaphragms are made from asbestos, which is a health hazard. New processes are instead based upon the use of ion-selective membranes. The performance of these processes is constantly being improved. They also offer a higher energy efficiency than the two other processes. The increased efficiency is a result of improved membranes, effective catalytic coatings on the electrodes and improved cell design, which contribute to a lower cell voltage.

One of the two products in the chlor-alkali process, chlorine, has received increasing concern with respect to its impact on the environment. In some countries a major fraction of the chlorine produced has been used as a bleaching agent in the production of pulp and paper. However, in the late 1980s it was found that dioxins are formed during pulp bleaching with chlorine. Regulations and consumer demand have lead to a decreased demand for chlorine in bleaching, and the use of chlorine in the pulp and paper industry is steadily decreasing. However, there is still a need for the caustic produced at the cathode for the cooking process in the pulp manufacturing process. Therefore it is of interest to develop electrochemical processes that still produce caustic in the cathode chamber but do not produce chlorine at the anode. One example is oxygen evolution or hydrogen oxidation as the anode reaction, using sodium sulfate instead of sodium chloride as electrolyte. This concept has already been discussed above as a method to purify waste solutions from sodium sulfate.

4 Electrochemical power sources for cleaner electrical energy

Thermal combustion of fossil fuels in power plants and vehicles is a major environmental problem in modern society. The immediate damage of air pollution has been estimated to cost about three times more than the fossil fuels themselves. Long-term effects, such as global warming, are not included. The most important gaseous impurities in the flue gas from electricity generation plants are CO_2, NO_x, SO_2 and dust particles. CO_2 is a major contributor to the greenhouse effect and NO_x contributes to the acidification of water and soil, eutrophication, and the formation of smog.

4.1 Batteries for electric vehicles

Approximately 20% of the primary energy used in the European Union goes to transportation. Road traffic alone generates more than 50% of the total emissions of nitrogen oxides, carbon monoxide and hydrocarbons. The authorities in California, where the transportation fleet is responsible for more than 75% of the air pollution in the Los Angeles basin, have enacted a law that requires that 10% of all new vehicles sold in the state must be so called zero emission vehicles by the year 2003. The only vehicles that are likely to meet these demands are electric vehicles.

In order to meet these new regulations 'The Big Three', General Motors, Ford and Chrysler in the USA decided in January 1991 to form a consortium, The United States Advanced Battery Consortium (US ABC), for cooperation towards improved power sources for electric vehicles. The joint research is also funded by the Department of Energy and EPRI. The total budget is $260 million for five years. The goals that have been set by the US ABC are shown in Table 1. These performance requirements are compared in the same table with some battery systems of special interest for electric vehicles and load levelling.

Table 1 US ABC criteria and performance of selected battery systems

Couple	Specific energy/ W h kg^{-1}	Peak specific power/W kg^{-1}	Deep-discharge cycles
US ABC criteria	80–100	150–200	600
US ABC, long term	200	400	1000
Pb/PbO_2	35–40	150–300	100–1000
Cd/NiOOH	50	80–150	1000
MH/NiOOH	60–80	200	750
Zn/air	100–120	150	< 300
Na/S	100	230	760
$Na/NiCl_2$	80	130	1200
Li/polymer (projected)	150	400	< 100
$LiAl/FeS_2$ (cells)	180–200	> 200	1000
Li–ion	80–90	200–300	400–1200 (cells)

Some of the systems that have been proposed to meet the mid-term goals include sodium–sulfur, sodium–nickel chloride, lithium–metal sulfide, lithium–polymer and lithium-ion batteries, metal hydride–nickel oxide, zinc–air and zinc–nickel oxide. None of these yet meet the long-term goals.

Electric Fuel Limited in Israel has developed a refuelable zinc–air energy system for powering electric vehicles.[23] In order to recharge the zinc anode rapidly, their system solution includes a refueling system for mechanically exchanging zinc anode cassettes and a regeneration system for recycling depleted cassettes. Zinc oxide is dissolved in a KOH solution, which is then fed into an electrowinning bath where zinc is deposited, collected and later reassembled into fresh cassettes. This system is being tested by Deutsche Post with Mercedes-Benz Vans and GM-Opel Corsa Combo Vans. The driving range is claimed to be over 300 km.

The overall advantages of electric vehicles with respect to the environment must be considered with respect to the total system design. The electric vehicle itself emits almost no pollutants. On the other hand, the electricity generating plants delivering electric energy to recharge the vehicles give additional pollution if they are based on fossil fuel combustion. However, these facilities are generally located outside the cities, and the control of their emissions is also easier and more cost effective. The efficiency of fuel utilization is also higher. When the electricity is produced by nuclear reactors, windturbines or solar cells the gaseous pollutants are negligible. Electric vehicles will primarily be recharged during off-peak hours, minimizing the need for increased utility capacity.

Even with an electricity generating mix which is highly coal orientated, such as in the US, a substantial reduction of air pollutants can be achieved in comparison to the standard gasoline driven car. EPRI estimates that together with new clean coal technologies it is possible to achieve reductions of 99% of volatile organic compounds (VOC), 99% of CO and 83% of NO_x.

Batteries are still too expensive and do not meet the requirements with regard to energy and power densities for electric vehicles, but the intensive research that is going on worldwide will hopefully lead to a breakthrough for the electric vehicle in the future.

4.2 Electrochemical capacitors

Batteries can be used in all-electric vehicles or, alternatively, in hybrid vehicles that use also combustion engines for propulsion. The batteries are then mainly used for acceleration and for citydriving, while the combustion engine gives a reasonable range. In this application, a high peak power density of the battery is a major requirement, while the energy density, which determines the all-electric range, is less important compared to all-electric vehicles. An interesting alternative, or complement, to batteries is electrochemical capacitors (also called ultracapacitors or supercapacitors), which can give peak power densities greater than 1 kW kg^{-1} while the energy density is only 2–10% of that stored in a battery to deliver the same power.[24]

An electrochemical capacitor stores the electrical energy electrostatically by charging of the electrochemical double layer at the electrode/electrolyte interface. In some systems intermediates are adsorbed on the electrode surface or intercalated into the electrode material, which gives an additional so called pseudo-capacitance that may be 10 to 100 times higher than the double layer capacitance.[25] In a finely porous electrode with a high specific surface area, fairly high amounts of electrical energy may be stored per unit volume or mass.

Research and development has been going on since the early 1990s to develop ultracapacitors using various types of carbon, doped conducting polymers, and metal oxides as electrode materials. The electrolyte may be aqueous, organic or a solid polymer. Ultracapacitors with aqueous electrolyte can store 1.5 W h kg^{-1} and deliver 1 kW kg^{-1}, while the best values reported for devices using an organic electrolyte are 5–7 W h kg^{-1} and 2 kW kg^{-1}. Future development is expected to result in ultracapacitors with an energy density of 10–15 W h kg^{-1} and a power density of 3–4 kW kg^{-1} in the near-term.[24] With increasing energy density the possibility increases of using only electrochemical capacitors as storage device for electrical energy in hybrid electric vehicles.

4.3 Fuel cells

The fuel cell represents another major challenge for electrochemists, electrochemical engineers and material scientists. Fuel cells are of great interest because of their efficient conversion of the chemical energy in fuels to electricity, as well as the very small pollutions. Therefore atmospheric pollution would be lowered and the energy sources used in a more efficient way, if fuel cells were used in stationary power stations and in electrically driven vehicles. Recent monographs on fuel cells are available.[26, 27]

The principle of the fuel cell was demonstrated more than 150 years ago but did not receive significant attention until the American space program in the sixties. In a fuel cell, a fuel (generally hydrogen) is oxidized at the anode, and an oxidant (oxygen in pure form or in air) is reduced at the cathode. The overall reaction in this 'electrochemical combustion' is thus the same as at thermal combustion. The principle is illustrated schematically in Fig. 6 for the case of the hydrogen–oxygen fuel cell.

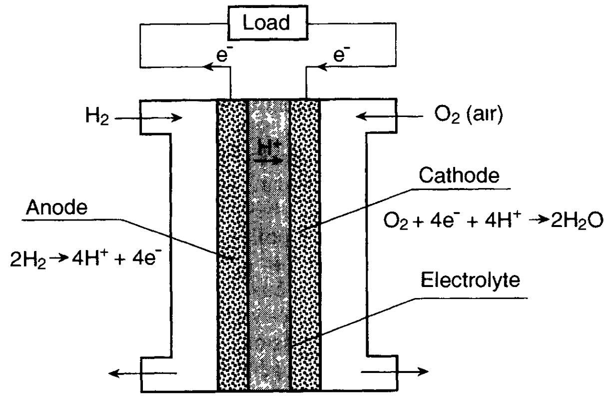


Fig. 6 The working principle of a fuel cell with acid electrolyte

The advantage of the fuel cell is that chemical energy can be converted directly to electric energy. For a reversible electrochemical reaction this is expressed in the well-known thermodynamic equation (8).

$$\Delta G = -nFE_{\mathrm{rev}} \tag{8}$$

In a thermochemical process the heat of combustion (= $-\Delta H$) is utilized in a cyclic process, the maximum efficiency of which is limited by the Carnot-efficiency ($\varepsilon_T = 1 - T_1/T_2$). In fuel cells, on the other hand, the ideal efficiency is given by eqn. (9).

$$\varepsilon_{\mathrm{T,\,ideal}} = \frac{-\Delta G}{(-\Delta H)} \tag{9}$$

From thermodynamic data, we can calculate the ideal efficiency of the hydrogen–oxygen fuel cell to be 83% at 25 °C. The real efficiency is lower because of the overpotentials and ohmic potential losses in the electrolyte, which mean irreversible losses. The cell voltage in working fuel cells is typically *ca.* 0.7–0.9 V at current densities of 1–5 kA m^{-2}. With E = 0.8 V for a hydrogen–oxygen fuel cell the real efficiency at 25° C is 54%, which is still considerably higher than the efficiencies that can be reached in conventional thermal cycles. A major part of the energy losses is due to the sluggishness of the oxygen reduction reaction at the cathode. Therefore an important issue in the development of fuel cells is the search for efficient and sufficiently cheap electrocatalysts for this electrode reaction. An alternative method is to reduce the overpotentials by operation at higher temperatures, using a molten salt or solid oxide as electrolyte. This introduces other material problems such as corrosion and mechanical stresses.

The ideal fuel cell would use hydrocarbons available from their natural sources directly. Even with platinum as catalyst, the direct anodic oxidation of hydrocarbons is a very slow electrode process, which requires a high overpotential. The only fuel which is practically useful today is hydrogen, and to some extent carbon monoxide in high temperature fuel cells.

Apart from applications in which fuel cells utilize hydrogen gas obtained as a side product in chlor-alkali and chlorate processes, the first step is to produce hydrogen from suitable primary fuels. In practice this is done by means of partial oxidation and steam reforming of coal, oil or natural gas. Gasification and reforming of biofuels such as wood and peat is also possible. Therefore, to a large extent, a fuel cell power station will be a chemical factory for up-grading of the primary fuel, as shown in Fig. 7. An important aspect is the purity of the gas, since common impurities such as CO and H_2S poison the catalyst.

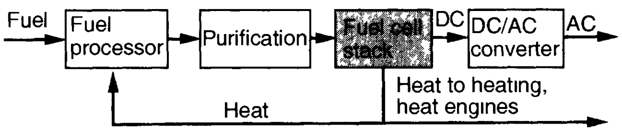


Fig. 7 Schematic drawing of a fuel cell power station

It is customary to classify fuel cells according to the electrolyte used. Fuel cells under development are alkaline fuel cells (AFC), phosphoric acid fuel cells (PAFC), proton exchange membrane fuel cells (PEMFC), molten carbonate fuel cells (MCFC) and solid oxide fuel cells (SOFC). Characteristic performance data for these different system are shown in Table 2.

The fuel cell which is closest to commercialization is the PAFC, which uses concentrated phosphoric acid as electrolyte and works at 160–200 °C. This type of fuel cell has been tested in Japan in an 11 MW power plant. Since natural gas is generally used as the primary energy source, the methane in this gas must first be converted to hydrogen through steam reforming ($CH_4 + H_2O \rightarrow 3\,H_2 + CO$) and shift ($CO + H_2O \rightarrow H_2 + CO_2$) reactions. The overall energy efficiency of a power plant using PAFC is *ca.* 40%. PAFC is intended for on-site integrated energy systems to provide electricity and heat for space heating and hot water. PAFC has also been considered for propulsion of electrically driven buses in the US.

The molten carbonate fuel cell, MCFC, operates with a carbonate melt as electrolyte at about 650 °C. At this high temperature sufficiently low overpotentials on the electrodes can be obtained without the use of expensive noble metal catalysts. The waste heat is also more valuable at the higher temperature, so that higher overall efficiencies can be obtained, especially if the heat produced is used for the reforming process. Estimates have been made that this concept can give an overall

Table 2 Characteristic performance data for different fuel cells

	AFC	PAFC	PEMFC	MCFC	SOFC
Temp./°C	60–120	180–210	80–100	600–700	900–1000
Anode fuel	H_2, high purity	H_2	H_2	H_2–CO CH_4	H_2–CO CH_4
Oxidant	O_2, high purity	Air	Air	Air + CO_2	Air
Electrolyte	KOH	H_3PO_4	Polymer	$(K,Li)_2CO_3$	Y_2O_3, ZrO_2
Anode catalyst	Pt	Pt	Pt	Ni	Ni/Zr_2O_3
Cathode catalyst	Pt	Pt	Pt	NiO	La–Sr–MnO_3

efficiency of up to 60% with internal reforming of the fuel gas to hydrogen. This is an impressive figure in comparison to conventional thermal engines. On the other hand, the competition will be strong in the future from advanced technologies such as combined cycles, especially for power stations larger than 10 MW. The remaining advantages are high efficiency even in small-scale applications and the low pollution. A 2 MW MCFC power station has been started up in Santa Clara, USA in 1996.

The solid oxide fuel cell is an all-solid-state fuel cell that operates at *ca.* 1000 °C. Yttria-stabilized zirconia is used as electrolyte. Strontium-doped lanthanum manganite and nickel–zirconia cermet are used as cathode and anode materials, respectively. The material currently used for the inter-connector is Mg or Sr-doped $LaCrO_3$. A major technical challenge is the fabrication of the component layers of the electrochemical cell stack. The thermal expansion coefficients of the four ceramic layers must be matched.

Three different designs of SOFCs have been developed: tubular, monolithic and planar.

Tubular SOFCs from Westinghouse Electric Corporation have been tested in 25 kW systems and are presently being built into a 100 kW power generation system.

Proton exchange membrane fuel cells (PEMFC) were introduced in the Gemini space project. Following the general working principle of fuel cells, as shown in Fig.6, the working unit of a PEMFC is the membrane electrode assembly (MEA) consisting of a thin, catalytic gas diffusion anode for electrochemical hydrogen oxidation, a catalytic cathode for oxygen reduction and a proton conducting membrane in between, forming the electrolyte as well as a separator for the two reactant gases. Platinum is used as electrocatalyst in both the anode and the cathode. The electrodes are supported by porous, inert materials. The solid electrolyte allows efficient sealing and safety of the fuel cell stack and permits the use of less corrosion-resistant construction materials. The performance as well as the cost of the PEMFC depend on the membrane and the utilization efficiency of the platinum catalyst. The high power density of the PEMFC, its simple and reliable construction as well as the possibility of rapid start-up even at low temperatures, make this fuel cell particularly suited as a power source for non-polluting vehicles.

A vision of the electrochemical future would include fuel cells both for electricity production in stationary power stations and for transportation. The high-temperature fuel cell systems (MCFC and SOFC) with their high system efficiencies would be most suited for the latter application, but also PAFCs and PEMFCs are being developed for stationary power production.

For transportation, the PEM fuel cell is generally the preferred choice. It allows rapid start-up from low temperatures and provides high power densities with values presently over 1 kW dm^{-3}. The first fuel cell powered ZEV bus was put into traffic by Ballard Power Systems of Canada in Vancouver 1993 with PEM fuel cells as the power source. A second generation zero emission transit bus was on the road in 1995. The new PEMFC engine produces 200 kW (275 hp), the same power as the diesel engine normally installed in the bus. Furthermore, the fuel cell engine occupies the same space as the diesel engine and gives the same or superior performance. The power density of the new fuel cell stacks is double that of the stacks in the first bus. The compressed hydrogen gas cylinders are placed in the roof space and are sized to give a range of 400 km. Refueling is a matter of minutes.[28]

The choice of fuel is a key factor. Most fuel cells operate best on pure hydrogen and oxygen. The use of air instead of oxygen means some loss of performance. Pure hydrogen can be carried aboard a vehicle either as compressed gas, as in the Ballard bus, or as a cryogenic liquid. However, the volumetric energy density of pressurized hydrogen gas is poor, which means a short range. The energy density of liquid hydrogen is somewhat better but less than a third that of gasoline, and the technology for storing small volumes of liquid hydrogen is not well developed. Hydrocarbons provide a simple way to store hydrogen at high density. They can be converted to hydrogen by on-board reforming and shifting. The PEMFC can tolerate CO_2 in the fuel stream, thus allowing the use of reformed hydrocarbon fuel.

Methanol is particularly interesting; it is a likely fuel to replace gasoline in the transportation sector, since it is easily integrated into the existing distribution system, and has about half the energy density of gasoline. To obtain hydrogen as a fuel to the fuel cell an on-board reformer must be used that allows rapid start-up and quick transient response. The long-term solution could be direct methanol fuel cells, in which methanol is fed directly to the anode of a PEM fuel cell.

5 Electrochemical sensors

An important issue in environmental engineering is the monitoring of toxic compounds. Electrochemical sensors are convenient and effective devices for this purpose, since they produce an electric signal that can be related directly to the concentration of the compound being measured. One of the major achievements within air pollution control is the introduction of the lambda sensor for monitoring oxygen in the exhaust gas from vehicle combustion engines, which is a prerequisite for the modern three-way catalytic converter that reduces considerably the emissions of carbon monoxide, unburned hydrocarbons and nitrogen oxides. The solid electrolyte in this sensor is of the same type as in the solid oxide fuel cell, stabilised zirconia.

Electrochemical sensors have been reviewed in *e.g.* ref. 29. They can be used for sensing pollutants either as potentiometric, amperometric or voltammetric sensors. Ion-selective electrodes work according to the first method and can be used to determine for example pH, fluoride and cyanide concentrations in water. The concentration of toxic gases such as sulfur and nitrogen oxides can also be determined with potentiometric sensors.

Amperometric sensors measure a current at a fixed potential, generally in the limiting current region. The current is then proportional to the concentration of the measured species. The mass transfer control is obtained by means of a porous barrier or a gas permeable membrane through which the gaseous species must diffuse in order to react on the sensing electrode. The Clark electrode for measuring oxygen concentration is the classic example.[30] Its general principle also works for toxic gases like CO, NO, NO_2, SO_2 and H_2S. A sensor can be made selective by a suitable choice of electrode potential and electrode material. An array of such selective sensors can be built into one device for monitoring flue gases and other gas streams containing several toxic components.

6 Photoelectrochemical methods

Recent advances in photoelectrochemistry have led to new, interesting possibilities, both for treatment of pollutants and for conversion of solar energy from light to electricity. In the first case, suspensions of semiconductor particles can be used to harness the light with production of electrons and holes in the solid, which can destroy pollutants by means of reduction and oxidation, respectively. In this way, air or water containing organic, inorganic or microbiological pollutants can be effectively treated. These photocatalytic methods have been reviewed recently.[31]

Photoelectrochemical cells for electricity production offer a sustainable way to generate electricity, *e.g.* for charging batteries in electric vehicles. With semiconductor electrodes using dye sensitized nanocrystalline TiO_2 films an efficiency of 12% has been reported.[32] Compared to conventional photovoltaic cells, this type of photoelectro-chemical cell is less expensive, since it uses inexpensive raw materials, is easily fabricated and does not require expensive crystal purification processes.

7 Conclusions

In this review, a variety of selected electrochemical processes and devices for environmental protection have been presented, which have been tested successfully on laboratory scale. Some, but not all of them, have also been tested at pilot scale and some have reached commercialization. There are many reasons why not all of them are yet commercial. In some cases, it is only a matter of time, further development work (and investment) being required. In other cases, chemical or biological processes are preferred because they are competitive and do not require expertise in electrochemistry and electrochemical engineering.

It may be expected that the number of electrochemical processes for treatment or prevention of pollution will increase in the future due to their specific advantages in a number of applications.

A major beneficial impact of electrochemistry on the environment would be the future introduction of fuel cell or battery driven vehicles.

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