ELECTROCHEMISTRY FOR A CLEANER ENVIRONMENT

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ABSTRACT

A status report of electrochemical processes and devices that could offer cleaner technology for environmental compatibility is presented. Electrochemical processes for treatment of wastewater solutions/effluents, flue gases and contaminated ground water and soil are discussed. Emerging electrochemical power sources for cleaner generation of electricity in fuel cell power stations and for electrically driven vehicles are also given. An overview of the contributions that battery-powered devices have made in medical science towards modern health care is given. The role of electrochemical sensors in monitoring toxic substances and the role of photoelectrochemistry with its interesting possibilities for treatment of pollutants and energy conversion as well as storage is discussed. The beacons and barriers in each strategy are viewed critically and suggestions for improvements of existing electrochemical processes or products in order to minimize the environmental impact are also provided.

Keywords:

Electrochemical processes, cleaner technology, electrochemical sensors, fuel cells, power sources, photoelectrochemical devices, solar energy conversion, energy storage systems, batteries, effluent treatment.

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CONTENTS

1. INTRODUCTION

The rapidly growing world population, increasing number of reports on detrimental effects on the environment and the concern for its protection is major issues today. The strategy for environmental protection in industry necessitates the processes for waste treatment as well as the development of new and alternative processes and products, which have no or less harmful effects on environment. Electrochemistry offers promising approaches in both types of strategies. The inherent advantage is its environmental compatibility, due to the fact that the main reagent, the electron, is a ‘clean reagent’. Electrochemical processes can be used for recovery or treatment of effluents from industrial plants. Industrial electrochemistry has undergone a remarkable development towards cleaner processes and environmentally friendly products. Electrochemistry offers unique ways to generate pure electric power at high efficiency in fuel cell systems or to store it in batteries. These power sources found their role in stationary power systems. The use of batteries in tackling problems related to human health has a proud heritage and a bright future. Electrochemical sensors are particularly attractive because of the chemical species, which are directly measured and transuded into electrical signals. As for electrical components, two types can be distinguished: active sensors, which give a voltage (potentiometric sensors) and passive sensors, for which an electrical source is necessary to impress a signal, the response of which is analyzed afterwards (amperometric, coulometric and conductometric sensors). Photoelectrochemical cells for electricity production offer a sustainable way to generate electricity e.g., for charging batteries in electric vehicles. Compared to conventional photovoltaic cells, photoelectrochemical cells is less expensive since it uses inexpensive raw materials, easily fabricated and does not require expensive crystal purification processes.

Attractive advantages of electrochemical processes include: (1) *Energy efficiency:* Electrochemical processes generally require lower temperatures than their equivalent non-electrochemical counterparts e.g., thermal incineration. Electrodes and cells can be suitably designed and organized to minimize power losses cost by inhomogeneous current distribution, voltage drop and undesirable side reactions. (2) *Cost effectiveness:* Cell constructions and peripheral equipments are generally simple and, if appropriately designed and assembled, also less expensive. (3) *Automation:* The systems are amenable to automation emerging from inherent variables of electrochemical processes i.e., electrode potential and cell current are suitably adjusted for facilitating process automation. (4) *Versatility:* Direct or indirect oxidation and reduction, phase separation, concentration or dilution, biocide functionality, applicability to a variety of media and pollutants in gases, liquids and solids, and the treatment of small to large volumes from microliters up to millions of liters are also possible.

The applications of electrochemistry for the protection of environment have already been exclusively discussed in number of books and reviews[1-9]. Many of the concepts discussed in early publications are still of interest today but progress in material science (new electrode materials and membranes) and aspects in electrochemical engineering (new and effective cell design) have offered possible effective and appealing solutions. This review provides a broad perspective on the use of electrochemistry for the future of human beings. Electrochemistry can be 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).

2. ELECTROCHEMICAL PROCESSES FOR EFFLUENTS AND WASTE TREATMENT

Electrochemistry, dealing with oxidation or reduction of compounds at well-controlled electrode potentials by adding (at the anode) or withdrawing (at the cathode) electrons, offers many interesting possibilities in environmental engineering. Anode 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 wastewater solutions down to very low concentrations. In both types of electrode processes, the operating conditions must be carefully chosen and controlled in order to avoid the side reactions. Not only the two electrodes of the electrochemical cell can be used in purification processes, but also the ion-selective membrane(s) that are often placed between the electrodes can help in selective transfer of anions or cations. New electrodialytic processes using such membranes have been developed, which can be useful for a variety of environmental problems.

2.1. Anodic Oxidation of Toxic Species

It is essential to set high electrode potentials to achieve 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 or chlorine evolution in chloride solutions, which lower the current efficiency. Therefore, the anode material must have a high overpotential for oxygen evolution reaction. For example, lead dioxide posses this property and extensively used in oxidations at high potentials. Dimensionally stable anodes used in chlor-alkali plants or in water electrolysis processes do not provide high oxygen overpotentials. In this context, platinized titanium exhibits better activity but is expensive. Doped SnO_2 – coated Ti electrodes were developed[10] exhibiting significantly higher oxygen overpotentials than both PbO_2 and Pt. As a test reaction phenol oxidation was carried out on these three electrodes and it was found that the rate of phenol removal was higher at SnO_2 than at PbO_2 and Pt. Similar results were obtained for the oxidative treatment of waste water[11]. The efficiency was ~30-40%, which was five times higher than the efficiency observed on a Pt anode. No interference with the cathode was found. This indicates irreversible oxidation to reaction products that cannot be reduced at the cathode. The attempts for electrochemical treatment of wastewater or wastes can be sub-divided into two categories:

(1) Direct oxidation at the anode and

(2) Indirect oxidation using appropriate anodically formed oxidants (Cl_2, hypochlorite, peroxide, ozone, Fenton's reagent, peroxodisulphate).

A special case of indirect oxidation frequently called mediated electrochemical oxidation (MEO) is the use of metal ions with high oxidation potential (e.g., Ag (II) and Co (III)) which can be electrochemically generated in a closed cycle.

2.1.1. Direct Oxidation at the Anode

For the direct oxidation two properties of anode are prerequisites for its suitability: high oxygen overpotential and stability towards corrosion. The process of anodic oxidation of an organic molecule assume the following major steps:[12]

Step I: Discharge of water with the formation of an adsorbed hydroxyl moiety

$$S[\ ] + H_2O = S[OH] + H^+ + e^- \qquad (1)$$

Step II: The adsorbed OH in an 'active state' participate in O-transfer reaction to the organic molecule R.

$$S[OH] + R = S[\ ] + RO + H^+ + e^- \qquad (2)$$

Step III: Oxygen evolution as side parallel process by oxidation of water, diminishing the current efficiency.

$$S[OH] + H_2O = S[\ ] + O_2 + 3H^+ + 3e^- \qquad (3)$$

Phenol and derivatives are the most studied examples. Main intermediates are found to be benzoquinone, maleic acid and hydroxy diphenyls, which could be further oxidized to CO_2 as well as with small amounts of CO.

A voltammetric study at a platinum rotating ring disk electrode with phenols, chlorophenols, organic acids and a surfactant (fluorinated octanic acid) was carried out by Huang et al[13]. Different anodic materials like Pt[14] as reference, Ni, glassy carbon and titanium supported oxide electrodes such as IrO_2, RuO_2, PbO_2 and SnO_2[15] and Bi as well as Fe doped PbO_2[12] were also employed. For phenol concentrations >>1 mM fouling of the noble metal anode was observed by films of polymeric material. By using a packed cell a high rate was achieved with PbO_2 anodes[16,17]. At optimum pH and temperature conditions, a complete oxidation of phenol was achieved. The main products were CO_2 and the side products were benzoquinone and maleic acid.

Comninellis and Pulgarin[15a] studied oxidation of phenol 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 SnO_2 anode with phenol to CO_2 or react with oxygen in a side reaction. Aromatic intermediates were formed in small concentrations on SnO_2, while they were formed in large concentrations on Pt. The rate of phenol removal is almost the same for both anodes, while Ti/SnO_2 anode showed higher rate of total organic carbon (TOC) removal.

It is known that in electroplating and surface finishing industry one still use large amount of cyanide to obtain very finely grained metal deposits. Therefore, the wastewater must be treated with respect to its cyanide content. In conventional chemical method, hypochlorite is used as an oxidizing agent to oxidize the cyanide to less harmful cyanate. In electrochemical process, cyanide is oxidized anodically and this approach is economically feasible at higher concentrations of cyanide (>1 g dm^{-3}). At the cathode, most of the metal ions may simultaneously deposit with hydrogen evolution as side reaction. The overall reaction at the anode (generally used anodic materials are graphite or stainless steel) is:

$$CN^- + 2\,OH^- \rightarrow CNO^- + H_2O + 2e^- \qquad (4)$$

Cyanate further reacts in alkaline solution to form Na_2CO_3, N_2 and NH_3. O_2 evolution is a side reaction. The current density 500 A/m^2, the energy demand is 10 – 40 kWh kg^{-1} cyanide at the reaction temperature 232 – 363 K. The remaining cyanide at low concentrations at the outlet stream has to be oxidized by hypochlorite. To achieve lower residual concentrations and a better process economy NaCl was added to the electrolyte so that chlorine is formed at the anode. The efficiency of the direct electrooxidation process can be improved by using three-dimensional electrodes, which will be discussed subsequently.

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 dilute wastewaters, because of high cost of transportation, the high consumption of fuel and in some cases, corrosion problems. Other treatment options include membrane separation, adsorption on activated carbon and stripping, chemical oxidation with air, ozone or other oxidants. Chemical reduction methods such as catalytic dehalogenation with hydrogen or other reducing agents are also employed. Biological techniques using specific microorganisms or enzymes are under development. Electrochemical dechlorination is an alternative, which could be employed either anodically or cathodically.

Wabner et al.[17b] showed that p-chlorophenol and pentachlorophenol could be destroyed anodically on PbO_2 anodes. The decomposition of p-chlorophenol follow concentration – time curves that are similar to those of phenol, showing the similarity in the mechanism in both cases involving hydroxyl radical formed from water. In the first step, chlorine is substituted by this hydroxyl radical. In subsequent steps, further oxidation yields quinone, which decomposes into maleic acid, oxalic acid and CO_2. The side products formed at the anode are O_2 and O_3. There is a risk that the chlorine 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 extended for dechlorination of other chlorinated aromatic compounds in aqueous solutions such as hexachlorobenzene, parachlorobenzene (PCB)[18] and tetrachlorodibenzodioxin.

Other substrates that have been researched for direct anodic oxidation includes: sugars, alcohols distillery effluents, dyes and aromatics[19]. The oxidation of azodyes leads to the formation of CO_2, N_2 and Na_2SO_4 apart from the formation of aromatic esters, phenols, aliphatic carboxylic acids, cyclic and aliphatic hydrocarbons and aromatic amines. In the presence of chloride, the oxidation of azodyes takes place primarily through the formation of "active chlorine"[19]. Scott[20] investigated the anodic oxidation of aromatic and aliphatic compounds using batch and flow electrolysis in divided and undivided cells. The suitability of various anodic materials for the oxidation of phenols was examined. For the intermediates (especially aliphatic species) the anodes are however, less effective. Graphite and SnO_2 anodes are suitable for the oxidation of formic acid. Lu and Ammon[21] have carried out kinetic study for the direct oxidation of SO_2 in solution using Pt, Pd, Ru, Ir, Rh, Re and Au. It was found from using DSA that PdO_X/Ti showed the highest catalytic activity in these experiments, whilst $RuO_X – TiO_2 / Ti$ and $IrO_X – TiO_2 / Ti$ were inactive. Reasonable current efficiencies were achieved using Pt/Ir coated Ti electrode for sulphite to sulphate oxidation in an undivided cell[20]. Direct oxidation of SO_2 as a tool for flue gas treatment was studied on several electrodes[22]. At graphite electrodes, the products were sulphate and dithionate. A continuous neutralization of generated acid is a necessity in these processes. Numerous fundamental investigations have been carried out for the anodic treatment of aqueous effluents containing inorganic pollutants, e.g. cyanide[23], thiocyanate[20] and sodium dithionate[24]. A major problem for the oxidation of SO_2 is to avoid the formation of elemental sulfur at the cathode. Ebonex® was tested as cathode material for these experiments[20].

2.1.2. Indirect / Mediated Electrochemical Oxidation

In this process, the oxidant is electrochemically generated. For example, chlorine or hypochlorite. It is known that dilute alkaline cyanide solutions can be oxidized homogeneously by anodically formed ClO^-. ClO^- is an efficient oxidant, but it has the disadvantage that it forms toxic chlorinated compounds. Other examples include peroxide, Fenton's reagent[25], peroxidisulphate and ozone. Hollow, cylindrical fluoro-carbon-impregnated carbon anodes were used for ozone generation in a solid polymer electrolyte cell[19]. Mediators of types Ag^{II}, Co^{III} and Fe^{III} were also used and the standard potentials vs. SHE are 1.987, 1.842 and 0.77 V respectively. The higher the redox potential, higher is the columbic efficiency.

AEA technology in Dounreay, Scotland[19] developed a process using Ag^{II}. Ag^{I} is anodically oxidized to Ag^{II} on platinized titanium in concentrated nitric acid in a membrane divided cell. Some Ag^{II} might oxidize the organic compounds directly in the anolyte, which then react with organics. Ag^{II} is probably stabilized in the solution as a nitrate complex, $AgNO_3^+$. In cathodic chamber, which is separated from the anodic chamber by means of a cationic selective membrane, nitric acid is reduced to nitrous acid, which is reoxidized to nitric acid by air in a separate reactor. The reduction of nitric acid followed Vetter mechanism[26] to form NO, which can be regenerated back to nitric acid by the oxidative absorption in columns[27]. Comninellis studied the electrochemically generated Mn (III) in sulphuric acid[28], which leads to the formation of aldehydes in counter current columns and complete oxidation of NO to HNO_3. Water is recycled to the anodic chamber to replace the water loss by electro-osmosis through the membrane. The net effect is that dissolved organics are converted to CO_2 and H_2O by oxidation with air. This technique is employed successfully to destroy a variety of organic compounds, including benzene, phenols, oils and chlorinated organic compounds. The use of metal ions with high oxidation potential like Ag (II) and Co (III) can completely oxidize the organic compounds to CO_2. This technique was originally employed in nuclear industry to dissolve refractory plutonium dioxide in nitric acid[30]. Ag (II) was found to be the most efficient oxidant for this purpose, and this experience initiated the treatment of mixed radioactive wastes (e.g., tributyl phosphate, solvent of the purex process) at Savanah River Laboratory[31], at AEA Dounreay[32] and at Forscungszentrum Karlsruhe[33], where for the first time intermediates and mechanism for the oxidation of phenol and chlorinated phenols were examined, and this method was applied for a plurality of hazardous wastes. For total oxidation, only redox couples with a high oxidation potential are suitable [Co (III) / Co (II), Ag (II) / Ag (I) and Fe (III) / Fe (II)]. The formation kinetics of the oxidizing state of the mediators was investigated by the rotating disk electrode (RDE) experiments[34]. The formation of Ag (II) is mainly diffusion controlled with an average value for β of 0.488 cm^2 sec^{-1} (β = Diffusion coefficient). For the Ag (II) system, under favorable flow conditions high current densities of more than 5 kA m^{-2} could be obtained.

Reports on the studies on Co (III) generation showed that anodic oxidation of water and Co (III) formation are probably simultaneous reactions. The kinetics of the oxidation of water by the mediator as a function of temperature was carried out[34]. Degradation of chlorinated organic compounds leads to the intermediate precipitations of silver chloride, which are redissolved in excess of Ag (II) by oxidation of chloride to perchlorate. This is enriched in the anolyte and can be separated from time to time by cooling as potassium perchlorate[35].

2.2. Cathodic Processes

2.2.1. Removal of Heavy Metal Ions

Waste water containing heavy metal ions generated in metallurgical, electroplating, photo development processes, printed circuit board production or battery technology, requires special treatment to remove toxic metal ions or recycling of valuable materials. The conventional purification of these streams uses hydroxide precipitation, which gives a voluminous metal hydroxide sludge that has to be disposed off 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 wastewater is an attractive alternative process, since the metal can be recovered in the pure metallic form or as a concentrated solution that can be recycled or the extraction of the pure metal in an electrowinning process may be possible. The basic problem is that the mass transport controlled limiting current density for cathodic metal deposition from dilute solution 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. A possible solution to this problem is to use a rotating cylinder cathode or use expanded metal mesh electrodes immersed in a fludized bed of small glass beads. The efficient electrochemical engineering approach is to employ the packed bed electrode or more generally, three-dimensional electrodes as shown in **Fig. 1**.

Most three-dimensional electrodes used for metal removal are of fixed bed type. The anode may also be a three-dimensional electrode or just a planar electrode. The cathodic materials employed are graphite particle, expanded metal, graphite felt, metal wool, graphite fibers and reticulated vitreous carbon. The engineering aspect is of importance, since the potential drop in the dilute electrolyte is along the depth of the electrode in the direction of current flow. This determines the extent of the side reactions such as hydrogen evolution[36]. If the bed is too thick, operation at the limiting current density across the whole depth of the electrode would give 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 few minutes[37]. Operational costs are favorable compared with the classical wastewater treatment systems. In some cases, the removal efficiency is higher, and the space required by the process is also low.

The deposited metal in the cathode may be recovered as a concentrated solution by chemical dissolution 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. A better approach would be the concentrated metal ion solution could be recycled to the process, which has generated the waste solution. An alternative regeneration procedure is to use three-dimensional electrodes made of foamed graphite or carbon felt to recover the deposited metal in an external procedure according to the principles of electro-refining. Processes utilizing packed–bed electrodes have been employed in the chemical industry mainly for waste solutions containing Cu and Hg[38]. Outlet concentrations of less than 1 ppm can be achieved. The energy consumption is of the order of 1 kWh^{-1}. For less noble metals such as Zn and Cd, the side reaction of hydrogen evolution predominates and the current efficiency is low, particularly at lower concentrations. Therefore it is not possible to decrease the concentration of these species below 1 ppm in an acceptable overall current efficiency. A further complication is that excessive cathodic hydrogen evolution may increase the pH, so that the metal precipitates as hydroxide. This phenomenon can be used to remove Cr (VI) as $Cr(OH)_3$.

2.2.2. Electrochemical Dechlorination

Schmal et al.[39] studied the feasibility of electrochemical reduction of wastewaters containing halogenated organic compounds. The electrode materials employed were graphite/carbon fiber with high surface area. A reasonably a high over potential for competing hydrogen evolution reaction was achieved and there was a complete removal of chlorine from organic molecules in aqueous solution. The dehalogenation results in a decreased toxicity and an increased biodegradability, thus enabling further biological treatment. The energy consumption and conversion rates of this process are technically and economically viable. The dechlorination of organic toxicants can occur not only anodically but also cathodically according to the overall reaction:

$$RCl + H^+ + 2e^- \leftrightarrow RH + Cl^- \qquad (5)$$

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, epichlorohydrin and of aromatic halides[40] has also been demonstrated.

2.2.3. Optimization of cell design

Most of the metal ions were removed by cathodic deposition. Electrochemical processes have been developed, some of which are already commercialized and being used now in the industry[41-44]. The removal of metal ions $Me^{z+}$from wastewater is based on the cathodic metal deposition:

$$Me^{z+}_{sol} + ze^- \Leftrightarrow Me \qquad (6)$$

From a thermodynamic point of view, the Nernst equation predicts that it should be possible to decrease the Me^{z+} concentration in solution to an arbitrarily low level, if the potential E of the Me/Me^{z+} electrode is maintained sufficiently negative with respect to the standard potential $E°_{Me/Mez+}$:

$$c_{Me^{z+}} = c^{+}\exp [zF/ RT] (E - E°_{Me/Me^{z+}}) \quad (7)$$

However, at extremely low concentrations, the rate of the mass transport controlled process strongly decreases. In practice, electrolysis at concentrations below 0.05 ppm is no longer economical due to increasing electrolysis time and unacceptable space-time yield. Since the current densities at low metal ion concentrations are small, the specific energy demand for an electrochemical wastewater purification process is generally quite low, typically in the order of 0.05 M. Another important point for consideration is that the specific investment costs, which are inversely proportional to the space-time yield of the reactor. For the cathodic metal deposition in an electrochemical reactor of volume V, the space-time yield is defined as the amount of metal dm (in grams of current units) deposited in a time interval dt:

$$\rho = \frac{1}{V} \frac{dm}{dt} \quad (8)$$

According to Faraday's law, dm is proportional to the electrolysis charge, $A\phi^{c}i\ dt$:

$$dm = A\phi^{c}i\ dt \ \frac{M}{zF} \quad (9)$$

Where ϕ^{c} is the current efficiency, A the actual electrode area, and M the molecular weight of the metal deposited. The optimal process conditions are met when the rate of the heterogeneous reaction attains its maximum at the limiting diffusion current density, $I = i_{l}$:

$$i_l = - zFD_{Me^{z+}} \frac{c_{Me^{z+}}}{\delta} = - zFk_m c_{Me^{z+}} \qquad (10)$$

Where $D_{Me^{z+}}$ is the diffusion coefficient, δ the Nernst diffusion layer thickness, and $k_m = D/\delta$ is the mass transport coefficient. On replacing the current density i in Eq. (9) by i_l the space - time yield can be expressed as:

$$\rho = \phi^c M a_c k_m c_{Me^{z+}} \qquad (11)$$

This is the key formula for the design and construction of an electrochemical reactor for wastewater treatment and metal recovery. For a given metal ion concentration $c_{Me^{z+}}$ a high mass transfer coefficient k_m and a large specific electrode area $a_c = A/V$ are essential to obtain high space - time yields.

The reactor performance is not independent of the properties of wastewater. Therefore, Kreysa[46,47] introduced the definition of a normalized space velocity ρ_s^n for the characterization of the reactor performance for a given degree of conversion:

$$\rho_s^n = \frac{I\phi^c}{(c_i - c_e)VzF} \log \frac{c_i}{c_e} \qquad (12)$$

This figure gives the volume of wastewater in cm^3 treated by reducing the inlet concentration c_i by a factor of 10 ($c_e = 0.1\ c_i$) within 1 s in a reactor volume of 1 cm^3.

Different types of cell constructions have been designed in the recent years. Efficient cell designs have been directed towards optimizing of the space-time yield ρ according to the key formula (Eq. 11), i.e. high specific electrode area a_e and/or large mass transport coefficient k_m.

With respect to these criteria, the electrochemical cells may be classified in the following three groups.

- Cells with improved mass transport and thus increased current density by setting the electrodes in motion or by applying turbulence promoters, but with a relatively small electrode area in a given cell volume. Examples are the Pump cell[48,49], the Chemelec cell[50], the ECO cell[51-55], the Beat rod cell[54,55] and cells with vibrating electrodes or electrolytes[56].
- Cells to accommodate large electrode area in a small cell volume. This has resulted in the developments such as the Multiple-cathode cell[57], the Swiss-role[58] or the ESE (extended surface electrolysis) cells[59].
- Cells with improved mass transfer coefficients and enlarged specific electrode area by the use of three-dimensional electrodes. Examples are the Porous flow-through cell[60], the RETEC cell[61], the packed-bed cell[62-64] the fluidized bed cell[65-69] and the rolling tube cell[70,71].

The design of the three-dimensional electrodes originates from the fact that in contrast to the planner configuration the electrode area is distributed throughout all three dimensions. Due to the specific fluid dynamic conditions inside such a three-dimensional bed electrode, this arrangement provides not only a large specific electrode area but also large values for the mass transport coefficient. The pictorial representations and discussions on the diagram and operation of various types of cells are presented elsewhere[9].

2.3. Electrodialytic Processes

Anion selective membranes, which allow only anions to pass, can be used in cells with three-dimensional electrodes for metal deposition. 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 carryout the main part of the work by splitting the inlet flow into one more concentrated and no more dilute stream. Recent studies on anion exchange membranes and electrodialysis methods to permeate specific anions through the membranes are reviewed by Sata[72]. The studies are classified as: (1) to increase cross-linkage of the anion exchange membranes, (2) to form tight surface layers on the anion exchange membranes, (3) to decrease hydrophilicity of the anion exchange membranes or their surfaces by introducing specific anion exchange groups in the membranes, (4) to impregnate hydrophilic compounds in the anion exchange membranes to increase hydrophilicity of the membranes, (5) to control permselectivity of anions by photoirradiation using membranes with a photoresponsive group and (6) to control permselectivity of anions through thermally responsive anion exchange membranes with temperature. Permselectivity of specific anions through the anion exchange membranes is governed mainly by the balance of hydration energy of anions with hydrophilicity of the membranes, partially by hydrated ionic size of the anions, except the membranes having an oppositely charged layer on the membrane surface.

Cation exchange membranes introduced commercially in the membrane cells for chlor-alkali production can also be used in electrochemical processes for environmental protection. Electrodialysis has since been used for salt or brine production and in desalination processes for obtaining fresh water. It can be combined with the process of electrolysis for desalinating water streams.

Aqueous streams containing NaCl and Na_2SO_4 are generated in many chemical-processing operations such as flue gas scrubbing, metal pickling, fermentation and rayon manufacture. Large volumes of highly concentrated sodium salts resulting from neutralization of acidic or alkaline solutions are economic motivations to reinforce the demand for zero effluent technology[3, 9]. As a result, there is an increasing interest in technologies to recover the sodium salts back to sodium hydroxide and acid. Since the reversal of the neutralization reaction is accompanied by a positive change of the enthalpy, such a process can only be realized by an electrochemical route. An example is the electrolytic splitting of sodium sulfate solutions into sodium hydroxide and sulfuric acid solutions in a three-compartment cell with cation or anion exchange membranes. Protons H^+ and hydroxyl ions are produced during oxygen and hydrogen evolution at the anode and cathode of the cell as shown in **Fig. 2.** In such a cell, hydroxyl concentrations of ~ 10 mass% can be achieved. The cell voltage and thus the energy demand are 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[73], as shown in **Fig. 3.**

However, in this case a pure sulfuric acid solution is not obtained as in the three-compartment cell. The energy consumption is 1600 – 1800 kWh tonne^{-1} caustic at a concentration of 13-18%. Energy savings may also be achieved by using bipolar ion exchange membranes, which consist of three 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 have 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 constructed as a compact stack. The energy requirement for producing sodium hydroxide is in the range 1300 - 2000 KWh tonne^{-1} at 1000 m^{-2} and a current efficiency of 80%. This energy demand is lower than that of the conventional chlor-alkali processes. This technique may be used to produce sodium hydroxide without the simultaneous generation of chlorine.

Gutbealet *et al*[74] described the combinations of ion exchange membranes and conventional ion exchanger resins for the treatment of water and processed solutions with continuous regeneration of the ion exchanger. This approach significantly reduces stack resistance, power consumption and increases the available surface area of conventional electrodialysis processes. The ion exchanger materials are continuously regenerated electrochemically by H^+ and OH^- ions that are produced by water splitting in an applied electrical DC field. The major application of this technology is the production of ultra-pure water and the removal and recovery of heavy metals and precious metal ions from industrial effluents.

Ganzi *et al*[75] employed three different concepts in their technology. The ion pure (Millipore) and the electrodiaresis (Euva) concept are employed for de-ionisation of pure water[76a,b]. The third concept was directed towards the separation, concentration and recovery of metal ions from solutions. *e.g*: $CuCl_2$ recovery (See **Fig. 4**. for typical representation).

The feed solution was passed through separate beds of cation and an anion exchanger. Under applied electrical field, protons and hydroxyl ions are generated by electrolysis and pass the ion exchanger membranes for continuous regeneration of the resin beds, replacing the Cu^{2+} and Cl^- ions, which are released into the central chamber of the concentrate. The process works with a current efficiency of 30%.

The conventional process for chlor alkali electrolysis is the amalgam process[77]. This technology is associated with the emission of mercury into the air and mercury - containing wastewaters. With the development of fluorinated ion exchanger membranes a new process became available which represents a cleaner technology. This new technology employ the zero gap cell concept, which is characterized by electrodes pressed directly onto the diaphragm in order to minimize the IR drop caused by the gas evolution. Such membrane cell technology has been commercialized by AZEC in Japan. Another interesting improvement to the process has been achieved by ICI with the FM21 electrolyzer, which is a plate and frame cell block only 40 cm in height and up to 2 m wide. The low height of the electrolyzer avoids gas accumulation and contributes to further energy savings. The progress in decreasing the specific energy consumption for chloralkali electrolysis by the invention of this new process is depicted in **Fig. 5**.

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 in **Fig 6**. The ground water or an externally supplied fluid is used as electrolyte. Acar and Alshawabkeh[79a] and Probstein and Hicks[79b] reviewed this technique. The main electrode reactions are generally oxygen evolution at the anode and hydrogen evolution at the cathode as shown below.

$$H_2O \rightarrow \tfrac{1}{2} O_2 + 2H^+ + 2e^- \quad (13)$$

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^- \quad (14)$$

As in ordinary electrolysis, movement of ions will 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. This method is not restricted to ionic contaminants but can also be used to extract organic compounds by means of the electro osmotic flow that is generated by the electric field in fine-grained soils with pores that are of micro-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, electro-osmotic flow will be effective in smaller pores. For ions, mass transfer by migration will generally be higher than that by electro- osmosis.

This technique can be employed in situ, on-site and off-site the flow around the electrodes and through the soils can be controlled so that the contaminating species in the fluid may be removed either at the electrode 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 equations (13) and (14). 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 alkali 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 fashion, species are concentrated in the region where the two pH-fronts meet and pH changes abruptly. These problems may be solved by means of pumping solutions. For example, the hydroxide precipitation at some distance from the cathode may be avoided by adding an acid solution to the cathode region.

Electro kinetic remediation has been tested successfully in field studies in Netherlands and in USA. Estimated costs for the technique[79b] indicate that they may be several times lower than that involved in conventional methods.

2.5 Electrochemical Gas Purification

The processes discussed deal with pollutants 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 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[80] as represented in **Fig.7**. 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. An increasing demand for off-gas purification, especially for smaller scale power plants, heating combustion units or chemical plants requires the development of new concepts of electrochemical gas purification techniques. Many gaseous pollutants such as chlorine, hydrogen sulfide, nitrous oxides or sulfur dioxide permit electrochemical conversion in an aqueous environment, since the standard potential of the corresponding reactions are all within the stability range of aqueous electrolytes:

$$2Cl \Leftrightarrow Cl_2 + 2e^- \qquad E^\circ = 1.360\ V \tag{15}$$

$$H_2S \Leftrightarrow S + 2H^+ + 2e^- \qquad E^\circ = 0.142\ V \tag{16}$$

$$NO + 2H_2O \Leftrightarrow NO_3^- + 4H^+ + 3e^- \qquad E^\circ = 0.957\ V \tag{17}$$

$$NO_2 + H_2O \Leftrightarrow NO_3^- + 2H^+ + 3e^- \qquad E^\circ = 0.775\ V \tag{18}$$

$$SO_2 + 2H_2O \Leftrightarrow SO_4^{2-} + 4H^+ + 2e^- \qquad E^\circ = 0.138\ V \tag{19}$$

Different concepts of electrochemical gas purification have been well discussed in literatures[80].

The reduction or oxidation may occur directly at the electrode or indirectly through a redox mediator, the mediator has to be generated electrochemically. In any case, the initial step is absorption of the pollutant species into a liquid phase. Since the solubility of several gases in aqueous-solutions is small, the transfer from the gas phase into the solution phase must be supported by a reaction, which converts the primarily dissolved species permanently to a more soluble one.

Homogeneous and heterogeneous catalysts were employed as redox mediators. The advantage of heterogeneous mediators, such as oxides, is that a separation of the reaction products from the mediator is not necessary. Both the electrochemical conversion of the pollutant and the electrochemical regeneration of the redox mediator can be achieved either by inner cell or an outer cell processes as illustrated in **Fig. 7**.

Direct electrochemical conversion of gases by an inner cell process can be carried out in a specially designed electrochemical absorption column, which consists of a three-dimensional packed bed electrode of conducting particles in contact with a cylindrical feeder electrode and a counter electrode separated by a porous diaphragm or ion exchanger membrane[81].

The schematic design of such a device, which usually operates under counter current flow conditions of the gas and the liquid phases is shown in **Fig. 8.** The dissolved pollutant is directly converted at the surface of the packed bed electrode. Such a construction exhibits high a space-time yield end has been successfully employed for electrochemical absorption of sulfur dioxide and chlorine[81b,82].

Indirect, electrochemical processes with homogeneous redox mediator are the so-called `peracidox' process developed by Furgi [83] using peroxodisulphate as the redox mediator for SO_2

oxidation, and the modified `Mark 13 A' process developed at the joint European Research Center Ispra,[84] using bromine as a mediator for the indirect oxidation of SO_2. (in both cases, the electrochemical regeneration of the redox mediator is performed by an outer cell process in a separate electrochemical cell.

$$SO_2 + Br_2 + 2H_2O \rightarrow H_2SO_4 + 2HBr \quad (20)$$

$$2HBr \rightarrow Br_2 + H_2 \quad (21)$$

Strafelda and Krofta[85] suggested PbO_2 as a heterogeneous redox mediator to catalyze the oxidation of SO_2. Kreysa *et al.*[86a] employed a copper catalyzed (Cu_2O / Cu_4^{2+}) process for the combined electrochemical and catalytic removal of SO_2. Iliev *et al.*[86b] employed porous gas diffusion electrodes for the conversion of SO_2 using pyrolized phthalocyanines as electro-catalyst. Electrode technology borrowed from the fuel cell technology has also been used for effluent gas treatment. A cell construction similar to that of a molten carbonate fuel cell with porous electrodes and a molten Na_2S-Li_2S electrolyte at 623 K has been examined for removal of SO_2 and H_2S[87]. 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.

$$SO_2 + O_2 + 2e^- \rightarrow SO_4^{2-} \quad (22)$$

High temperature solid state electrochemical cells based on yettria stabilized zirconium dioxide YSZ and porous palladium electrodes have been studied by Hibino[88] for the electrochemical removal of both NO and CH_4 at 923-1023 K in an oxidizing atmosphere. NO is reduced to N_2 and CH_4 is oxidized to CO_x.

Since flue gases not only contain SO_2 but also NO_x the simultaneous removal of both components is the subject of recent investigations[89]. In an indirect outer cell process that employs Ce^{4+}as homogeneous redox mediator the simultaneous oxidation of SO_2 and NO_x to sulphuric acid and nitric acid respectively has been released. The process scheme and the reactions are depicted in **Fig 9**.

The acidic, solution is continuously fed down to the anode, where Ce^{4+} is regenerated. When the solution reaches a critical concentration of 30 – 40% HNO_3 and H_2SO_4, separation of the nitrate effluent from the sulfate solution and recycling of Ce^{3+} are performed in a separate unit, in which HNO_3 is first separated by distillation and the excess H_2SO_4 is then continuously removed by liquid / liquid extraction technique[90].

Lead dioxide dithionate process,[89c,d] which combines direct and indirect conversion of SO_2 and NO_x respectively in two steps with dithionate as homogeneous redox mediator for the indirect reduction of NO_x and lead dioxide as heterogeneous catalyst and mediator for the direct oxidation of SO_2. The gas mixture, first enters an absorption column, where NO is absorbed by the complex forming agent Fe (II) EDTA and simultaneously reduced with dithionite, $S_2O_4^{2-}$. The redox mediator dithionate is continuously regenerated by cathodic reduction of SO_3^{2-} in an electrochemical cell. The second compound, SO_2, passes through the NO absorption column without reaction and enters an electrochemical cell, where it oxidized directly to sulphuric acid at the anode. Micro-kinetic studies of NO_x absorption revealed that the degree of NO conversion can be improved at the low content of Fe (II) EDTA in absorption solution. Since, addition of Fe (II) EDTA at the partial pressure NO at the outlet is drastically decreased and remains at lower level as long as dithionate is present in solution. The products were NH_4^+, amidosulphonic acid and SO_3^{2-}. The formation of N_2 was negligibly small, optimization of this process requires further investigations on the complex chemistry of NO_x[74,91a,b].

Non-faradaic electrochemical modification of catalytic activity (NEMCA) was described for over 60 catalytic systems[92]. It includes the significant increase in the catalytic activity and selectivity of metal and metal oxide catalyst deposited on solid electrolytes such as Y_2O_3 -

stabilized ZrO_2 (YSZ) or β" - Al_2O_3 by electrochemical polarization of the catalyst electrode. The rate of the catalytic reaction is typically increased by a factor of 5-100. A positive influence of NEMCA on the catalytic reduction of NO by C_3H_6 in the presence of O_2 leading to the formation of CO_2 and N_2 has been recently reported[93].

3. ELECTROCHEMICAL POWER SOURCES

The development that has been made on energy sector during the last two decades indicates that it is actually a transition time for improving strategies regarding energy production, storage and conversion. The demand for the usage of fossil fuels like coal, oil and natural gas is increasing day by day due to the increase in population. The population figures for the period between 1989 and 1998 are given in **Table 1**. The data on world energy consumption for this period are given in **Table 2** [94]. World energy consumption is increasing enormously as shown, mainly because of the growing demand for energy in developing countries as they attempt to improve their living standards. If the growth of world population continuous at this rate, it will be difficult to deliver energy equitably at the present consumption levels of the developed nations as well as to satisfy the needs of the developing countries.

The fact that the resources such as oil, coal and natural gas are limited has led to a growth of scientific efforts to find alternative energy sources which have one following basic attributes: (1) The energy should be inexpensive as possible, (2) a secured supply should be ensured, (3) its use should lead to minimum environmental pollution, and (4) it should be socially acceptable. It is hard to meet all these requirements at the same time. For instance, the use of coal may be secure and relatively inexpensive but is not environmentally acceptable. Synthetic fuels produced from coal may also prove to be environmentally incompatible and at the same time expensive. Electricity from non- thermal generators does satisfy two of the requirements, namely security of supply as well as minimal environmental effects. It is known that all other energy sources like fission, fusion, photovoltaic, ocean thermal gradients and wave power can be used to produce electricity. Similarly, all energy requirements can be met at least partially through electricity. In spite of these advantages of electrical energy, it should be pointed out that storage of electricity is expensive and it has to be produced when and where it is required. Otherwise, one has to incur transmission expenses and the concurrent power losses in transmission. Storage of electricity as chemical energy is more convenient and comparatively inexpensive. This is why chemists, chemical engineers have a key role to play in the energy conversion processes.

Today we are using fossil fuels as energy sources, because these are readily available and relatively convenient to use i.e. to find, transport, refine and consume. But they have drawbacks, like non-renewability, uneven distribution around the globe and problems of environmental pollution. Air quality has been deteriorating rapidly over the years resulting in health hazards. The principal pollutants derived from fossil-fuel consumption, which are most harmful to health, are listed in **Table 3**. This table also shows the sources and types of pollutants including the extent of emissions in a particular year. The combination of two or more of any of these pollutants gives rise to secondary pollutants (**Fig. 10**), which multiply health hazards. The effects of various pollutants on human health are outlined in **Table 4**.

Adopting electrochemical methods is one of the ways of ensuring pollution free operation[94b].

3.1 Electrochemical Capacitors

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 absorbed 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[95]. 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.

An interesting alternative, or complement to batteries is electrochemical capacitor (also known as ultra capacitors or super capacitors), which can give peak power densities greater than 1 K W Kg^{-1} while the energy density is only 2-10% of that stored in a battery to deliver the same power[96].

Research and development is going on since the early 1990s to develop ultra capacitors using various types of carbon doped conducting polymers, and metal oxides as electrode materials. The electrolyte may be aqueous, organic or a solid polymer. Ultra capacitors in aqueous electrolyte can store 1.5 W h kg^{-1} and deliver 1kW kg^{-1}, while the best values reported for devices using an organic electrolyte are 5-7 Wh kg^{-1} and 2 $kWkg^{-1}$. Further development is expected to result in ultra capacitors with an energy density of 10-15 W h kg^{-1} and a power density of 3 - 4 kW kg^{-1} in the near future[96]. With increasing energy density the possibility increases of using only electrochemical capacitors as storage device for electrical energy in hybrid electric vehicles.

3.2 Batteries for Electric Vehicles

Batteries or galvanic cells, are electrochemical energy systems / devices in which chemical energy is directly converted to electrical energy. 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 Angels 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 during Jan 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 $1260 million for five years. The goals that have been set by the US ABC are shown in **Table 5**. These performance requirements are compared in the same table with some battery systems of special interest for electric vehicles and load leveling.

Some of the systems that have been proposed to meet the mid-term goals include batteries like sodium-sulfur, sodium - nickel chloride, lithium - metal sulfide, lithium - polymer and lithium - ion batteries, metal hydride - nickel oxide, zinc - air and Zn - 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[97]. In order to recharge the zinc anode rapidly and 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 electro-winning 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 GN - OpelCorsa Comb Vans. The desiring range is claimed to be 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 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. The efficiency of fuel utilization is also higher. Batteries are still to 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 world wide will hopefully lead to a break through for the electric vehicle in the future.

3.3. Batteries for Modern Health Care

The invention of the cardiac pacemaker thirty - nine years ago marked the beginning of the era of the treatment of health disorders by battery powered implantable devices. Since that time several different battery powered implantable devices have been developed and are in use. Batteries play an important role in external medical devices as well, ranging from surgical tools to motorized wheel chairs. At both battery technology and device development progress, the use of batteries in the treatment of disease will continue to be an important feature of medical care.

For example, implantable defibrillators save thousands of lives annually. Drug delivery systems provide carefully controlled administration of medication inside the patient. Neurostimulators, which relieve severe pain and treat conditions such as epilepsy, are in routine use. Left ventricular devices provide life-saving `bridge' for patients awaiting heart transplants.

In addition to these internal devices, batteries have played an important role in powering external medical devices. Portable external defibrillators powered by rechargeable batteries are present in most emergency response vehicles. Holter devices for cardiac monitoring rely on batteries for energy. Ambulatory external drug delivery systems are powered by batteries. Motorized wheel chairs, increasingly rely on secondary batteries for their power. Surgical tools without cords enable surgeons to operate with less inconvenience. The list goes on and on. The development of the devices mentioned above has been made possible in part by the advances in battery technology in the last 40 years. The evolution of implantable biomedical devices proceeds as the development of advanced primary lithium batteries has evolved. The advances currently under way in the field of secondary batteries provide the promise of lighter, smaller and longer lasting power sources for external medical devices. Especially batteries using unique materials will allow the development of medical devices for demanding environments such as the magnetic resonance treatment arena. Power sources for medical devices show many important features. Size and weight are always important considerations, particularly for implantable devices. Longevity is a crucial factor. Above all, the requirement is for the highest standards of quality and reliability. Life-saving devices simply must work right, and the battery is a crucial component in ensuring reliable performance. Methods of assessing quality and reliability of medical batteries have been developed and are used to ensure that power sources meet the requirements.

(A) The Cardiac Pacemaker

* Greatbatch and Chardack, between 1958-60 made the first successful cardiac pacemaker. Zinc/mercuric oxide batteries was the power source[98]. Early pacemakers used as many as ten of these batteries in series/parallel combinations. This cell, invented by Puben[99] was used for first 10 years, but significant drawbacks were present. The cell generated hydrogen gas as a by - product of the cell reaction and this prevented hermetic sealing of the pacemaker. The cell showed significant self-discharge at body temperature. The end of the life time of the cell was rather abrupt, with little indication that cell depletion was imminent. Later versions of the cell developed by companies such as Leclanche', Mallory, and General Electric showed some improvement in longevity and self-discharge[100].

* In 1970s, rechargeable pacemaker was developed using a specially designed nickel/Cd battery[101]. The cell was recharged through the skin by an alternating field. But patient compliance was a problem.

* Nuclear batteries were developed for pacemakers. These cells used plutonium to generate heat, which was converted into electrical energy by thermopiles[102]. This system was reliable and successful but it associated with regulatory burden.

* The real progress in achieving a truly long-lived pacemaker came with the development and commercialization of lithium primary batteries in the late 1960s and early 1970s. Lithium metal, which offers 3.86 ampere hours of capacity per gram made possible the development of pacemakers with years of longevity which could be hermetically sealed and the cell depletion could be detected easily by the circuitry of the device. The first lithium battery to be used in a cardiac pacemaker was the lithium / iodine - polyvinyl pyridine (PVP) system, invented by Schneider and Moser[103] and developed by Greatbatch, Mead and Rudolph[104]. Several other lithium-based systems found significant use in pacemakers, especially the lithium / silver chromate system[105], the lithium/cupric sulfide system[106] and the lithium/thionyl chloride system[107]. Gradually the other systems gave way to the lithium/iodine-PVP system, and today all cardiac pacemakers use this system. The advantages of lithium/iodine-PVP system include: There is no gas generation unlike Zn/Hg oxide battery, so the cell and the pacemaker can be hermetically crated; the energy density approached 1.0 W h cm^{-3}, providing greater longevity in a much smaller package and self-forming, self-healing electrolyte/separator provides inherent reliability and the system exhibited excellent record of reliability and safety[108]. The limitations are: (1) The system contains solid electrolytes which grow thicker as the cell is discharged the resistance of the cell is rather high and

increases with discharge, leading to a voltage drop under load, which increases as the cell is depleted and results in current - delivery limitations. (2) The cell shows excellent volumetric energy density, the gravimetric energy density is not as advantageous, because iodine itself is rather dense and the cell is encased in stainless steel.

It has been proposed that using a solid cathode, liquid electrolyte system could help to alleviate these drawbacks. The lithium / carbon monofluoride system has been proposed for future pacemakers. This system can be encased in a titanium enclosure, resulting in a cell which retains the volumetric energy density of the lithium / iodine-PVP system while doubling the gravimetric energy density. The resistance of the cell remains under 50 ohms throughout discharge, unlike the lithium/iodine - PVP system, which exhibits a resistance of thousands of ohms in the final stage of discharge. The solid cathode liquid electrolyte systems, including lithium / carbon monofluoride and lithium/manganese dioxide are likely to find their application in pacemakers in the near future[109].

(B) Implantable Defibrillator/Cardioveter

Implantable defibrillator/cardioveter was developed by Morowski *et al.*[110] in 1970s. It was believed that ventricular fibrillation, a major cause of death, could be treated by an implantable device, which could detect the onset of the condition and provide a shock to the heart, stopping the fibrillation and restoring normal cardiac rhythm. By 1980, a working model was implanted in a human. This device places a challenging demand on the battery. The power source must operate efficiently at low current drains necessary to power the monitoring circuitry and, when ventricular fibrillation is lined, must provide a very high energy power (~ 35 joules) to change the capacitors and provide the shock to the heart.

The first power source used in this application was Li/V_2O_5 cell developed by Horning and Viswanathan at Honeywell Corporation[171]. They exhibited shorter longevities than needed, and this source was soon replaced by batteries using silver vanadium oxide as cathode material based on original technology developed by Liang *et al.,*[112] and adapted for the implantable defibrillator application by Keister *et al*[113a,b]. The Li/Silver vanadium oxide energy source was used in over 75,000 implantable defibrillators. Recent clinical studies established the effectiveness of the device in prevention of sudden cardiac death.

(C) Implantable Neurostimulators

Few types of chronic intractable pain can be effectively managed by electrical stimulation of the spinal cord[115]. Implantable neurostimulator has been used for this purpose. Advanced models of these devices permit the patient to control the level of stimulation in response to the level of pain involved. Further development have shown that direct stimulation of the brain may be effective in controlling the tremors associated with Parkinson's disease[116]. Neurostimulation has been developed to treat epilepsy. A multi-programmable implantable pulse generator delivers electrical signals to the left vagus nerve via bipolar electrodes. These electrical signals showed in clinical trials to be effective in reducing the frequency and severity and epileptic seizures[117]. These devices currently are powered by lithium/thionyl chloride batteries, which can provide the milliampere - level current drains necessary for effective stimulation[118]. It is anticipated that the future will employ solid cathode, liquid electrolyte batteries in these devices.

(D) Implantable Drug Delivery Systems

Implantable drug delivery systems began in 1970s and first such units employed bellows pump activated by liquefied freon[119]. The device provided a constant flow of a drug through the expansion of the bellows and so control of the drug administration other than that provided by the mechanical pump. Later, electrically powered pumps and advanced electronics were employed to provide a more controlled administration of drugs. The use of implantable pumps administer several drugs for therapies such as cancer, multiple sclerosis, cerebral palsy and injuries [120]. The classic example is insulin[121]. The most commonly used battery system for these devices is the lithium/thionyl chloride system. This system offers the ability to deliver the milliampere-level current drains required by the device and the higher voltage (3.65 V) needed by the electronics. Drug pumps of the future may employ solid cathode liquid electrolyte systems such as lithium/manganese oxide or lithium/carbon monofluoride.

(E) Implantable Atrial Defibrillators

Atrial fibrillation is an arrhythmia in which rapid, irregular atrial impulses and in effective atrial contractions occur. Because all the blood is not pumped out of the atrium, blood can pool and clot, resulting the possibility of stroke. A device has been developed to treat atrial fibrillation by electrical stimulation,[122] which resembles cardiac pacemaker, and implanted pectorally. The defection and stimulating leads are placed transvenously into the heart. The device detects the onset of atrial fibrillation, and after careful diagnosis of the appropriate electro-physiological signals, applies electrical pulses to the heart. Units are currently in clinical evaluation[123]. Typically, energy levels of about three joules or less are necessary to achieve reversal of the condition. This energy is adequately provided by implantable batteries capable of delivering milliampere - level pulses. Solid cathode, liquid-electrolyte cells such as the lithium/vanadium oxide systems are employed in these devices.

(F) Left ventricular assist devices (LVAD) / total artificial heart (TAH)

For more than 10 years the development of LVAD & TAH has been under way[124]. Nickel / Cd batteries are employed. Current progress in lithium-ion secondary battery technology offers the promise of lighter; smaller battery packs in future versions of this type of device.

(G) External medical devices

Batteries allow patients to be equipped with portable monitoring or therapeutic devices while remaining ambulatory. They allow surgeons to use electrical tools and visualization devices without the encumbrance of power cords attached to house power. They make it possible for the wheel chair users to travel about without providing manual propulsion of their devices. On interruptible power sources prevent the loss of line power from causing severe problems in hospitals. The specific examples of the many types of external devices are given elsewhere[125].

Batteries indeed contribute in an important way to the maintenance of health and saving of lives. We can look forward with confidence to more exciting applications of battery-powered devices as scientists, engineers and physicians continue to make progress.

3.4 Fuel Cells

From today's perspective, the present status of our industrialized world requires new approaches to solve energy and environmental problems. Fuel cells are becoming widely accepted as a preferred means of generating electricity for distributed electrical power generation because of their high fuel conversion efficiency, environmental compatibility and reliable and quiet operation. Fuel cells differ from conventional internal combustion engines in that they do not suffer from Carnot's limitation. It differs from the secondary battery in that they are not chargeable in the conventional manner. It differs from primary batteries in that the reductant (fuel) and the oxidant (typically air or oxygen) are continuously supplied and not prepacked. The challenges this approach is supposed to meet could dominate energy conversion systems introduced in the energy market in the foreseeable future.

Possible *advantages* of such a scenario are:

- Providing power for both stationary and mobile applications.
- Preserving material and energy resources.
- Minimizing environmental problems on a local basis (*i.e.,* emission, noise and summer smog).

- Reducing emissions (greenhouse effect) on a global basis and considering new fuel concepts.

On the other hand, the *economic and technological challenges* include:

- Competing with established low-cost technologies showing considerable development promise (efficiency improvement, reduction of pollutant emissions).
- Solving specific problems associated with new technology
- Providing acceptance of the new technology and
- Discussing the application prospects of new fuels.

Steady progress has been made in various aspects such as catalysis, electrolytes, electrode structure design, theoretical understanding of gas diffusion and fuel cell engineering. Possible configurations of fuel cells and their relative merits are given in **Table 6**[126]. The schematic representations of various types of fuel cells such as alkaline fuel cell (AFC), polymer electrolyte membrane fuel cells (PEMFC), direct methanol fuel cell (DMFC), molten carbonate fuel cell (MCFC) and solid oxide fuel cells (SOFC) are given in **Fig. 11**, along with their respective reaction at the electrodes. Excellent reviews and books are available on various aspects of different types of fuel cells[127-141].

Fuel Cells for Electric Vehicles

New drive systems with fuel cells and the energy carriers required could play a major part in improving the overall environment.

- Within the past 2 years 18 prototype fuel cell vehicles have been produced[142].
- Most of the major OEM's are gearing up for a year 2004 launch of fuel cell cars.
- Ford's P2000 and Daimler Chrysler's NECAR 5 are currently undergoing real world test in California partnership driving for the future.
- Jürgen E. Schrempp of Daimler Chrysler, at the launch of the NECAR 5 was quoted saying, "Today we declare the race to demonstrate the technical viability of fuel cell vehicles over. Now, we begin the race to make them affordable"[143].

All these points can be seen as evidence that fuel cell cars are on their way soon. The technical systems under discussion will have to be evaluated on the basis of three reference criteria namely: performance, lifecycle and cost. In particular, electrically powered fuel cell drive systems will have to compete with

- Combustion engines (on the basis of clean primary energy carriers),
- Hybrid drive systems (with higher drive weight and higher cost and
- Electric drive systems with batteries (with higher cost, shorter range and higher drive weight).

One question that still seems to be unanswered though is whether the customer will be refueling their vehicle directly with hydrogen or via the hydrogen-rich carrier, methanol. This is an important issue not just from a refueling infrastructure perspective but also from the public perception and from the gearing up of production, retraining of staff and mechanics, developing guidelines and dealing with safety issues that will need to put in place for the new fuel.

As compared with conventional cars, fuel cell cars would be equipped with novel drive units, that is, the fuel-cell unit (PEFC) and, in addition, fuel processing or gas production unit in the case of methanol or hydrocarbons (clean gasoline or clean diesel), when used instead of hydrogen. These new fuel-cell systems for road traffic are confronted with the following key requirements:

- Low manufacturing costs (< 70 DM/k W_{el}),
- Light and compact construction (< 6 kg/k W_{el}, < 61/k W_{el}),
- Efficient energy management,
- Efficient water management,
- Efficient gas processing,
- Quick start-up and systems dynamics,
- Compliance with environmental standards,

- Adequate life cycle (>10 years),
- Mass production,
- Driving comfort and
- Safety considerations.

The efficiency rates achieved in various units of gas producing systems, including gas after treatment and fuel-cell systems with net power generation for the electrically powered drive systems, are interrelated process parameters which determine the energy management in the New European Driving Cycle (NEDC) in terms of both the drive system and the overall energy requirements at the wheel basis.

In fuel cell systems, that is PEFC systems that are ready for operation at ambient temperature with optimum operational temperatures between 60 and 80°C are integrated in electrically powered drive systems, the overall energy management depends on various performance parameters that determine not only the energy and emission balances but also the material balances. Major variable performance parameters showing particular impact on the power yield in the fuel-cell system are:

- Temperature
- Pressure at the anode and cathode unit
- Excess air in the cathode unit
- Fuel - gas processing in anode unit
- Fuel - gas rarefaction or pollution (e.g. CO)
- Design of membrane and electrode
- Quality and quantity of electrode / catalyst, and
- Energy and water management

All these parameters influence the current/potential characteristics of the cells, thus defining the energy efficiency rate of power generation as a function of the drive load. At the same time, they determine the overall energy management for fuel gas supply, net electricity generation of the fuel-cell system, current transformer and electrically powered drive with electric motor and, it appropriate, transmission mechanism.

The various fuels that can be employed as the reductant in fuel cells are listed in **Table 7.** It is seen from the table that hydrogen is the most promising fuel because of its maximum energy density and the maximum voltage that can be derived which is close to the theoretical value. However, the use of hydrogen is always associated with the complexity in storing and handling, which drives one to reflect on an alternative fuel. Next to hydrogen, methanol is the favored fuel from the aspects of cost, efficiency, availability, existence in liquid state, stability, oxidizing ability and electrical yield per gram of fuel[144].

The direct methanol fuel cell (DMFC), based on a PEFC, uses methanol directly for electric power generation and promises technical advantages for power trains. A direct methanol fuel-cell system offers higher system efficiencies because there is no energy consumption for fuel processing. As a consequence, a significantly smaller size and lower costs at comparable power densities may be achievable. In addition, there are two concepts for using methanol directly. The fuel can be delivered to the fuel cell in a gaseous or liquid form. The actual power densities of a DMFC are clearly lower than those of a conventional hydrogen-fed polymer electrolyte fuel cell. The main problem is that the electrochemical reaction of methanol is kinetically hindered. In addition, methanol permeates through the electrolyte and oxidizes at the cathode. This results in a mixed potential at the cathode. Furthermore, part of the fuel cannot be used for power generation and the efficiency of the system decreases.

Methanol crossover is controlled by cell temperature, fuel molarity and operating current. Numerous investigations have addressed the problem of methanol permeation to find ways to reduce it[145].

In summary, fuel-cell cars operating on hydrogen prove to be zero-emission vehicles, fuel-cell cars operating on methanol offer emission levels considerably lower than the SULEV standard required for CO, NOx and NMVOC emissions in the American driving cycle and the EURO4 standard in the European driving cycle. For fuel-cell cars operating on hydrocarbons, this is only partially the case. In general, fuel-cell developments for mobile applications are focusing on the following trends and options:

- Choosing the "right" fuel
- Proving the feasibility of the new technology, especially in long-time operation
- Achieving the cost reductions necessary from today's point of view
- Contributing to minimizing energy demand and emissions, and
- Implementing the steps necessary to gain access to the market.

4. ELECTROCHEMICAL SENSORS

Chemical sensors are used in a variety of applications such as chemical processes, analysis setups, food industry, environmental control (water, air, industrial wastes, combustion monitoring etc.), and biomedical applications (analysis and monitoring) as well as in integrated home systems. Electrochemical sensors are attractive due to their detection ability, that is, chemical quantities measured are directly transduced in electrical signals. As for electronic components, two types can be distinguished: active sensors, which give a voltage (potentiometric sensors), and passive sensors, for which an electrical source is necessary to apply a signal followed by the analysis of the response (amperometric, coulometric and conductometric sensors).

Basic electrochemical concepts were established in the 19th century by volta (classification of redox couples), Faraday (relation between electricity and quantity of matter), Kohlrausch (conductivity measurements), and Nernst (thermodynamic approach), but the first sensors were developed at the end of the century. The pH electrode using a glass membrane was discovered by Cremer in 1906[146] and then on, spate of investigations have been carried out in this area.[147-159] The key finding were: After a first approach made by Nikolskii in 1937,[147] a theoretical model was established by Eisenman[148] to explain interfering phenomena in sensory using a glass membrane. pH electrode were employed for pCO_2 measurement by Severinghaus and Bradley in 1957[149]. After the ion-selective electrode (ISE) for Cl^- ion, introduced in 1937,[150] other ISE's based on silver salt or on a LaF_3 monocrystalline membrane were developed in 1960s[151]. Ceramics were first used for O^{2-} analysis in molten salts in 1960[152].

Kiukkola and Wagner[153] employed solid oxide cells for thermodynamic measurements. The first oxygen gauges were tested in 1961[154a,b]. Similar sensors for halogens,[155a,b]sulfur oxides[156] and hydrogen[157] were developed. Amperometric and coulometric oxygen sensors are more recent[158a,b]. The first conductometric sensors using a TiO_x-based material were developed in 1970s[159].

Nowadays, ionic materials, amorphous,[160] or crystalline materials are used to improve the selectivity[161]. New systems coupling amperometric and potentiometric measurements have been proposed. Excellent reviews are available in this field[162a-m] and the goal of this presentation is to explain using electrochemical concepts, the working principle of electrochemical sensors and to show their limits of utilization.

4.1 Potentiometric Sensors

Principles of potentiometric sensors using solid electrolytes are extensively dealt with in literature[162i,163a-h]. Potentiometric sensors are based on the existence of equilibrium at the interface between a solid ionic conductor (SIC) and the analyzed medium, by exchange of electrochemical species.

- *Ionic junction of the first kind*:

  In this case, only a single electrochemical species (X^{2+}, mobile ion) is exchanged between the SIC and the analyzed solution (sol). Typical examples are: LaF_3/F^-, stabilized zirconia/O^{2-}, AgCl/Ag^+ or Na^+-based glass/Na^+ interfaces in ISE.

- *Ionic junction of the second kind:*

  In this case, the mobile ion of the SIC reacts with the analyzed ion to give a complex or an insoluble chemical product at the interface.

$${}_yX^{z+}{}_{SIC} \; + \; {}_zB^{y+}{}_{sol} \quad \Leftrightarrow \quad X_yB_z \qquad (31)$$

The thermodynamic relation is,

$$Y\mu^\circ{}_xZ^+{}_{(SIC)} \; + \; yRT \text{ In a } (X^{2+})_{SIC} + YzF\phi_{SIC} + z\mu^\circ{}_B{}^{y-}{}_{(Sol)}$$

$$= \; RT \text{ In a } (B^{y-})_{Sol} - YZF\phi_{Sol} \; = \; \mu X_yB_z \qquad (32)$$

If XyBz forms a separate phase, its chemical potential is equal to the standard potential μ°. The Galvanic potential is given by

$$\phi_{SIC} - \phi_{Sol} = \frac{1}{yzF}\left(\mu^\circ XuBz - y\mu^\circ{}_xZ+(SIC) - Z\mu^\circ{}_{By-(Sol)}\right)$$

$$- \; \frac{RT}{zF} \text{ In a } (X^{2+})_{SIC} - \frac{RT}{YF} \text{ In a } (B^{y-})_{Sol} \qquad (33)$$

As in (31), if the concentration of X^{2+} in SIC is high, the voltage is proportional to the logarithm of the activity of the analyzed ion. Of course, the variation is a function of the numerical value of y. Typical examples are AgCl membranes and Ag_2S - Cl mixtures to determine the activity of Cl^- ions. If AgCl is a separate phase equation (33) can be applied and the Nernst equation is obeyed.

Other factors such as electrode reactions, ionic exchange at the interface and interfering phenomena are dealt in detail elsewhere[164]. The characteristics of common ISEs and new sensors in this field are summarized in **Table 8.**

Limit of Detection: Interferences can restrict the measurement of ion concentrations, if the interfering ions are highly concentrated or if their selectivity co-efficient is high. The solubility of the membrane in solution is another limiting factor.

The various gas potentiometric sensors are summarized in **Table 9.** Severinghaus and Bradley employed ISE to measure an active gas pressure. The gas is supposed to be in equilibrium with an ion (typically proton) in an intermediate solution (carbonate solution for CO_2 measurement), which is in contact with the external medium, through a material permeable to the gas (TEFLON®). A pH electrode can be used for CO_2, NH_3, SO_3 and NO_2, S^{2-}-ISE for H_2S, Ag^+-ISE for HCN, F^--ISE for HF and Cl^--ISE for Cl_2[170].

4.2 Amperometric Sensors

Amperometric sensors are based on electrochemical reactions, governed by the difussion of the electro active species through a barrier[171]. The barrier usually consists of a hole or a porous neutral layer.

Up to now, only gas sensors are based on amperometric principles, essentially oxygen sensors. The SICs used for oxygen sensors are generally based on stabilized zirconium (e.g. YSZ), as for potentiometric sensors[172]. The conductivity must be as high as possible to avoid an excessive ohmic drop. Another problem is that the diffusion is slow at low temperatures[173]. A working temperature of about 400°C is often employed. An example of an amperometric oxygen sensor with an air reference is shown in **Fig.12**. Liaw and Weppner[175] have proposed tetragonal zirconia for measurements down to 250°C. Bi_2O_3-Eu_2O_3 solid solutions are good candidates for low-temperature sensors[176]. Amperometric oxygen sensors based on $PbSnF_4$ already operate at room temperature[177].

Similar SICs can be used to analyze species such as CO_2 or H_2O by electrochemical reduction. The various electrode reactions are:

$$O_2 + 4e^- \rightarrow 2O^{2-} \qquad (34)$$

$$CO_2 + 2e^- \rightarrow CO + O^{2-} \qquad (35)$$

$$H_2O + 2e^- \rightarrow H_2 + O^{2-} \qquad (36)$$

To apply Faraday's law, the voltage at which the above reactions occur must be compatible with the electrolytic domain of the SIC. When this condition is not satisfied, an electronic conductivity, either n or p type will appear. Generally, with an electronic transport number of a few percent, the Faradic efficiency is close to one and the error is less disastrous than for potentiometric devices.

A protonic conductor was employed for a H_2 amperometric sensor by Miura *et al*[178]. Chlorine sensor proposed by Liu and Weppner[179] is based on β"-alumina as SIC with an AgCl layer. The electrode reaction is given by

$$Ag^+ + e^- + \tfrac{1}{2} Cl_2 \rightarrow AgCl \qquad (37)$$

The lifetime of this sensor could be limited by the formation of a covering AgCl layer at the electrode. A reducing gas can be analyzed indirectly by first oxidizing it, for instance, with an excess of oxygen produced by an oxygen pump. The O_2 excess is then measured by an amperometric oxygen sensor[180].

4.3 Coulometric Sensors

Coulometric sensors are similar to the amperometric devices. The gas species is dosed by the Faradic effect, but, in this case, the diffusion flux between the chamber and the analyzed atmosphere is negligible during the measurement. The electro active gas is supposed to be an ideal gas and so its partial pressure is equal to

$$Pin = \int_{t}^{t+\Delta t} \frac{R\,T\,I\,(t)\,dt}{ZFV^{o}} \qquad (38)$$

Where, z is the charge number to reduce (or to oxidize) one molecule of the electro active gas, V^o the volume of our chamber, and I (t) the dc current during Δt (time delay to obtain Pin → 0 or reverse). If the current is kept constant during Δt, the above equation simplifies to

$$Pin = \frac{R\,T\,I\,\Delta\,t}{zFV^{o}} \qquad (39)$$

4.4 Pump-Guage Devices

Pump-guage devices are derived from amperometric and coulometric devices. They consist of a pumping part, to which a variable current can be applied, and a gauge part, which is used for measuring the resulting voltage. Only oxygen sensors are based on this principle.

(a) Direct current mode

In the model proposed by the Hetrick *et al.*[181] a pumping gauge system works in steady-state condition. The current is related to the pressure difference between the analyzed gas and the internal chamber.

$$I = 4FA\ (Pout - Pin) \qquad (40)$$

Where, A is a coefficient; the internal pressure Pin can be calculated from the gauge voltage E by using the Nernst equation,

$$Pin = Pout\ \exp\ (4\ FE\ /\ R\ T) \qquad (41)$$

The above two equations, lead to

$$I = 4FA\ Pout\ \ (1 - \exp(\ 4\ FE\ /\ R\ T)\ ) \qquad (42)$$

The current can be modified by an external source and a plot of I as a function of

$$1 - \exp\ (4\ FE\ /\ RT)$$

allows Pout to be measured.

(b) Alternating current mode

Maskell *et al.*[182a,b] have proposed an AC mode for amperometric devices. A sinusoidal current $I = I^o \sin \omega t$ is applied to the pumping part and the voltage is measured on the potentiometric part. A low frequency (lower than 10 Hz) is required to achieve equilibrium in the chamber. The corresponding voltage may be given as,[183]

$$ES = \ - RT/\ nF\ In\ \ [In - (RTI^o\ /\ 4F\ V^o\ \omega\ P_{out})\ \cos^2\Psi \qquad (43)$$

Where P_{out} is the oxygen partial pressure in the analyzed gas and Ψ is a parameter depending on the geometric factor of the pore, the diffusion coefficient and V^o, the volume of the chamber. The above equation can be simplified if $R\ T\ I^o/4FV\ \omega\ P_{out}$ is small. The amplitude of ac voltage is then proportional to P_{out}^{-1}.

Benammar and Masskell[184] have proposed a more sophisticated sensor to limit the parasitic phenomena. Here, an ac current $I = I^o \sin \omega t$ is applied to the pumping part, with a low frequency (<10 Hz) to obtain equilibrium in the chamber.

The potentiometric voltage is equal to,

$$E = RT/4F \, [\ln (P_{out} / P_{in}) - \ln (1 + RTI^o / 4FV^o\omega \, P_{in}) \cos\omega t \qquad (44)$$

Where, V^o is the internal volume, P_{in} and P_{out} are the internal and external oxygen partial pressures respectively. By employing an electronic system to maintain the mean value of E equal to zero and to transform the emf into a dc voltage Edc, an approximate equation is obtained.

$$E_{dc} = \quad [R^2T^2I^o / 8 \, \pi \, F^2 \, V^o \, \omega] \;\; [1/ P_{out}] \qquad (45)$$

The measured dc voltage is then proportional to P_{out}^{-1}.

4.4 Conductometric Sensors

In this section, conductometric sensors in which the ionic conductivity of the material plays a role are considered. For example: TiO_x, exhibits a variable stoichiometry as a function of the oxygen pressure. Semiconductor materials like SnO_2 are used in Figaro sensors for analyzing the reducing species, work on principles of heterogeneous catalysis[185a,b]. The working principle of TiOx, and various electrochemical parameters employed for analysis is given elsewhere[164].

<u>Achievements:</u>

At the present time materials such TiO_x doped with Fe, Mn, Cr, or Ba oxides, or alkaline earth ferrates are used essentially for oxygen sensors[185]. In these devices, the area/volume ratio plays an important role. The grain size and the grain boundaries are two parameters, which should remain constant as a function of time. The higher the temperature, the faster morphological changes of the ceramics will occur. The working temperature is generally higher than 600°C (at low temperature it becomes a semiconductor sensor). It was also proposed to use two sensors in a differential mode at the same temperature, one in contact with the analyzed atmosphere, the other insulated from it.

Thin-layer technologies for fabrication of conductometric sensors are being developed[186a,b]. Such devices have two advantages: the response time is improved and mass production is less expensive.

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 the flue gases and other gas streams containing several toxic components.

5. PHOTO ELECTROCHEMICAL METHODS

This approach is especially appealing since an important energy input contribution from light might be expected, thus diminishing electricity consumption. Recent developments in photo electrochemistry 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. This photo catalytic methods have been reviewed sometime ago[187].

It is known that, metals are unsuitable for light energy conversion because their excited electronic states have extremely short lifetimes and energy is rapidly dissipated as heat. Only semi-conducting materials can store the energy obtained from incident light and allow the stored energy to be converted to other forms.

Table 10 provides an outline of some semiconductor conversion devices.

The photo-electrolysis of water to hydrogen and oxygen using semi-conductors as photo electrodes has been studied extensively during last few decades - as a method for converting solar energy into hydrogen, which can be used as a storable fuel. Photo electrochemical reduction of CO_2 on semiconductor electrodes, which is regarded as a kind of artificial photosynthesis has recently received attention from the viewpoint of the global environmental problem.

Lewis[188] recently covered the frontiers of research in photoelectrochemical solar energy conversion. A historical perspective was presented to frame the recent scientific and technological progress that has been made in this field. The exploitation of a deliberately nanostructured interface which could provide useful enhancements to the kinetics of interfacial charge transfer events and that allow the use of catalysts without suffering concomitant efficiency losses was discussed. A model system was provided for the elucidation of the interconnections between the chemical modification, electrical properties, and electrochemical behavior of photoelectrode surfaces. Tryk et al[189] discussed the recent topics in photoelectrochemistry in terms of its achievements and future prospects. The properties of nanocrystalline electrodes are reviewed with particular emphasis on electron transport in dye-sensitized nanocrystalline photovoltaic cells by Peter et al[190].

The considerable amount of research that has been carried out in the two closely related fields of semiconductor photoelectrochemistry and photocatalysis during the past three decades continues to provide fundamental insights and practical applications. However, we are not addressing the underlying theory or physics of photoelectrochemistry, for several excellent reviews on these topics are already available in literature[197-203].

Beginning with work on photoelectrochemical water electrolysis or `splitting', in the late 1960s[204,205], there has been much work carried out primarily aimed at solar energy conversion as an alternative approach to that of the solid state junction photovoltaic cell. The latter has enjoyed continuous development, with the efficiency now reaching over ~24% in laboratory cells[206], although practical wafer-based cells give efficiencies in the range 12–16% [207]. One of the driving forces behind the photoelectrochemical approach is the perceived ability to form rectifying junctions in simpler ways compared to the relatively sophisticated techniques required in solid state processing. Another is that barrier height can in principle be varied easily by choosing appropriate match-ups between semiconductors and redox couples. These ideas and interesting results continue to drive research in this area. Efforts have been made to improve the performance of conventional semiconductor electrodes for solar energy conversion, both for regenerative cells (i.e. photogeneration of electricity) and electrolytic cells (i.e. photogeneration of useful products such as hydrogen).

Nanostructured surfaces : Nanometer-scale control of the solid semiconductor electrode is sensitively related to the photoelectrode behavior and hence to the energy conversion efficiency. For example, Kawakami et al. have recently prepared porous n-Si photoelectrodes, by photoetching in HF, with macroporous layers at the surface, consisting of micrometer-sized pores and Si pillars[208]. The walls and tops of the Si pillars are further covered with 0.2–0.5 μm thick nanoporous layers. The solar cell characteristics for the porous n-Si electrodes with Pt coating in aqueous HBr/Br_2 are improved by thinning the nanoporous layer. A maximum solar energy conversion efficiency of 14% (V_{oc}, 0.573 V; j_{sc}, 34.7 mA / cm^2; fill factor, 0.701) was obtained, which is one of the top records for n-Si photoelectrochemical solar cells, equaling that of Gibbons et al., working in nonaqueous electrolyte[209].

Sugiura et al.[210] fabricated TiO_2 nanostructure by photoelectrochemical etching with nanohoneycomb pattern made up of rectangular cells, of few hundred nanometers wide and several micrometers deep. These cells are regularly ordered, depending upon the crystallographic orientation. The large specific surface area and high crystallinity of the etched TiO_2 make it an attractive material for photoelectrochemical applications, including photocatalysts and dye-sensitized solar cells.

Surface modification and thin film electrodes:

Nakato et al. modulated the band energies of an n-type Si chip by the formation of silicon-halogen termination on one side of the chip[211]. This surface asymmetry produces an efficient solar-to-chemical conversion owing to the presence of band bending within the n-Si chip in a photostationary state, leading to efficient electron-hole separation, in contrast to the case in which both sides of the semiconductor have the same type of termination. Torimoto et al. modified size-quantized CdS nanoparticles with 2-aminoethanethiol and immobilized them on an electrode with the use of glutaraldehyde as a cross linking agent [212]. Quantum size effects of the immobilized nanoparticles on the metal electrode were retained in the photoelectrochemical behavior of the electrode. Shiga et al. prepared a TiO_2 film electrode by coating a TiO_2 colloidal solution on a F-doped SnO_2-glass substrate[213]. After the thermal treatment, this film electrode exhibited photoelectrochemical current-potential curves similar to those for single crystal n-TiO_2 electrodes. It was suggested that a Bardeen-type junction is plausible for the electric contact at the TiO_2 particle/substrate interface.

Multiple-band-gap photoelectrochemical cells:

The aim of using multiple-band-gap cells is to capture a greater fraction of the solar spectrum, which has motivated work in the area of photovoltaic solar cells. Only recently, this idea has been applied in the photoelectrochemical area. Licht et al., have developed a series of such cells [214-217]. They have provided systematization for multiple-band-gap photoelectrochemical cells based on whether the solid-state p-n junctions are arranged in a bipolar (e.g. pnpn) or inverted (e.g. pnnp) fashion[216]. These workers have achieved a solar-to-electrical efficiency of 19.2% using an AlGaAs (wide band-gap) — Si (narrow band-gap) bilayer[214]. Most of their work thus far has involved ohmic rather than Schottky-type semiconductor-electrolyte junctions, which unfortunately negates one of the inherent advantages of the photoelectrochemical approach. In the most recent example of this approach, an overall efficiency of 18% was achieved in the charging of a Ni-metal hydride battery with the application as constant voltage power source[217].

Khaselev and Turner at the National Renewable Energy Laboratory (NREL) in U.S. have adapted a multiple-band-gap approach to photoelectrochemically split water[218]. The solid-state tandem cell consists of a GaAs bottom cell connected to a $GaInP_2$ top cell through a tunnel diode interconnect. The $GaInP_2$ band-gap is 1.83 eV. The GaAs band-gap is 1.42 eV. The theoretical maximum efficiency for a dual band-gap is ca. 41% but the maximum efficiency for this combination of band-gaps is 34%. The difference between this type of cell and the fully photovoltaic tandem cell is that the top junction is p/Schottky rather than p/n. H_2 is produced at the semiconductor electrode, which is thus cathodically protected. H_2 evolution starts 0.40 V positive of open circuit. This system yields 12.4% conversion efficiency for an incident light intensity of 1190 mW cm^{-2}. Of course, there is an advantage to using concentrated sunlight, but theoretically this effect is relatively small [219]. The H_2 production photocurrent of 120 mA/ cm^2 is multiplied by 1.23 V, which is the ideal fuel cell limit at 298 K (lower heating value of H_2). The authors state that one key aspect appears to be that the bottom cell current is limiting, which is different from the case for the solid-state p/n/p/n device, in which current matching is desirable.

Photoelectrochemical reduction of CO_2:

The fixation of carbon dioxide is one of the most important area[220,221]. The reduction of CO_2 is an uphill process. It is desirable to carry out this reaction with a very low consumption of energy and/or with the use of a renewable energy source[222]. The photoelectrochemical reduction of CO_2 is hence an attractive pathway.

In the course of the development of photoelectrochemistry, a variety of p-type semiconductor electrodes such as p-CdTe, p-GaP[223], p-GaAs, p-InP, p-Si, and p-SiC have been examined. Semiconductor electrodes whose surfaces are modified with metal particles are often known to exhibit improved photoelectrochemical behavior. p-Si electrodes modified with metal particles (Cu, Ag, or Au) were used by Hinogami et al. to reduce CO_2 in aqueous solution, resulting in the formation of CH_4, C_2H_2, CO, etc.[224a]. The reduction process was shifted in potential approximately 0.5 V positive compared to that obtained with the corresponding metal electrodes.

A high-pressure CO_2-methanol system has been found to offer a number of advantages for the photoelectrochemical reduction of CO_2 by Hirota et al.[224b]. This reaction was examined in a 40-atm CO_2-methanol medium using the p-type semiconductor electrodes p-InP, p-GaAs, and p-Si. With p-InP photocathodes, current densities up to 200 mA/ cm^2 were achieved, with current efficiencies of over 90% for CO production, while hydrogen gas evolution was suppressed to low levels. At high current densities and CO_2 pressures, the CO_2 reduction current was limited principally by light intensity. Of the various factors that were found to influence the product distribution, including the concentrations of added water and strong acid, the CO_2 pressure was the most critical factor. It was proposed that the adsorbed $(CO_2)_2^{-\cdot}$ radical anion complex reaches high coverages at high CO_2 pressures and is responsible for both the high current efficiencies observed for CO production and the low values observed for H_2 evolution. In addition, this adsorbed complex is responsible for stabilizing all the three semiconductor electrode materials at high CO_2 pressures, even at current densities as high as100 mA/ cm^2. Aulice Scibioh and Viswanathan[225] have recently reviewed the various aspects of photo/ photoelectrochemical reduction of CO_2.

Dispersed semiconductor particle suspensions are attractive, as each particle is made up essentially of a short-circuited photo anode and photo cathode. They find their utility in water splitting, as well as other reactions, including CO_2 reduction.

Water splitting:

It is well known that the distribution of energies in the solar spectrum does not allow most semiconductor materials to decompose water completely into hydrogen and oxygen. For materials whose valence band energy is not sufficiently positive, a sacrificial donor is used as a source of electrons for hydrogen evolution, while for those whose conduction band energy is not sufficiently negative, a sacrificial acceptor is used as a sink for electrons in order to facilitate oxygen evolution. The complete water splitting reaction, i.e. both H_2 and O_2 generation, by semiconductor particles without the benefit of sacrificial agents has been an elusive goal.

Since the early 1980s, ion-exchangeable layered oxide compounds such as $K_4Nb_6O_{17}$ loaded with Ni have been reported to be capable of generating both H_2 and O_2 under UV illumination. Recently, water splitting under visible light illumination was achieved by Takata et al. with hydrated layered perovskites such as $RbPb_2Nb_3O_{10}$ (>420 nm) and $A_2La_2Ti_3O_{10}$, where A is an interlayer cation (K, Rb, Cs), modified with Ni [226]. The photocatalytic activities for water splitting for a series of 25 tantalate compounds in powder form were thoroughly examined and compared by Kato and Kudo [227]. Among these candidates, $NaTaO_3$ loaded with NiO showed the highest quantum efficiency (28%) for water splitting for UV light with wavelengths of 270 nm or less [228]. Doping with excess Na (donor doping) was found to be highly beneficial. Materials with rectangular[229] or pentagonal prism[230] tunnel structures are capable of carrying out complete water splitting with UV illumination by Ogura et al. and Kohno et al., respectively. Sayama et al. found that the addition of sodium carbonate or other sodium salts to the aqueous suspension remarkably improved the efficiency of complete water splitting in the case of TiO_2[231], Ta_2O_5 and ZrO_2

loaded with Pt, NiOx or RuO_2 [232]. For Pt-TiO_2, it was supposed that the loaded Pt is covered with titanium hydroxide, resulting in the suppression of the back reaction.

It is known that doping can improve the photocatalytic activity for water splitting. For instance, doped perovskites such as niobates and titanates layered in the (110) direction were employed by Kim et al. [233]. These were highly donor-doped and loaded with Ni. An overall quantum yield of 23% was reported for UV light of wavelengths of 300 nm or below. Where as Ishihara et al[234] employed different types of acceptor-doped $KaTO_3$ materials, the highest activities were found for Zr^{4+} and Hf^{4+} doping.

Cu_2O is a promising candidate for the complete photocatalytic water splitting reaction under visible light illumination, particularly in view of the long-term stability exhibited over a period of 1900 h by Hara et al.[235]. Surprisingly, this material displayed a so-called mechanocatalytic water splitting reaction, i.e. without illumination, but the reaction was enhanced under illumination, as found by Ikeda et al.[236]. One possible explanation of this phenomenon might involve a piezoelectric effect.

There are a number of efforts to develop novel types of photocatalysts for various applications, including water splitting as well as others. For example, the improvement of the visible light absorption characteristics could have far-reaching consequences. Ion implantation of transition metal ions in TiO_2 by Anpo et al. resulted in a shift of the action spectra towards longer wavelengths [237]. In the case of Cr-implanted TiO_2, the solar-based efficiency was improved by 20%. Also by the same group, immobilization of semiconductor particles in zeolite cavities was found to improve the photocatalytic activity. For example, TiO_2 anchored in zeolite cavities by ion-exchange method exhibited high photocatalytic reactivity for the direct decomposition of NO to N_2, O_2, and N_2O[238].

A variety of sensitizing dyes have been examined to improve the characteristics of both semiconductor photoelectrodes and dispersed semiconductor particle systems. Quantum efficiency and long-term stability are the most essential points for practical use. The most successful dyes so far reported are the Ru-bipy complexes, which have been intensively studied by Grätzel et al.,[191] A typical one is *cis*-X_2bis (2,2'-bipyridyl-4,4'-dicarboxylato) Ru(II), where $X=Cl^-$, Br^-, I^-, CN^-, and SCN^-. In the case of $X=SCN^-$ and the dye-modified TiO_2 film electrode, the solar conversion efficiency exceeds 10%, and the quantum current efficiency can reach to practically unity[239]. Further improvements were reported by Nazeeruddin et al. for this type of dye in conjunction with a TiO_2 film electrode[240]. A black trithiocyanato-ruthenium (II) terpyridyl complex in which the terpyridyl ligand is substituted with three carboxyl groups in the 4,4',4"-positions achieved very efficient panchromatic sensitization of nanocrystalline TiO_2 solar cells over the whole visible range, extending into the near-IR region to ~920 nm. The efficiency of photocurrent generation was practically 100% over a wavelength range from 400–700 nm, with a photocurrent density of 20 mA / cm^2 was obtained.

The high efficiencies of dye sensitization are attributed to the high rate of transfer of electrons from the excited dye molecule to the conduction band of the semiconductor. The electron injection of Ru^{II} (2,2'-bipyridyl-4,4'-dicarboxylate)$_2$(NCS)$_2$ to a TiO_2 film electrode was found to be biphasic, with 50% occurring in <150 fs and 50% in 1.2–2 ps[241]. A particularly challenging problem is the development of all-solid-state versions of dye-sensitized photoelectrochemical cells. There are several advantages that such cells would have compared to those with liquid electrolytes, including ease of manufacturing and robustness. There has been recent progress reported in this area, with relatively high incident photon-to-current efficiencies[242,243]. However, the overall efficiency is still slightly less than 1% due to other types of losses.

Photo electrochemical cells for electricity production offer a sustainable way to for charging batteries in electric vehicles. With semiconductor electrodes using dye sensitized nanocrystalline TiO_2 films an efficiency of 12% has been reported[244]. 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.

At present, the prospects for widespread application of solar photoelectrochemical devices appear to be somewhat dim for several reasons, as already discussed. However, it is important for research efforts to continue in these areas, because the time may surely come when this technology will be needed. It should also be stated that there is an important role to be played by the more innovative approaches, for example, attempt to mimic natural photosynthesis[245]. The situation with the photocatalytic water splitting approach deserves to be monitored carefully. This area has not received as much attention worldwide as that of the photoelectrochemical cell.

6. CONCLUSION AND OUTLOOK

Electrochemical methods have reached a mature status, that they are able to sense very low concentrations of hazardous species and converting them to non-hazardous or even useful materials. This has become possible, because of the potential window that could be handled by increasing the possibilities with respect to electrodes as well as the media to disperse the depolarizer. Electrochemistry being amenable to the modern electronic resolution by the pulsed modes and hence increased the levels of sensibilities for analysis. In fact, electrochemical means are exactly identical with the natural processes taking place in living or non-living cells and membranes and hence, appear to offer the best way to succeed to keep our environment cleaner as well as suitable for living beings. The developments in electrochemistry in the last two or three decades very stimulating and hence can be expected to handle the environmental problems posed by the modern developments in process and manufacturing industries. In fact, this is one of the options available to mankind to combat environmental problems, at the same time converting the pollutants into useful products. It is possible that electrochemical methods will occupy prominent position, in future, in the compact for the environmental pollution and the analysis and control.

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LIST OF FIGURES AND TABLES

Table 1.

Population figures (in millions) for the period between 1989- 1998.

Country	1989	1990	1991	1992	1993	1994	1995	1996	1997	1998
North America	358.51	363.42	368.12	373.04	377.78	382.47	387.09	391.57	396.28	400.97
Central South America	347.99	354.53	360.91	367.34	373.53	379.81	385.94	392.22	398.23	404.56
Western Europe	452.92	456.55	458.98	461.39	464.16	466.33	468.39	470.37	471.99	473.66
Eastern Europe & former USSR	385.20	389.68	391.74	390.69	391.35	391.60	391.69	391.28	390.90	390.46
Middle East	126.37	130.05	134.93	137.86	141.50	145.19	148.26	151.92	155.38	159.23
Africa	601.46	617.43	634.70	653.70	673.40	690.10	707.63	725.87	746.05	764.28
Far east & Occeania	2,896.3	2,944.22	2,992.64	3,040.21	3,086.79	3,132.99	3,178.8	3,232.79	3,277.7	3,323.34
World	5,168.75	5,255.87	5,342.03	5,424.23	5,508.50	5,588.48	5,677.8	5,756.03	5,836.6	5,916.39

Table 2.

The world primary energy consumption for the period between 1989 and 1998 (Quadrillion (10^{15}) Btu)

Country	1989	1990	1991	1992	1993	1994	1995	1996	1997	1998
North America	100.43	100.02	99.95	101.56	103.90	106.31	108.12	111.74	112.07	112.57
Central South America	14.11	14.16	14.83	15.05	15.70	16.50	17.24	18.15	18.95	19.73
Western Europe	63.67	63.99	65.01	64.24	64.54	64.58	66.31	68.39	68.60	69.52
Eastern Europe & former USSR	74.88	74.11	69.45	65.03	60.53	54.58	52.87	52.58	50.34	48.96
Middle East	10.90	11.13	11.17	11.19	12.72	13.33	13.88	14.51	15.38	15.90
Africa	9.15	9.34	9.74	10.01	10.18	10.51	10.77	11.07	11.51	11.77
Far east & Occeania	71.68	74.09	77.35	80.57	85.63	91.44	96.53	99.80	101.19	99.27
World	344.83	346.83	347.51	348.46	353.21	357.25	365.72	376.25	378.04	377.72

Table 3.

Sources and types of major air – pollutants

Sources	Types – quantity (millions of tons per year)				
	CO	NO_X	SO_X	HC	SP
Transportation (motor vehicles)	75.0	11.5	1.0	13.0	1.5
Stationary fuel (Electric power & Heating)	0.7	10.0	25.0	2.0	6.0
Industrial process	14.5	0.5	5.0	2.5	10.0
Solid waste Disposal and Miscellaneous	4.4	0.5	0.4	12.9	1.4
Total	94.6	22.5	31.4	30.4	18.9

Table 4.

Effects of pollutants on human beings

Types	Effects
Primary pollutants	
CO	Heart disease, strokes, pneumonia, pulmonary tuberculosis, congesti Brain and lungs
SO_x	Acute respiratory infection (chronic pulmonary or cardiac disorders)
NO_x	Chronic respiratory infection
HC	Lung and stomach cancer
SP	Tissue destruction of the respiratory epithelium
Pb & PbO_x	Brain damage, cumulative poisoning (adsorbed in RBC & bone marr
Secondary pollutants	
PAN & NO_2	Attacks of acute asthma and allergic respiratory infections
O_3	Chest constriction, irritation of mucous membrane, head ache, cough and exhaustion
SO_4^{2-} and NO_3^-	Asthma, infant mortality and acute respiratory infections
Aldehydes, Olefens, Nitrosomines, PAH etc.	Respiratory tract carcinoma
Acrolein	Irritation to the eyes

Table 5.
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 terms	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	100
Li - ion	80-90	200-300	400-1200 (cells)

Table:6 Configuration of Fuel Cells

Fuel Cell System	Temperature Range	Efficiency (Cell)	Electrolyte	Advantages	Disadvanta
Alkaline Fuel Cell (AFC)	60-90° C	50-60%	35-50% KOH	1. Low temperature operation 2. Rapid O_2 reduction kinetics 3. Non-noble electrocatalysts	1. Do not reject C 2. Pure H_2 & O_2 a
Polymer Electrolyte Fuel Cell (PEFC)	50-80° C	50-60%	Polymer membrane (Nafion/Dow)	1. Electrolyte-good proton conductor 2. Minimum corrosion problem 3. Long life period 4. Able to withstand large pressure differentials	1. Water manage critical, limitat operating temp 2. Higher catalys than PAFC bot anode&cathod
Phosphoric Acid Fuel Cell (PAFC)	160-220°C	55%	Concentrated phosphoric acid	1. Operate at high acid temperature range 2. Water management is easy	1. Phosphoric aci ionic conducto temperature 2. CO poisoning catalyst
Molten Carbonate Fuel Cell (MCFC)	620-660° C	60-65%	Molten carbonate melts (Li_2CO_3/Na_2CO_3)	Noble metals are not required	High operating tem
Solid Oxide Fuel Cell (SOFC)	800-1000° C	55-65%	Yttrium-stabilized zirnondioxide (ZrO_2/Y_2O_3)	1. Noble metals are not required 2. Rapid O_2 reduction kinetics	High operating tem

Table 7. Chemical and Electrochemical Data on Various Fuels

Fuel	ΔG^0 (kcal/mol)	E^0_{theor} (V)	E^0_{max} (V)	Energy density (kWh/kg)
Hydrogen	-56.69	1.23	1.15	32.67
Methanol	-166.80	1.21	0.98	6.13
Ammonia	-80.80	1.17	0.62	5.52
Hydrazine	-143.90	1.56	1.28	5.22
Formaldehyde	-124.70	1.35	1.15	4.82
Carbon monoxide	-61.60	1.33	1.22	2.04
Formic Acid	-68-20	1.48	1.14	1.72
Methane	-195.50	1.06	0.58	-
Propane	-503.20	1.08	0.65	-

Table 8.
Summary of ion selective electrodes

Ion (x)	Membrane	Concentration range	Main interfering ions $K_{x,y} \geq 10^{-2}$	Ref.
Ag^+	Ag_2S	10^{-1}-10^{-7}	Cl^-, Br^-, SCN^-, CN^-, S^{2-}, Hg^{2+}	165a
Br	Ag_2S + AgBr AgBr	1-10^{-5}	I^-, SCN^-, CN^-	165a-c
Cd^{2+}	Ag_2S + CdS	10^{-1}-10^{-7}	S^{2-}, Pb^{2+}, Ag^+	165a,b
Cl^-	Ag_2S + AgCl	10^{-1}-5 x 10^{-5}	CN^-, I^-, Br^-, Ag^+, S^{2-}, SCN^-	165a,b
CN^-	Ag_2S + AgI	10^{-2}-10^{-6}	I-, S^{2-}, Ag^+	165a,c,d
Cu^{2+}	Ag_2S + CuS	10^{-1}-10^{-8}	Ag^+, Hg^{2+}, S^{2-}, Cl^-, Br^-, SCN^-, CN^-	165c,d
F^-	LaF_3	1-10^{-6}	OH^-	165a,b
H_30^+	Glass	1-10^{-14}		165a,d
Hg^{2+}	Ag_2S + AgI		Ag^+, Cl^-, Br^-, SCN^-, CN^-	165e
I^-	Ag_2S + AgI AgI	1-5 x 10^{-8}	Ag^+, S^{2-}, CN^-	165a-c
Na^+	Glass NASICON	1-5 x 10^{-7} 1-10^{-4}	H_3O^+, K^+, Li^+ H_3O^+	165a,f 165f
Pb^+	Ag_2S + PbS	1-10^{-7}	Ag^+, Hg^{2+}, Cu^{2+}, Cd^{2+}, Cl^-, Br^-, SCN^-, CN^-	165a-c
S^{2-}	Ag_2S	1-10^{-7}	Ag^+, Hg^{2+}	165a,b
SCN^-	Ag_2S + AgSCN	1-5 x 10^{-6}	I^-, OH^-, S^{2-}, Cl^-, Br^-, CN^-	165d,g

Table 9.

Examples of electrochemical gauges (gas potentiometric sensors)

Analyzed species	Electrolyte	Operating Temp. Range (K)	Concentration Range (ppm)	Ref.
O_2	ZrO_2-based ceramic $PbSnF_4$ LaF_3	750-1100 370-520 300-373	$0.1\text{-}10^6$ $10^3\text{-}10^6$ $10\text{-}10^6$	166,167a 168b,c 168d
Cl_2	$SrCl_2$-KCl $BaCl_2$-KCl	350-500 350-500	$0.1\text{-}10^6$ $0.1\text{-}10^6$	155b 167b
I_2	KAg_4I_5	313	$10^3\text{-}10^6$	155a
H_2	H.U.P β’- Al_2O_3 NASICON $BaCeO_3$-based ceramic	300 300 300 770-1100	$>10^4$ $>10^4$ $>10^4$ $10^3\text{-}10^6$	167c 168a 167d 167d,e
CO_2	Na_2CO_3 / NASICON $Li_2CO_3/LiTi_2(PO_4)$	570-1000 620-1000	>10 in dry air $80\text{-}10^4$	168e,f, g 168g,h
SO_2-SO_3	K_2SO_4 Ag_2SO_4+Li_2SO_4 Na_2SO_4/β’- Al_2O_3 Na_2SO_4/ZrO_2-based ceramic	500-1200	>10 in air	168i
NO_2	$NaNO_3$/β’,β’’- Al_2O_3	400	0.1×10^3in air	169a
(NO_x)	$NaNO_3$/NASICON			
AsH_3	Na^+β’- Al_2O_3	1000	$50\text{-}2 \times 10^3$	
As_4O_8			1-190	169b
H_2O	$SrCeO_3$-based ceramic Ag^+ - Glass	870-1270 300		169c 169d

Table 10.

Features of semiconductor conversion devices

Devices	Materials Used	Efficiency,%	Remarks
Solid state p-n junction	Si, GaAs, n-CdS/p-CdS	12-22	Single-crystal,high cost, well established
Schottky barrier M/SC or MO/SC	Au/n-GaAs	9-12	-
Photogalvanic cells	Pt/Fe^{2+};Fe^{3+} & Th^{+}/Th/ Pt	<0.2	All other PG systems have low efficiency
*PEC(liquid-junction) Cells	n-CdS/ $Fe(CN)^{3-/4-}$ pH=13/ Pt	5-6	Higher efficiencies (10%) for semi-conductor coated with sensitizer dye
Photoelectrolysis (H_2O	C/VCl_4, VCl_3/p-InP	10-14	Lab device working for several weeks
	n-TiO_2/NaOH/Pt	1	Bias voltage required
	n-$SrTiO_3$/NaOH/Pt	1	No bias voltage
	Pt/ HCl/ p-InP(Ru)	12	Low stability

* One of the many systems studied.

This table is taken from Ref. 94b.