Electrodes Based on Noble Metals

ESSENTIAL COMPONENTS FOR ELECTROCHEMICAL TECHNOLOGY

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Electrochemical technology is playing an increasingly important role in modern society and especially in the chemical industry, see Table I. Major reasons for the shift towards electrochemical technology include:

(a) the unique ability of electrolysis to bring about selective chemical change without the use of toxic reagents or hazardous conditions;

(b) the myriad possibilities for the recycling of metals, chemicals and process streams;

(c) the need for clean and efficient energy sources, especially for transport systems; and

(d) the many opportunities for designing small and portable sensors which use electrochemical detectors.

The key components of all electrochemical cells are the electrodes and, in some cases, the separators. There is little doubt that developments in both electrode materials and ion permeable membranes during the last quarter of a century have allowed the successful implementation of many novel concepts. In fact, in almost all cases where process economics require the optimisation of cell performance, electrodes made from noble metals or noble metal oxides are the components of choice. Although noble metals are expensive, their properties are such that the overall costs of the process are reduced through their use.

Common features which recur in the development of materials for electrodes, with many diverse applications are:

• the use of platinum group metals and their oxides as coatings on inert substrates

• the minimisation of the platinum metal loading

• the use of platinum group metal alloys or mixtures of oxides to enhance electrode stability, to improve product selectivity and/or to minimise overpotentials

• the fabrication of membrane/electrode combinations to reduce interelectrode gaps and hence energy inefficiencies.

In this review some of the roles of the platinum group metals, in particular platinum, iridium and ruthenium, in present and potential applications of electrochemical technology will be highlighted.

Dimensionally Stable Anodes

The late 1950s saw an event of great importance for electrochemical processing – the development of dimensionally stable anodes (2). These introduced a new approach to the manufacture of coated electrodes and increased expectations of the performance of electrodes. The first examples of dimensionally stable anodes consisted of ruthenium dioxide (RuO_2) coatings on titanium and these were prepared very simply by repeatedly spraying or painting a pretreated titanium surface with a solution of ruthenium trichloride, followed by thermal decomposition in air. These electrodes found rapid application in the chlor-alkali industry because of a unique combination of properties – a very low overpotential for chlorine evolution and a very long service life – both in stark contrast to graphite, the previous anode of choice, see Table II. Moreover, this coating technique could be used on titanium substrates which had been fabricated into almost any shape. Hence,

Table I
Typical Applications of Electrochemistry (1)

The Manufacture of Inorganic Chemicals
including $Cl_2/NaOH$, KOH, ClO_3^-, ClO_2^-, BrO_3^-, H_2, O_2, F_2, O_3, H_2O_2, MnO_2, Cu_2O, MnO_4^-, $Cr_2O_7^{2-}$, $S_2O_8^{2-}$, N_2O_5, NH_2OH, SnO_3^{2-}, Ce^{4+}, AsH_3

The Synthesis of Organic Compounds
typically monomers, fine chemicals, pharmaceutical and agrochemical intermediates

The Extraction of Metals
including Al, Na, K, Mg, Li, Cu, Zn, Ga

The Recycling of Chemicals and Process Streams
metal recovery and refining, recycling of redox reagents, salt splitting, electrodialysis for stream concentration and purification

Water and Effluent Treatment
salt removal, treatment with ClO^-, H_2O_2 and O_3, the removal of metal ions to < 1 ppm, and the removal of organics, nitrate and radioactive ions

The Total Destruction of Toxic Materials
such as the destruction of contaminated waste from the nuclear industry, and the destruction of polychlorinated biphenyls

Metal Finishing
in processes such as electroplating, anodising, electropainting and surface modification

The Manufacture of Electronic Components
including printed circuit boards, deposition of metal contacts and semiconductor layers

Metals Fabrication
in processes such as electrochemical machining, electroforming and electrogrinding

Corrosion Control
by, for example, anodic and cathodic protection, sacrificial anodes

Batteries and Fuel Cells
such as batteries for electronic devices, household and portable devices, fuel cells for vehicles and on site power generation

Sensors
for monitoring atmospheres, toxic hazard warning, optimisation of engine/furnace performance, monitoring water quality, process streams, medical applications and others

Table II
Performance of Anode Materials in Cells
Used for the Manufacture of Chlorine and Sodium Hydroxide
Reaction conditions: 25 per cent brine at 363 K; current density 3 kA m^{-2}

Anode	Cl_2 overpotential, mV	Anode weight loss
Graphite	≈ 400	2–3 kg/tonne Cl_2
Pt†	≈ 200	0.4–0.8 g/tonne Cl_2
RuO_2/Ti	≈ 50	< 0.03 g/tonne Cl_2

† Platinum anodes can also passivate leading to a substantial further increase in overpotential

Fig. 1 Scanning electron micrograph of a modern oxide coated titanium anode for a chlor-alkali cell. Scale: 1 cm represents 20 μm
Photograph reproduced courtesy of ICI Chemicals & Polymers Ltd.

these coated titanium anodes made possible the construction of sealed cells with a range of electrode configurations; thereby introducing a new flexibility into cell design. The result was a new generation of improved performance cells including the highly successful membrane cells for chlor-alkali production.

Coating Compositions

Dimensionally stable anodes rapidly became more complex in composition (2–5). It became apparent that for some applications it was advantageous to have an undercoat. This could be a titanium dioxide (TiO_2) layer, a mixture of RuO_2 and TiO_2, or a layer with a gradient in composition. It also became customary to include other platinum group metals, valve metals, tin and/or transition metals in the coating, with the objectives of:

• reducing the chlorine overpotential even further

• increasing the resistance of the coating to damage during electrolysis

• further enhancing the lifetime or reducing the catalyst loading

• improving the current efficiency for chlorine (that is, decreasing the oxygen content of the chlorine by increasing the overpotential for the competing water oxidation reaction) or just

• establishing a stronger patent position for a technology which had become both highly successful and very profitable.

Variations in the coating composition are easily achieved by changing the composition of the spray/paint solution. Such oxide coatings usually have the "cracked mud" appearance when examined by scanning electron microscopy, see Figure 1.

Modern coatings for the anodes used in mercury, diaphragm and membrane cells in the chlor-alkali industry differ in composition, to allow for differences in the operating conditions and the environment close to the anode surface. Anodes for membrane cells are now generally a mixture of RuO_2 and iridium oxide (IrO_2) and, with a platinum group metal loading of 10–20 $g\,m^{-2}$, have a guaranteed operating life of five to eight years. Such coatings give a very stable, low chlorine overpotential and a low oxygen content in the chlorine. In common with other cell components, the anodes are also now asked to operate at higher current densities. For many years the accepted current density was 2 to 3 $kA\,m^{-2}$ and the emphasis was on reducing the energy consumption of the cell. However, the recent trend is towards using further improvements in cell performance to lower the capital cost of the plant, and it would be advantageous for the anodes to operate at 4 to 5 $kA\,m^{-2}$ without significant loss in performance.

Such developments clearly demonstrated the possibilities for modifying the electrocatalytic properties of coatings on titanium by changing the composition of the oxide. This is well illustrated by two examples. Dimensionally stable anodes for oxygen evolution are now widely used for applications including cathodic protection, electrogalvanising and electrowinning of metals from aqueous acid (5, 6). For these anodes, the coating is based upon IrO_2 which gives a low overpotential for the oxidation of water to oxygen. Minor changes to the coating composition have led to a substantial improvement in oxygen anode performance, particularly the wear rate. Perhaps the most spectacular application of these electrodes is in electrogalvanising where steel strip is coated with zinc on a reel-to-reel system at high speed and the coated anodes operate at 7 to 10 kA m^{-2}.

Another type of anode has been developed for the production of chlorate. In this process the anode reaction is again the oxidation of chloride ions, but the reaction is carried out at a higher pH (pH > 6, compared with a pH of 3–4 in a chlor-alkali cell). The chlorine is immediately hydrolysed to hypochlorite which then disproportionates in solution to chlorate and chloride. The higher pH leads to a greater loss of current efficiency due to oxygen evolution and also to higher rates of dissolution of the RuO_2 layer. In attempting to overcome these problems, the Canadian company Chemetics International developed coatings based on $TiO_2/RuO_2/AlSbO_4$ (or $RhSbO_4$) with a low RuO_2 content (7). These compositions exhibit better catalytic activity, higher selectivity (with less oxygen production) and lower wear rates compared with RuO_2 or RuO_2/TiO_2 anodes. They also permit operation at a higher temperature, which significantly reduces the plant capital and operating costs.

Cathodes for Hydrogen Evolution

The overpotential for the cathode reaction in a chlor-alkali cell is, of course, also critical to the process energy consumption. Perhaps surprisingly, it has proved more difficult to eliminate the significant overpotential for this

electrode reaction: the reduction of water to hydrogen and OH$^-$ in strong caustic soda solution (usually > 30 per cent). The primary literature contains descriptions of many studies of the hydrogen reaction and many non-noble metal catalysts have been proposed. Even so, many chlor-alkali producers still rely on cathodes coated with noble metals, which are available from most electrode suppliers.

While their exact compositions are not disclosed, many are believed to be related to the platinum/ruthenium coatings described by Grove (8). Nickel is used as the substrate, to ensure stability against corrosion, and the coatings contain 3.0 to 3.5 g m^{-2} of platinum and 1.0 to 1.5 g m^{-2} of ruthenium. The coatings are prepared by immersion plating. After appropriate surface preparation, the nickel substrate is simply dipped into a solution of the noble metal chlorides and left to stand at room temperature until the required loading of noble metal is obtained. The nickel metal is the reducing agent in this cementation reaction. Once again, uniform coatings on complex surface shapes are easily obtained, for instance on expanded metal mesh and slatted louvres, as well as on flat surfaces, all of which are found in modern cell designs.

Typically the overpotential for hydrogen evolution is 100 mV with a current density of 3 kA m^{-2} in 35 per cent NaOH at 363 K and this performance can be maintained for more than 2 years. The major reason for loss of performance is due to coverage of the active catalyst surface by base metals, which have a high overpotential for hydrogen evolution. Hence, it is advantageous to operate with a catholyte which is free of metal ions, such as iron(II). However, some tolerance to iron poisoning has been claimed for noble metal cathodes and an upper limit of 60 ppm has been proposed (9).

Platinised Titanium Electrodes

Platinum electrodes are the workhorses of many laboratories, especially for the study of oxidations. They are regarded as being stable to anodic dissolution, and it is assumed that platinum coated titanium, either plated or as a cladding of thin platinum foil, will be a cost
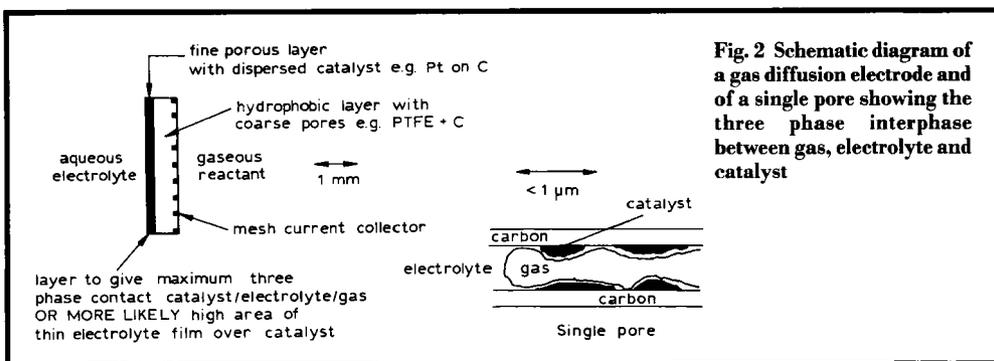
Fig. 2 Schematic diagram of a gas diffusion electrode and of a single pore showing the three phase interphase between gas, electrolyte and catalyst

effective, industrially useful alternative to bulk platinum metal; unfortunately, neither is entirely true.

On the longer timescale of pilot plant operation, platinum is often found to corrode significantly (5). There are only limited studies, but the available data suggest that platinum corrodes more rapidly in the presence of organics and certain anions. For example, in a scale-up of the conversion of methyl adipate to dimethyl sebacate, loss of platinum from the anode was found to be a significant factor in the process economics (10). Moreover, platinised titanium can have significantly different properties from platinum itself, presumably because of its higher surface area and perhaps also because of the poor adhesion of platinum to the titanium substrate.

Platinised titanium anodes however, have certainly found applications in electrochemical technology. They have been used in the electrosynthesis of several inorganic compounds, including persulfates and perchlorates, in electrochlorination plants and electroplating processes, for example, for chromium and gold. They are widely employed as the anodes for cathodic protection in sea water environments (for example, sea water intakes and heat exchangers, and for oil rigs) because their resistance to abrasion is superior than that of other anode coatings. At present, modern platinised titanium anodes are manufactured with an undercoating layer of platinum/iridium or noble metal oxide, and covered with a dense layer of platinum by electroplating. For cathodic protection in sea water,
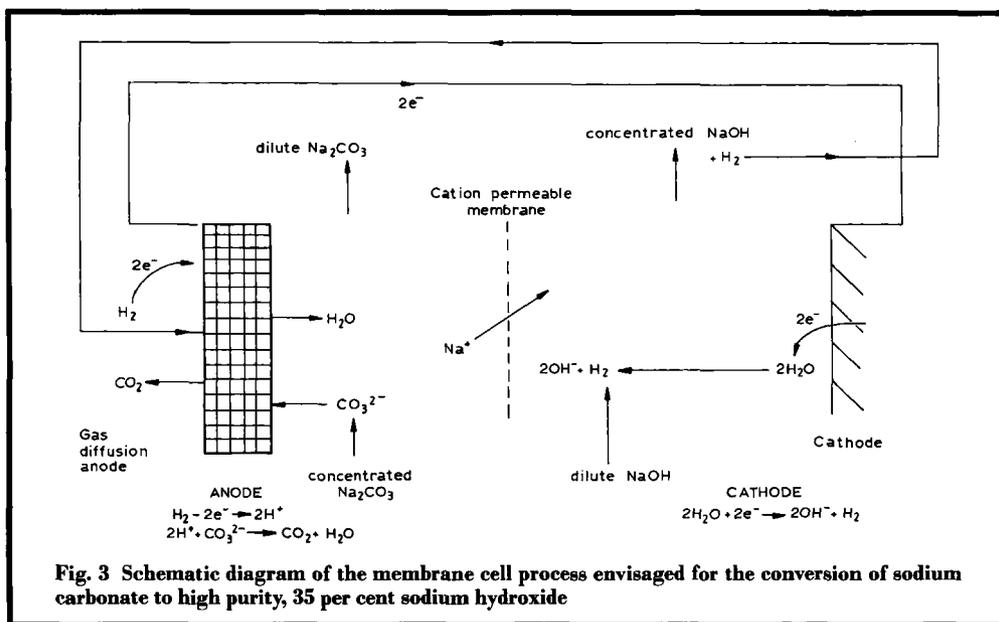
such anodes have a wear rate of 1 to 2 μg/A h.

Platinised titanium anodes were the first coated electrodes to be marketed, and in many applications they have been displaced by dimensionally stable oxide coatings that have been highly optimised for the particular electrolyte. However, there remains a market for anodes which can be used in relatively small scale processes and this could be met by high performance, platinised titanium anodes. Indeed, the number of such applications in electrosynthesis and environmental processing is expanding. It may be timely, therefore, to re-examine the manufacture and performance of platinised titanium anodes and to consider using platinum alloys for nonspecific applications; for example, platinum/iridium coatings on titanium are known to have superior properties in some applications.

Gas Diffusion Electrodes

Gas diffusion electrodes are porous structures, where the gas is fed to the back of the electrode away from the electrolyte, and a three-phase interphase between the gas, electrolyte and electrocatalyst is formed close to the electrode/solution interface. Most electrodes consist of a relatively thick layer of carbon and PTFE containing a current collector (such as a fine metal mesh) and a thinner layer of carbon containing the electrocatalyst on the solution side, see Figure 2.

The skill in the fabrication of electrodes is in selecting the appropriate catalyst, minimising the catalyst loading and designing a stable structure where the gas/solution interface is formed

Fig. 3 Schematic diagram of the membrane cell process envisaged for the conversion of sodium carbonate to high purity, 35 per cent sodium hydroxide

at the catalyst site. Such electrodes can be operated with almost insoluble gases at current densities in the range of 1–10 kA m^{-2}.

Fuel Cell Uses

Gas diffusion electrodes were originally developed for fuel cells where hydrogen and oxygen (from the air) are reacted at the anode and cathode to give water and a significant energy output. One such type of fuel cell is the proton exchange membrane fuel cell (PEMFC) which employs a perfluorinated membrane as a solid electrolyte (11–13). Due to their intrinsic simplicity and high power density, PEMFCs are suitable for both stationary and transportation applications. Major progress towards commercialisation has been made with these fuel cells, especially by Ballard Power Systems in collaboration with Johnson Matthey. Test units of up to 250 kW, as well as whole buses, have completed extensive trials (12).

The catalysts used for PEMFCs are typically platinum for the air cathode and platinum or platinum based alloys or mixed metals, such as platinum/ruthenium, for the anode. Optimisation of electrode structure – to improve catalyst utilisation – and better catalyst dispersion have led to noble metal loadings of typically 3 g m^{-2}.

Substantial developments have also occurred recently in direct methanol fuel cells (DMFCs) (14). Organic fuels have advantages over hydrogen in their relative ease and safety of transportation and distribution, and their lower cost. There are a number of factors responsible for the advances in performance. These include the use of solid polymer electrolytes, which allow the fuel cell to be operated at higher temperatures than is possible with traditional liquid electrolytes, and improvements in anode performance. For many years, the performance of DMFCs was poor due to poisoning of the platinum catalyst by intermediates in the oxidation of the fuel. One particular problem is carbon monoxide, which absorbs strongly and irreversibly onto the platinum surface, thus restricting the rates of methanol oxidation to 1 A m^{-2}. The use of catalysts, such as platinum/ruthenium materials often with additives, for example tin/tungsten or tin/zirconium, has reduced electrode poisoning, thus allowing the fuel cell to give a power output of 2 kW m^{-2} at a discharge rate of 4 kA m^{-2} (15, 16).

Gas diffusion electrodes have now become an accepted tool in electrochemical technology and
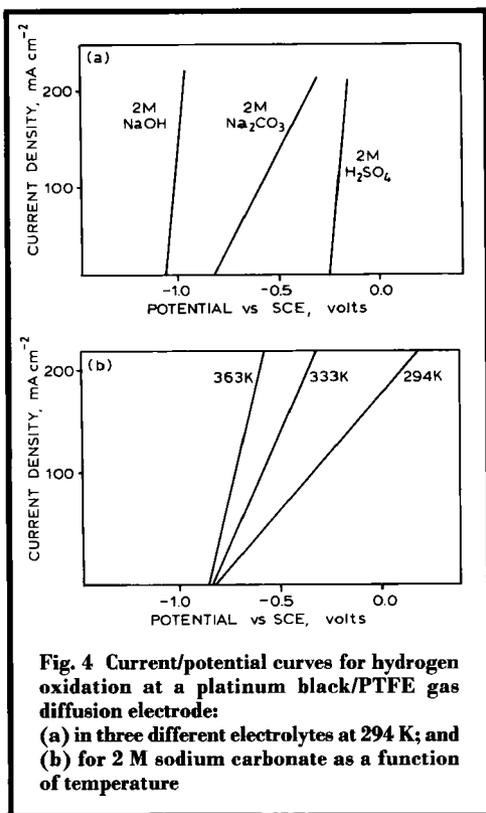
Fig. 4 Current/potential curves for hydrogen oxidation at a platinum black/PTFE gas diffusion electrode:
(a) in three different electrolytes at 294 K; and
(b) for 2 M sodium carbonate as a function of temperature

have found applications in batteries, sensors, metal recovery and synthesis. Processes for the reduction of oxygen to hydrogen peroxide at uncatalysed gas diffusion cathodes are being developed (17), and platinum catalysed gas diffusion electrodes find application in electrochemical processing as counter electrodes.

The replacement of hydrogen evolution by the $4e^-$ reduction of oxygen, or oxygen evolution by hydrogen oxidation can lead to substantial decreases in energy consumption by the cell. Thus, oxygen cathodes have been used, for example, in cells for the production of ozone (for water treatment) (18, 19) and hydrogen anodes have been used in cells for zinc electrowinning (20) or the regeneration of redox reagents such as Ti^{3+} (used for organic synthesis) (21).

The hydrogen anode plays a more central role in a novel process for the conversion of sodium carbonate to sodium hydroxide. This is effectively an electrolytic version of the old Soda

Lime Process – which is both energy efficient and benign to the environment (22). From the scheme of the cell chemistry, Figure 3, it can be seen that the cathode chemistry and catholyte are identical to those in a chlor-alkali membrane cell. The hydrogen formed at the cathode is, however, piped around to a noble metal catalysed gas diffusion anode in an anolyte stream consisting of aqueous 2 M Na_2CO_3. The chemistry which occurs at the anode is:

$$H_2 - 2e^- \rightarrow 2H^+$$
$$2H^+ + CO_3^{2-} \rightarrow CO_2 + H_2O$$
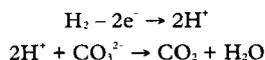
and the overall chemical change in the cell is

$$Na_2CO_3 + H_2O \rightarrow 2NaOH + CO_2$$
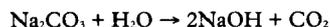
where the carbon dioxide is found in the anode gas stream. The Gibbs energy change associated with the cell reaction is only $\approx +54$ kJ (compared to $\approx +420$ kJ in a chlor-alkali cell), leading to the possibility of a very low cell voltage and low energy consumption. It should be noted that the process uses available and successful membrane cells, cathode coatings, membranes and the hydrogen oxidation anode. Moreover, with the exception of the anode, all the components are used in environments almost identical to those for which they were developed and optimised.

Hence, the key to success lies in the performance of the gas diffusion anode. Current/voltage characteristics for a preferred anode in three different electrolytes, are shown in Figure 4(a). Each characteristic shows the expected equilibrium potential for the pH concerned and is linear due to the voltage drop at these high currents. The response in sodium carbonate shows a much lower slope and this may arise partly from the higher resistance of this solution. However, the dominant factor is thought to be the local pH within the pores which decreases with increasing current density. Figure 4(b) shows the influence of temperature for the sodium carbonate electrolyte, and it can be seen that increasing the temperature is very beneficial to the process performance.

Using a flow cell operating at 363 K, with electrode areas of 7.5 cm², a Nafion 902 membrane

Table III
Energy Consumption for Various Electrochemical Technologies for the Manufacture of Sodium Hydroxide

Process	Energy consumption, kWh ton^{-1} NaOH
Chlor-alkali membrane cell	2500
Na_2SO_4 splitting	
3 compartment cell	4700
2 compartment cell	3600
2 compartment cell with H_2 anode	2800
bipolar membrane cell	1800
$Na_2CO_3 \rightarrow 2NaOH$	1100 (target 800)

and a catalytic cathode (see above), it has proved possible to produce very pure 13M NaOH with a current efficiency of over 98 per cent and a cell voltage of 1.6 V at 2.5 kA m^{-2}. This gives an energy consumption of 1100 kWh ton^{-1} of NaOH, which is much lower than is achievable by competing technologies, see Table III. Moreover, the energy consumption should be reducible to about 800 kWh ton^{-1}. The economics of the process depend on the balance of the markets for chlorine and NaOH, as well as on the value given to the liquid carbon dioxide recovered from the anode gas stream. Future work will focus on the long term stability of the anode and the influence of impurities in the sodium carbonate feedstock.
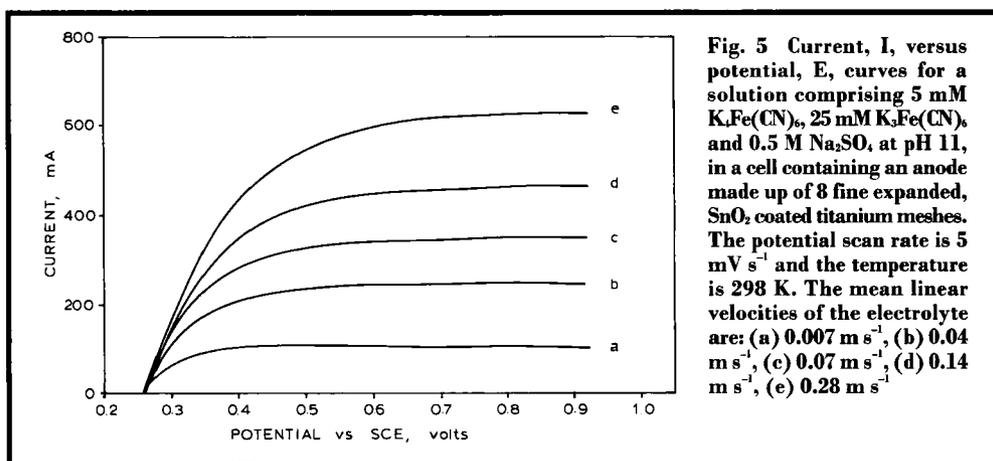
Three Dimensional Electrodes

Some electrolytic processes inevitably take place at low current densities because:
(a) the objective of the process is to remove a low level toxic component from an effluent
(b) the reactant for a synthesis has only a low solubility, or
(c) the rate of conversion is kinetically controlled. For such processes, scale-up may be achieved using a three dimensional electrode, fabricated, for example, from a bed of spheres or particles, a foam or a felt (23). Such structures made solely from noble metals are not available, and in any case, would be prohibi-

tively expensive. Hence, three dimensional electrodes using the platinum group metals must again be based on coated titanium.

The Olin Corporation has recently started to market a titanium felt type material called TySAR™ which is manufactured by welding together titanium fibres of thickness 50 to 60 μm (24). The material is 85 to 90 per cent porous, has a specific surface area of 6000 to 9000 m^2 m^{-3} and is available in sheets of size 0.5 m × 1.0 m with a thickness of 3.2 mm. Hence, in many respects it is similar to the metal and carbon foams which can be purchased. Although there is little data in the open literature, TySAR™ should be an excellent three dimensional electrode material, allowing reactions with acceptable space-time yields to be carried out in cells at low current densities. TySAR™ EP is a form supplied with an electroless metallic platinum coating of sub-micron sized, hemispherical platinum particles, giving a 60 to 95 per cent coverage of the titanium surface. The total platinum loading in a 1.0 m × 1.0 m × 3.2 mm electrode would be ≈ 80 g. Although this is still costly, TySAR™ offers one route to achieving a three dimensional platinum electrode. Expanded titanium mesh is a standard material suitable for coating with platinum group metals or oxides. Indeed, electrodes based on coated expanded titanium mesh are widely available.

Therefore, stacked coated titanium meshes

Fig. 5 Current, I, versus potential, E, curves for a solution comprising 5 mM $K_4Fe(CN)_6$, 25 mM $K_3Fe(CN)_6$ and 0.5 M Na_2SO_4 at pH 11, in a cell containing an anode made up of 8 fine expanded, SnO_2 coated titanium meshes. The potential scan rate is 5 mV s^{-1} and the temperature is 298 K. The mean linear velocities of the electrolyte are: (a) 0.007 m s^{-1}, (b) 0.04 m s^{-1}, (c) 0.07 m s^{-1}, (d) 0.14 m s^{-1}, (e) 0.28 m s^{-1}

provide a second convenient way to fabricate three dimensional electrodes where the active surface may be a platinum group metal, an alloy or an oxide. Stacks of fine meshes also make excellent three dimensional electrodes because they lead to high values of the mass transfer coefficient as well as moderate specific electrode areas (25).

Voltammograms of a solution of 5 mM ferrocyanide at a stack of 8 fine, coated titanium meshes are shown in Figure 5 (the coating is SnO_2 although the data for a mass transport controlled reaction is independent of the coating). It can be seen that very high limiting currents are obtained even for such a low reactant concentration (42 mA cm^{-3} mM^{-1}). In practice, limiting currents are about twice as high as at a metal foam anode for the same flow rates of solution; this would allow the design of very compact cells for high, single-pass, conversions. Unfortunately, with a loading of 10 g m^{-2} on the titanium surface and a stack of 8 fine meshes of total area 1 m^2, the platinum group metal content of such an electrode structure would contain approximately 50 g of metal.

Thus, it can be seen that high performance, three dimensional electrodes are very achievable; however, there is a great commercial benefit in minimising the thickness of the platinum group metal coating.

Conclusions

Electrochemical technology is now clearly identified as a "clean technology" for the manufacture of chemicals. It also finds application in processes for recycling chemicals and materials, treating effluents, destroying toxic materials, soil remediation and other diverse technologies. All this technology depends on stable electrode materials and, frequently, only platinum group metal materials fulfil this requirement. The objective of electrode/catalyst design is often, therefore, to place the noble metal in a stable matrix and to achieve the required performance with a minimum noble metal loading. Platinum group metals, their alloys and oxides used as coatings on inert substrates of titanium, nickel and carbon, have already found many applications, and further advances are sure to be a feature of the early 21st century.

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A Rhodium Solvated Molecular Wire

One-dimensional inorganic compounds have been investigated for a number of years because of their interesting electrical properties and their predicted high temperature superconductivity; indeed the square-planar platinum cyano-complex ion, $[Pt(CN)_4]^{2-}$, has been one of the commonest materials examined (1). Recently, there has been increased attention paid to molecular structures which can form molecular wires and act as connectors in molecular-scale electric devices (2). The controlling factors for the formation of these structures have been the ligands, which effectively govern the closeness between the metal atoms, and the electronic properties of the metals, which need incompletely filled bands to allow electron movement. However, there have been few infinite metal-metal bonded chains, because the ligands typically used in co-ordination compounds do not allow direct approach of the metal atoms along the axial direction.

Now, however, scientists from Michigan State University and Siemens in the U.S.A. and the Institut de Ciència de Materials de Barcelona in Spain, have succeeded in converting a discrete rhodium-rhodium bonded dimer into an infinite one-dimensional "polymer" array, $\{[Rh(MeCN)_4](BF_4)_{1.5}\}_x$, by the one-electron reduction of $[Rh_2(MeCN)_{10}](BF_4)_4$, in a cell also containing $[(nC_4H_9)_4N]BF_4$ in MeCN, with platinum electrodes and an applied current of 2 μA.

The unbridged rhodium compound was used in the investigation because it possessed only small, linear MeCN ligands, whose steric effects are minimal (3).

This rhodium polymer is the first, mixed valence, one-dimensional compound of rhodium, and is the only example of an infinite metal-metal bonded chain synthesised from a dinuclear precursor. The ligands are neutral donors, thus there is cationic charge on the chains which form the backbone. This contrasts with the partially oxidised tetracyanoplatinates which are anionic. The ligands may also be tailored, so it might be possible to produce insulating sheaths around the central chain of rhodium atoms, leading perhaps to liquid crystallinity, and allowing small changes in properties by varying the organic groups.

This novel rhodium chain polymer will enable the theory of one-dimensional materials to be tested, and using different ligands, will give insights into structures and transport properties.

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