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Nine years of research and development on advanced water electrolysis. A review of the research programme of the Commission of the European Communities

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The development of advanced water electrolysis was one of the main tasks of the R & D programme on hydrogen funded, within its main R & D programme on Energy, by the Commission of the European Communities. Most of the work has been concentrated on the development of alkaline water electrolysis, as this process appears particularly promising. (Water electrolysis based on 'acidic' solid polymer electrolytes, developed during the last 10 years, seems to be a potentially attractive alternative technology, at least for electrolysers of smaller scale (up to 100 kW). Even at this size, however, there is not yet evidence of any overall economic advantage over advanced alkaline cells.)

The results of 9 years of R & D in this field are critically examined, by reviewing the improvements achieved on the components of the electrolytic cell as well as the overall modification of the cell design. The anode, cathode and diaphragm have been the components investigated, but also the constituent materials, the nature of the electrolyte and its operating conditions have been dealt with. Three main lines of advanced electrolyser development were identified in the course of these investigations. The corresponding charcteristics are:

(i) low temperature (70° C to 90° C), low current density ($i = 0.1–0.3\,\mathrm{A\,cm^{-2}}$);
(ii) moderate temperature ($< 120°\mathrm{C}$), high current density (i up to $1\,\mathrm{A\,cm^{-2}}$), medium pressure (5–10 bars);
(iii) medium temperature (120–160° C), high current density ($i = 1–2\,\mathrm{A\,cm^{-2}}$), moderately high pressure (30 bars).

In cell design, very compact cell units have been devised, in which a 'zero gap' configuration (anode and cathode are placed directly on the diaphragm) is generally adopted, resulting in very low internal cell resistance (about $0.2\,\Omega\,\mathrm{cm^2}$). Potential energy savings of 20 to 30% can be anticipated for the advanced electrolysis.

In addition to this work on advanced alkaline water electrolysis, some limited research efforts on high temperature ($> 1100\,\mathrm{K}$) water vapour electrolysis have been made and are reported. The latter work has been concentrated on the production of thin-layer doped zirconia solid electrolytes ($d = 50\,\mu\mathrm{m}$), potentially leading to high performance cells. The economic implications of high-temperature vapour electrolysis, however, cannot be judged at the present status of development.

1. Introduction

Within the Energy R & D programmes of the European Communities (1975–79; 1979–84), the R & D on hydrogen was aiming at its large-scale production and use, since hydrogen was considered mostly as a large-scale energy carrier, capable of effectively supplementing the existing energy system. Its contribution to the energy market in this role is expected to be long term, because of the evolution of actual energy markets. During implementation of the above mentioned programmes it was shown, however, that electrolytic hydrogen could be used to an advantage as a feedstock in specific applications in which the overall cost balance was favourable, which is a real possibility even at medium term. This extends to smaller size equipment and systems which exploit most profitably the improvements achieved in the development of advanced water electrolysers.

The analysis of the potential penetration rate of electrolytic hydrogen into the energy market and in the feedstock market gives relatively uncertain results, as the evolution of all the contributing factors is still very uncertain at this time. Furthermore, it is

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impossible to evaluate in general the potential advantages of specific processes in which electrolytic hydrogen production is fully integrated, as specific evaluations are then necessary.

In qualitative and global terms, however, it seems likely that in countries like France and Belgium, where an increasing fraction of electrical power will be provided by nuclear power stations, increasing quantities of cheap off-peak electrical energy will be available. In these conditions production of electrolytic hydrogen can be an effective and convenient means for load levelling as soon as other 'interruptible' uses of this energy are saturated. In this field these countries will be forerunners of events that will take place at a later time elsewhere and may well begin to utilize the results reported here quite rapidly. Earlier, and even large-scale applications, are possible in other countries where hydroelectric energy is abundant and cheap, for example, Canada, Brazil, Zaire, etc. The possibility of hydrogen-born energy imports from Canada or Greenland seems to be of special interest for those countries of the European Communities who do not intend to extent their nuclear electricity production any further such as the Netherlands or – possibly after Chernobyl – the German Federal Republic.

Contrary to the more recent hydrogen production by thermochemical water splitting cycles, alkaline water electrolysis is a well-established technique since its first development more than 50 years ago [1, 2]. Due to the high cost of electricity, however, it does not account for more than 1–2% of the world's hydrogen demand and it is used for massive hydrogen production only where large quantities of cheap electrical power are available.

As a result of these circumstances and in contrast with the fact that the process was old at the time this R & D programme was started, alkaline water electrolysis has not yet been optimized to a full extent. In this field, therefore, rapid technical progress was expected, followed by an easy transfer to industrial practice. Thus, the aim of the R & D programme on electrolytic hydrogen production was to minimize its production costs by careful optimization of all factors involved, such as the electrical energy needed by the process and the capital investment for the equipment, so that the cost of electrolytic hydrogen would come closer to the cost of hydrogen produced by steam-reforming of oil or methane and eventually become competitive as the cost of these fossil fuels increases with time.

2. State of the art of water electrolysis at the start of the programme

When the European R & D programme started in 1976, a limited number of types of commercially available water electrolyser existed; their operation data and investment costs were comparable. The new, advanced electrolysers, which the hydrogen programme was intended to develop, had to be a real improvement in comparison with those already available.

All standard commercial electrolysers use an alkaline electrolyte (30 wt % KOH), operated at relatively low current density (0.1 to 0.3 A cm^{-2}), at modest working temperatures (between 70 and 90° C), and their unit cell voltages range from 1.85 to 2.2 V. As constitutive materials, normal steels are used for cell frames and electrode supports, relatively thick and rugged asbestos cloth or fabric is used as a diaphragm. Only a few electrolysers work under pressure (the Lurgi electrolyser working at 3 MPa was, and is, the most advanced in this category) [1].

The specific investment costs referred to the electrical power input of these electrolysers (utilities and gas conditioning included) was comparable for all types and ranged from 450 to 580 ECUS per kW at the end of 1982 [3].

To show more clearly the status of this technology, the voltage of a single cell technically achieved in these electrolysers may be compared with the theoretical cell voltage, computed from the thermodynamic relationships ($\Delta G = 2FU_0$ (minimum) [4]). Its value is given in Fig. 1 as a function of the temperature at two different pressures (1 bar and 20 bars). From Fig. 1 it is obvious that the cell voltage of 1.8 to 2.2 V is considerably above the theoretical cell voltage. Even if the actual cell voltage is compared to the theoretical voltage derived from the enthalpy of the process (i.e. addition of the entropic term $T\Delta S$ to ΔG), which is about 1.5 V, cells working with cell voltages of 2.2 to 1.8 V have an overall efficiency of only 70–80%.

There are several reasons for this unfavourable situation, caused by the relatively high losses of the process itself, whose main components are:

(i) the relatively high internal electrical resistance of conventional electrolysers, and

(ii) the relatively high overvoltages experienced at the cathode and at the anode.

These losses are shown on the schematic presentation of the different components of the cell voltage, as

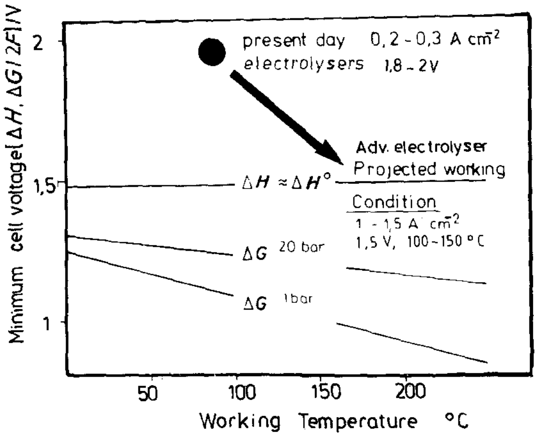

Fig. 1. Minimum cell voltages for electrolytic splitting of water as a function of temperature based on ΔG^0 for 1 and 20 bars. Current standard electrolysers work at cell voltages of about 1.8 to 2 V at low current density. Aim of development is obtaining a cell voltage of approximately 1.5 V with increased current density.

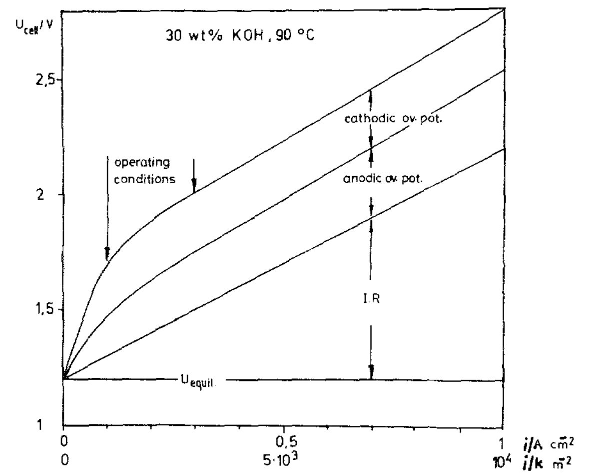

Fig. 2. Cell voltage currrent density correlation for the current electroyser technology. The internal cell resistance is approximately $1\,\Omega\,cm^2$.

a function of the current density for a conventional electrolyser, given in Fig. 2.

3. The development of advanced alkaline electrolysers

For water electrolysis to become a more competitive and more efficient process, all the causes of energy loss had to be tackled while, at the same time, the total cost of the equipment had to be lowered. In detail the main goals were:

(i) The unit cell voltage should be reduced as far as possible, in order to minimize the unit cost of electrical power, since this is generally the main component of the hydrogen production cost.

(ii) The current density should be increased over that of conventional electrolysers, in order to lower proportionally the investment costs (approximately proportional to the total surface area of the electrodes). Further investment cost reduction would also be obtained by a more compact design of the cells, but this would only be possible if a more detailed knowledge of fluid flow and fluid dynamic behaviour of these compact cells were available.

These two goals are somewhat contrasting and a certain amount of optimization is always needed to suit specific conditions. In fact, according to Equation 1, which defines the cell voltage of an electrolyser, the increase of current density (which leads to a decrease in investment costs) unevitably results in an increase of cell voltage.

$$U_c = U_0 + iR' + \eta_{an} + |\eta_{cath}| \qquad (1)$$

where U_0 is the equilibrium cell voltage ($= \Delta G/2F$); R' is the specific resistance per unit surface ($\Omega\,cm^2$) (this resistive component includes the ohmic drop in the electrolyte, in the diaphragm and the increase of ohmic drop due to the bubble curtain formed during electrolysis); η_{an} and η_{cath} are the anodic and cathodic overpotentials which increase logarithmically with current density.

Therefore, the two conflicting requirements of simultaneously decreasing the energy costs and the investment costs can be satisfied only by the development of a completely new cell design having, intrinsically, a much lower internal resistance and by developing special electrodes having much lower overvoltages at high current density than present day electrolysers.

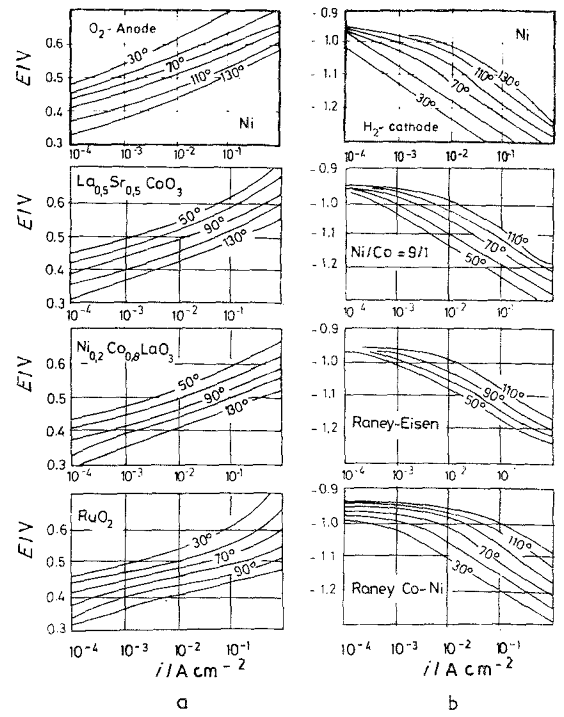

Fig. 3. Current-voltage correlation for unactivated and activated nickel electrodes at different temperatures [5]. (a) Anodic O_2 evolution (oxidic catalysts); (b) Cathodic H_2 evolution (Rancy-metal catalysts).

As shown in Fig. 3a, for oxygen evolution at the anode, and in Fig. 3b for hydrogen evolution at the cathode, non-activated nickel electrodes show (by chance), at 90° C, in 30 wt % KOH at current densities of $1\,A\,cm^{-2}$, nearly equal overvoltages of 350 mV (absolute) [5, 6]. These overvoltages should be reduced as far as possible because of their direct relevance to the hydrogen production cost. In practice the behaviour of the anode and cathode and of the respective anodic and cathodic electrocatalysts eventually applied to them is drastically different, as clearly analysed in [5, 6]. The electrode reactions at the anodes show the highest irreversibility and only small improvements of the resulting anodic overvoltage can be expected in practice with long lasting catalysts (although improvements seem possible with short lived catalysts). On the contrary, large improvements seem possible for the cathodes, by the use of appropriate electrocatalysts and of suitable operating conditions.

To show more clearly the main themes for which improvements are necessary, the characteristic data of water electrolysers of the current technology are presented in Figs 2, 3a, 3b and 4. In order to improve this technology by a sizeable extent the following programme steps were defined.

(i) The development of new cell configurations and of new types of diaphragms with the aim of lowering the internal cell resistance to a considerable extent. The component of the electrical resistance of the cell

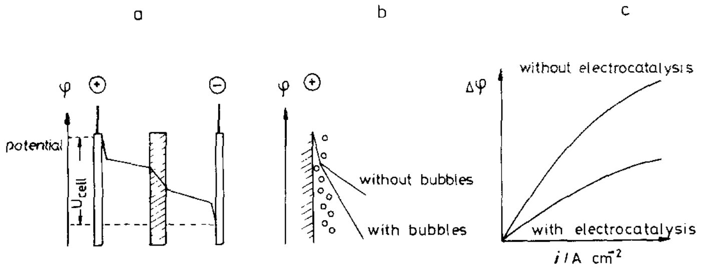

Fig. 4. Schematic representation of voltage losses in water electrolysers: (a) Potential drop across the cell includes interfacial potential differences at the electrode/electrolyte interface and ohmic voltage drops across the interelectrodic gap including the diaphragm; (b) The 'bubble curtain' in front of the electrode increases the effective electrolyte resistance; (c) The kinetic hindrance of the electrode processes is overcome by the overvoltage. Electrocatalysis reduces the overvoltage by acceleration of the chemical steps of the electrochemical reaction.

due to the effect of the bubble curtain produced by gas evolution should also be reduced or eliminated altogether by proper design and arrangement of the interelectrode gap.

(ii) Systematic search and development of new, very active and long-lasting electrocatalysts for evolution of O_2 and H_2 resulting in the development of more effective, long-lived and possibly cheaper electrocatalysts than those known and used until now.

(iii) Identification of types of materials to be used in the environments specific to electrolytic cells, working under hitherto unprecedented operating conditions such as higher working temperatures, higher electrolyte concentrations and much higher current densities. Furthermore, it was of interest to determine whether cheap plastic materials could be used in cells operating at relatively low temperatures (90° C and below).

(iv) Study of the conditions leading to safe operation of high current density, high power electrolysers working at a much higher power per unit volume (about $1\,\mathrm{MW\,m^{-3}}$) than conventional electrolysers, with special attention to the prevention of any hazardous condition.

Points (i) to (iv) were planned to cover the field of advanced alkaline electrolysis exclusively since it was felt strongly that the attempt to investigate water electrolysis in acid solutions would lead to hopeless difficulties with problems of material choice and of corrosion in general.

(v) A limited effort was forseen in the field of high-temperature vapour electrolysis using solid electrolytes, as this alternative route could lead, if successful in the long term, to much higher overall electrical efficiency than the alkaline process. The specific approaches were complementary to the large body of work already going on in this field, particularly in the Federal Republic of Germany [6].

4. Results

This review is based on the detailed data reported by the contractors in the final report of their contracts, in papers presented to specific conferences [7, 8], as well as on results presented at meetings and interviews with some contractors.

For easy reference, Tables 1 to 4 show – for the different projects of the first (1975 to 1979) and the second (1979 to 1983) programme – the project number*, the contractor, the subject for research (cathode activation, anode activation, diaphragms, cell configuration, materials). A further column also indicates whether the respective contractor worked on a total cell concept (t) or restricted the work to the development of specific components (c). The envisaged working temperature of the corresponding electrolysis concept is also given.

4.1. *General operating conditions*

4.1.1. Working temperature. Only a few of the projects (Nos 5, 21–29 in the first and 109 and 114 in the second programme) worked on the improvement of the anodic and cathodic electrocatalysts so that electrolysis might become competitive even at 90–100° C. All the others aimed at electrolyser versions working at higher temperatures, namely 120, 160 or even 200° C, as in these conditions the overvoltage reduction caused by the increased temperature adds to the overvoltage reduction obtained by the use of electrocatalysis. The endurance of electrocatalysts is, however, obviously lower in these conditions and the development of long-lived catalysts has been very laborious.

4.1.2. Current density. Generally, $1\,\mathrm{A\,cm^{-2}}$ was assumed to be a sufficiently clear target, approximately corresponding to a fair compromise between the necessity of lowering the energy consumption while keeping the equipment cost to an acceptable level. However, in projects Nos 11 and 25 the contractors lowered the current density to $0.5\,\mathrm{A\,cm^{-2}}$ because they did not succeed in reducing sufficiently the internal cell resistance. A global cost analysis shows, however, that the optimal current density lies between 0.5 and $1\,\mathrm{A\,cm^{-2}}$. Its value depends on material costs, very much on electricity cost and on plant availability (yearly hours of operation). In very special cases the optimal current density may be even higher than $1\,\mathrm{A\,cm^{-2}}$.

4.1.3. Electrolyte concentration. In order to reduce corrosion problems under working conditions potass-

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* The 'project' number shown in the tables is a conventional filing reference used throughout the programme for convenient identification of specific research lines.

Table 1. Advanced alkaline electrolysis, 1st programme (1975–79)

Project No.	*Contractor*	*Electrocatalysis*		*Diaphragm*	*Cell geometry*	*Temperature (°C)*	*Scope of project*
		Anodic	*Cathodic*				
1	TH Darmstadt	+	+	+	+	150–200	t
2	SCK/CEN Mol	+	+	+	+	120	t
5	TNO	+	–	–		80	c
11	Marcousssis	+	+	+	+	120–160	t
18	SRTI/IFP	+	+	+	–	150	t
21	Univ. Milano	+	–	–	–	70	c
23	O. De Nora	+	+	–	–	80	c
24	TH Eindhoven	bubble formation, bubble curtain effect					–
25	Krebs-Kosmo	–	–	+	–	80	c
29	Polit. Milano	–	–	+	–	70	c
30	City University	+	+	–	–	70	c
31	RTI/SODETEG	–	–	+	+	200	c
35	CEM	+	+	+	+	200	t

ium hydroxide has been generally adopted as electrolyte with concentrations $\geqslant 30$ wt %. For temperatures above 120° C, however, this concentration was raised to 40 or even 47 wt % (which is an upper limit, above which the electrolyte will solidify at room temperature). In general, it can be expected that in the final optimization the concentration of the electrolyte will correspond to that having the highest conductivity at the working temperature (compatibly with material corrosion) as this will limit the corresponding ohmic loss. In one case (Nos 2, 115) 20 wt % and even 12% NaOH was chosen, in order to prevent deterioration of one of the newly developed cell components.

4.2. *Cell configuration*

Minimizing the internal ohmic resistance of the electrolyser was imperative for all those projects which dealt with the development of total cell concepts, since this is an unavoidable component of the cell voltage and since the cost of the electrical power is the major component of the electrolytic hydrogen cost.

Therefore, on one hand, thin cells in which the interelectrodic gap was reduced to 1 or 2 mm were constructed (Nos 11, 35) and during the second programme, on the other hand, a general convergency of cell concepts towards a 'zero-gap' geometry was observed. This 'zero-gap' concept, already established for more than 15 years in some commercial electrolysers (though with thick diaphragms) was verified in four projects (Nos 115, 131, 135, 136). In this configuration the cell is essentially established by pressing particulate electrode structures, perforated plates or expanded metals against the diaphragm.

A sketch of this concept is given in Fig. 5. In this way the interelectrode distances are limited to a minimum and no free space is left between the electrodes (as the whole interelectrode space is filled by the diaphragm or membrane) for the gas bubbles evolved by electrolysis to influence significantly the internal resistance of the cell. In these conditions the greater part of the gas bubbles escapes from the back of each electrode and through the perforations and their contribution to the total ohmic drop is minimized.

4.3. *Diaphragms and membranes*

Up to now the general experience in the field of diaphragm development shows that 'composite' materials could, in general, meet the very stringent properties (porosity, mechanical strength, chemical stability, hydrophilicity) necessary for any material to meet the requirements of a diaphragm/membrane in large-scale alkaline water electrolysers under conditions of enhanced temperature. This does not imply that it is impossible to develop a specific material for this use; the stringent requirements, however, make this task difficult and long term.

Six different types of diaphragm were developed, characterized and subjected to long-term performance tests.

Table 2. Water vapour electrolysis, 1st programme

Project No.	*Contractor*		*Temperature (°C)*	*Scope of project*
3	SCN Grenoble	ZrO_2 flat discs	900	t
6	BBC Mannheim	ZrO_2 cylinders	900	t
33	Citroên	ZrO_2 flat cones	900	t
38	Dornier System	Ultra-thin ZrO_2 electrochemical vapour deposition	900	t

Table 3. Advanced alkaline electrolysis, 2nd programme (1979–83)

Project No.	*Contractor*	*Subject*	*Scope of project*	*Working temperature (°C)*	*References*
102	SODETEG/IFP	Anodic and cathodic electrocatalysts	t	160	[9, 10]
104	CEA (CENFAR)	Electrolysis with H^+-cond. membranes	c	100	–
105	SODETEG	High temperature diaphragm	t	160	[11]
106	University of Cork	Stabilization of RuO_2 as anodic electrocatalyst	c	100	[12, 13]
107	TH Eindhoven	Bubble curtain effect and I.R. drop	c	90	[14, 15]
109	City University	PTFE-bonded cathodes and anodes	c	90	[16, 17]
111	KFA Jülich	H_2O electrolysis in hydroxide melts	t	400	[18, 19]
112	Lab. Marcoussis	Safety problems in large scale H_2 prod.	t	–	[20]
113	INCO Ltd.	Sinter nickel: anodes, cathodes, diaphragms	t	90–160	[21, 22]
114	CEGB	Pilot plant electrolyser with PTFE-bonded electrodes	t	90	[15]
115	CEN Mol	Inorganic membrane electrolysis	t	120	[24, 25]
121	TH Darmstadt	Medium temperature, medium pressure electrolysis	t	up to 160	[36, 37]
122	Creusot Loire	Corrosion of nickel in caustic solutions	c	200	[26, 27]
123	IRCHA	PTFE-bonded diaphragms	c	160	[28]
125	University Milano	Anodic electrocatalysits of perovskitic mixed oxides	c	120	[29, 30]
126	Panclor	Medium scale electrolyser	t	100	–
128	Panclor	H_2O electrolysis with cation conducting membrane	t	200	–
130	Politecnico Milano	Stabilized asbestos of large scale	c	90	[31, 32]
131	SODETEG	Construction and testing of a 28 kW prototype electrolyser	t	120	[33]
132	CEN/Cobelcon	Construction and testing of a 100 kW prototype electrolyser	t	120	[47]
134	Politecnico Milano	Polymer reinforced diaphragms for higher working temperature	c	160	[32]
135	CEN Mol/SODETEG	PTFE-bonded diaphragms	c	160	[34, 35]
136	TH Darmstadt	Oxide-ceramic diaphragm, el. activ.	t	160	[36, 38, 40]

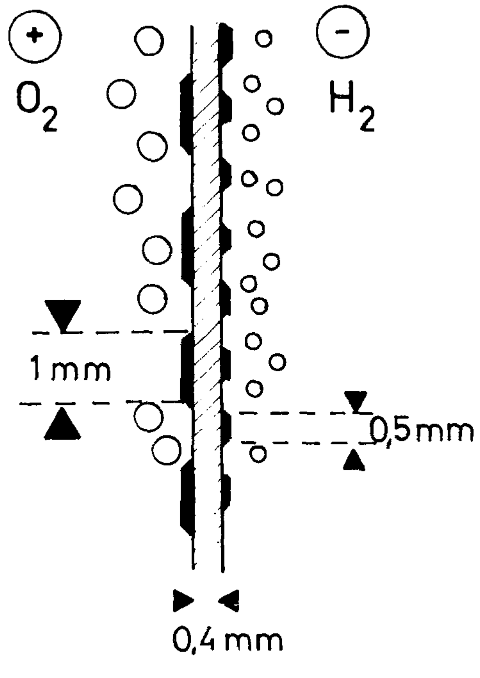

Fig. 5. Schematic representation of a zero-gap geometry for water electrolysers. Perforated plate type electrodes are pressed at either sides of the diaphragm. Because of the different bubble radii of O_2 and H_2 bubbles the optimum hole diameter of the perforated anode (1 mm) is greater than that of the perforated cathode (0.5 mm).

4.3.1. Polymer-reinforced asbestos diaphragms. These were developed and successfully tested over several thousand hours (Nos 29, 130). Because these diaphragms consist mainly of asbestos whose fibres are protected, but often not fully covered by the reinforcing polymers, they are not perfectly stable against dissolution by potassium hydroxide solutions at high temperature. These diaphragms can therefore be used safely only at working temperatures below 100° C*. They are thus typical components for advanced electrolysers working at low temperatures. Their advantages, in comparison to plain asbestos, are a superior chemical resistance and a much higher mechanical stability. This allows the use of very thin reinforced diaphragms ($d < 0.5$ mm).

This work has been successfully extended by producing polyphenylene sulphide (PPS)-reinforced asbestos. It is now being continued with the aim of preparing PPS-covered inorganic cloth potentially useful as an advanced high-temperature (160° C) diaphragm. This type of diaphragm exhibits, under

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* Recent tests showed, however, that by improving the homogeneity of the polymer distribution over the asbestos substrate (through a semicontinuous process) the resulting diaphragm could be used up to 120° C.

Table 4. Water vapour electrolysis, 2nd programme

Project No.	*Contractor*	*Subject*	*Scope of project*	*Working temperature (°C)*	*References*
108	CEN Grenoble	Sintering procedure for ZrO_2 discs of larger scale	t	900	[41]
118	Dornier System GmbH	Ultra-thin ZrO_2 membranes: their incorporation in cell structures	t	900	[42, 43]
137	University Grenoble	Catalysis of solid state cathodic processes	t	900	[44]
138	UHDE/USC	Techno-economic evaluation of several projects			

operation conditions, only $0.16\,\Omega\,cm^2$ surface resistance per unit surface (No. 134).

As a further development for the longer term, specific spinnable, highly stable polymers are being developed. Eventually a woven diaphragm or needle felt may be produced, which could be utilized in a very broad range of temperature.

4.3.2. Teflon tissue hydrophilized by radio-grafting of hydrophilic polymers. An extended investigation, whose aim was to make PTFE tissue hydrophilic by radio-grafting hydrophilic polymers onto it, ended eventually without success because the radio-grafting polymer was chemically unstable against potassium hydroxide solutions at the relatively high temperature (150° C) for which it was intended, although the composite diaphragms obtained might be sufficiently stable at a lower temperature (Nos 31, 135). This point is, however, still very uncertain, as degrafting is much accelerated by electrolysis, even at 120° C.

4.3.3. Polyantimonic acid impregnated by polysulphone (inorganic membrane electrolysis, IME). This diaphragm was developed for a moderately high working temperature (120° C) and needs, for stability, an unusual electrolyte, i.e. 12–20 wt % NaOH. It has been tested successfully to date for more than 10 000 h and can, accordingly, be said to be a very reliable electrolyser component. Its semi-technical production and relatively large scale (1 × 1 m) is now already established. The specific resistance per unit surface at 120° C in 12 wt % NaOH is 0.16 to $0.2\,\Omega\,cm^2$ (Nos 2, 115*).

4.3.4. Sinter nickel diaphragms. At the beginning of the first programme sinter nickel was assumed to be a promising candidate as a diaphragm material which would be corrosion-resistant in advanced electrolysers, working at temperatures above 120° C. (Zero-gap geometries would be, however, impossible with such a diaphragm, because of its electrical conductivity.) It has however, been impossible to produce sinter nickel diaphragms which are sufficiently resistant against oxidation and corrosive deterioration during electrolysis. Protection by cathodic polarization makes this diaphragm stable, but the necessity of the polarization is a further disadvantage in practical uses (No. 113).

4.3.5. PTFE-bonded zirconia diaphragms. The idea of using zirconium oxide as a hydrophilic agent for a particulate PTFE-structure was developed only very recently. The results are sufficiently promising for the production of a diaphragm stable in 30 wt % KOH at 160° C and exhibiting, under operation conditions, a specific resistance of about $0.2\,\Omega\,cm^2$ to be a real possibility at this temperature (No. 135).

4.3.6. Composite diaphragm made of porous sintered oxide ceramics supported by a nickel net. This type of diaphragm was introduced for high-temperature alkaline electrolysers in the first programme. It was successfully fabricated with nickel–titanate as its oxide–ceramic component. In long-term performance tests nickel–titanate was, however, not stable as it was slowly reduced at the cathodic side. Replacement of nickel–titanate by a proprietary cermet which is absolutely stable against reductions by hydrogen has been a major improvement leading to very good performances of this type of diaphragm. It has successfully undergone thorough long-term testing which has shown that:

(i) it is stable at 160° C in 50 wt % KOH;

(ii) its specific resistance per unit surface amounts at 160° C to $0.16\,\Omega\,cm^2$;

(iii) chemically it is the most stable diaphragm type within the programme, but it is also the most expensive, in relative terms ($\sim 300\,DM\,m^{-2}$).

Table 5 collects the most relevant data for the different diaphragm types developed in the framework of this R & D programme. It lists the maximal working temperature, the specific resistance per unit surface under operating conditions ($1\,A\,cm^{-2}$) and the estimated production costs.

4.4. *New electrocatalysts*

4.4.1. Electrocatalysts for cathodic hydrogen evolution. Most contractors adopted high surface area deposits of nickel as the basis of their electrocatalysts, to which other transition metals were added, using specific

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*This type of diaphragm has become the basis for a completely new electrolysis technology which has been commercialized since mid-1985.

Table 5. Characteristic data for newly developed diaphragms/membranes

	Specification	*Thickness* d/(*mm*)	*Surface-specific resistance* R′ ($\Omega\,cm^2$)[a]	*Maximum working temp.* t (°*C*)	*Estimated price* ($\$\,m^{-2}$)	*Remarks*	*Contractor*
(a)	Polymer reinforced asbestos	0.2–0.3	0.15–0.2	90	30	Semi-technical	Politecnico Milano
(a1)	Specific polymers for woven diaphragms	–	–	up to 140	–	Laboratory	Politecnico Milano
(b)	Teflon-tissue hydrophilized by radiografting	0.2–0.3	0.5–0.6	160	–	Failed	SODETEG
(c)	Polysulphone impregnated by Sb_2O_5 polyoxides	0.2–0.5	0.16–0.2	120	35	Technical	CEN, Mol
(d)	Sinter nickel	0.2–0.5	0.3–0.6	160	–	Failed[b]	INCO-Nickel
(e)	PTFE-bonded zirconia	0.2–0.5	0.25–0.25	160	40	Laboratory	IRCHA, CEN-Mol
(f)	Nickel-net backed $BaTiO_3$ diaphragm	0.3	0.15–0.2	160	140	Semi-technical	TH Darmstadt

[a] Under operating conditions.
[b] Unless properly polarized.

techniques. As a high surface area base, either sinter nickel (Nos 11, 35) or a type of Raney prealloy (Ni–Al or Ni–Zn) were used. The latter was applied to the base electrode surface and leached with potassium hydroxide to form, *in situ*, the high surface nickel (No. 136). Similarly Ni–NiS deposits were produced cathodically on the base electrode which, by successive cathodic reduction, resulted in a layer of high surface area nickel formed inside the electrolytic cell under operation conditions (Nos 115, 102). Stabilization against ageing is obtained in some cases by doping with molybdenum, titanium and zirconium oxides. A different approach consists in the preparation of high surface area powders of mixed transition metal sulphides which are then bonded by PTFE to the electrodes (Nos 30, 109). By using the techniques outlined above, the cathodic overvoltage at $1\,A\,cm^{-2}$ and 90° C in 30 wt % KOH has been decreased from the value of $-350\,mV$ for unactivated nickel to between -150 and $-200\,mV$ for catalysed electrodes.

4.4.2. Electrocatalysts for anodic oxygen evolution. The choice of electrocatalysts for anodic oxygen evolution is comparably more restricted than in the case of cathodic H_2 evolution. Apart from the use of sintered nickel anodes which are unstable in anodic conditions (Nos 11, 35), mixed oxides of spinel-type or Perovskite-type, all containing cobalt oxide, are used as anodic catalysts (Nos 102, 136). Up to the present, the oxide Co_3O_4 seems to be one of the most powerful electrocatalysts for anodic oxygen evolution (Nos 109, 136) [5, 6]. PTFE-bonded anodes of mixed oxides have likewise been developed. Generally, the improvement of the overpotential at the anode is smaller than in the case of the cathodes. The anodic overvoltage is decreased by 70 to 90 mV at 90° C and $1\,A\,cm^{-2}$ in 30–40 wt % KOH ($\eta = +260$ to $+280\,mV$) with the best electrocatalysts. Operation at higher temperature (160° C) allows reduction of the anodic overpotential to less than $+250\,mV$.

This reflects the inherent irreversibility of the anodic process [45], whose several steps are unlikely to be improved to obtain a large decrease of the overvoltage. Tables 6 and 7 present the most important data of differently activated cathodes and anodes.

5. Materials for cell construction

For the construction of low-temperature versions of alkaline electrolysers (70–100° C), apart from the use of ordinary steel, the less costly and more easily workable polypropylene may be used. Polyphenylenethersulphone, which is mechanically strong and stable in potassium hydroxide solutions up to 120° C, is econo-

Table 6. Cathodic electrocatalysts

Composition	*Method of preparation*	*Working temp.* t (°*C*)	*Overpotential* η (*mV at 1 A* cm^{-2})	*Contractor*	*Project No.*	*Reference*
Raney-nickel	Plasma-spray of Al/Ni alloy	160	-150	SODETEG	131	[9, 10]
'NiS'-PTFE NiCoS-PTFE	Emulsion-paint of sulphide and PTFE, annealing at 300° C	90	-100	City University	109	[16, 17]
Sinter-nickel	Sintering of carbonyl-nickel	120–160	-200	INCO–Nickel	113	[21, 22]
'NiS'-reduced	Cathodic deposition of rough Ni/NiS-mixture activation of deposit *in situ*	120	-150	CEN, Mol	115	[24, 25]
Raney Ni	Cathodic deposition of Zn/Ni, Zn/Ni/Co and Ni	90	-250	TH Darmstadt	136	[37, 38]
Raney Ni/Co			-150			
'NiS'						

Table 7. Anodic electrocatalysts

Composition	*Method of preparation*	*Working temp.* t (° C)	*Overpotential* η (mV at 1 A cm^{-2})	*Contractor*	*Project No.*	*Reference*
Cobalt containing Perovskites, e.g. $La_{0.5}Sr_{0.5}CoO_3$	Spray-thermal decomp. sintering	160	+250	SODETEG	102	[9, 10]
RuO_2 stabilized	Spray sinter	90	Not stable	Univ. Cork	106	[12, 13]
$NiCo_2O_4$-PTFE Co_3O_4-Li-PTFE	Freeze-drying of nitrates therm.-decomp. PTFE-emulsion bonded	90	+270	City Univ.	109	[16, 17]
Sinter nickel	Sintering of carbonyl Ni	100–160	Not stable	INCO-Nickel	113	[21, 22]
Co_3O_4	Spray-sinter	120	+280	CEN, Mol	115	[24, 25]
Perovskites, Spinels	Spray-sinter	120	+280	Univ. Milano	125	[29, 30]
Co_3O_4	*In-situ* activation	80–120	+280	TH Darmstadt	136	

mically more advantageous than steel because of the reduced production costs due to the possibility of using molding techniques for making the cell components, not to mention the absence of cathode deterioration processes, generally due to uncontrolled, disordered cathodic re-deposition of corrosion-dissolved iron (Nos 131, 132).

For electrolysis at higher temperatures (up to 160° C) only pure nickel or nickel-clad steel can be used for the stressed or pressure-bearing components, e.g. cell frames, separators and tubes, etc. (No. 136) [34, 35]. At this temperature, however, severe local corrosion of nickel in crevices has been observed, a fact that demands extreme care in the design of all parts of electrolytic cells working in these conditions, though it is only at 200° C that this phenomenon is rapid and potentially dangerous (No. 122).

Special care in the choice of gaskets is absolutely necessary, as, at higher temperature, very few gasket materials are chemically and dimensionally stable in long-term operation and leak-free, long-term operation is obviously a major prerequisite for industrial application of advanced electrolytic cells. Zirconia- and carbon-filled PTFE or filled polyphenylensulphide seem to be particularly suitable materials for gaskets.

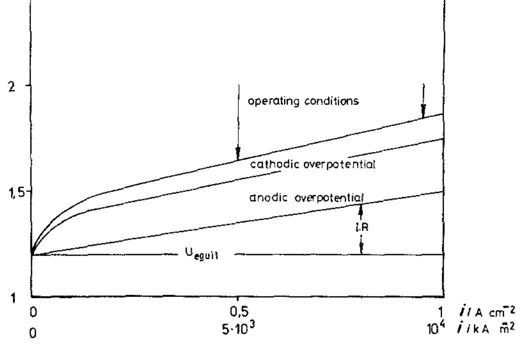

Fig. 6. Typical cell voltage–current density correlation for newly developed water electrolysers. The internal resistance of cells is about 0.3 Ω cm^2. The anodic and (even more) the cathodic overpotentials are considerably reduced.

6. Synthesis of the overall results and preliminary economic analysis

Analysing the overall results of this R & D programme is not an easy matter, as the degree of development of the different choices of electrodes, diaphragms etc. is not uniform and often still in the laboratory stage.

To ensure a reasonable validity to such overall analysis, this task was assigned to an engineering consultant [46] (UHDE). The present synthesis is based on the conclusions drawn by this consultant, elaborated further by means of a specific dedicated computer code of CEN, Mol [46] from which further conclusions can be advanced here.

Fig. 6 depicts the cell voltage–current density correlation of a cell which is composed of new components of optimal choice. Typically the ohmic resistance is reduced by at least a factor of three and the anode and cathode overvoltages become appreciably smaller.

No specific analysis has been performed for the high-temperature (1000° C) vapour electrolysis; since this technology is still far from practical application only comparative estimations have been made [47] for assessment of the future potential of this concept. This type of electrolysis will therefore be mentioned only briefly.

An additional investigation [48] into the influence of storage costs on the efficient costs of electrolytically produced hydrogen yielded an important insight into the market chances of hydrogen in the immediate future and around the turn of the century in Belgium and France.

As basis for the techno-economic evaluation by UHDE the data of three different versions of advanced alkaline water electrolysers, which had been developed to a pilot plant scale of 3–10 kW by the nuclear research center of Mol, Belgium (SCK/CEN Mol) by Laboratoires de Marcoussis and by Sodeteg located at Buc, France (SODETEG), were used. Table 8 shows

Table 8. Characteristic data of three different advanced electrolysers

Origin	*Diaphragm*	*Cathode/anode activation*	*Electrode distance*	*Current density* ($A\,cm^2$)	*Temperature* (°C)	*Cell voltage* (V)
CNR Mol	Sb_2O_5/polysulphone	(Ni, Co)S/Co_3O_4	zero gap perforated plates	0.3–1	120	1.65–1.8
Lab. de Marcoussis	PTFE-bonded K-hexatitanate	MoNi/FeMoNi	0.4 cm sheet electrodes	0.3	120	1.85
SODETEG	Stabilized asbestos	Raney Ni/Co-oxide impregnated Raney Ni	zero gap perforated plates	0.3	120	1.8–1.9

selected data on these three versions. Marcoussis electrolyser is a narrow-gap electrolyser with between 4 and 7 mm interelectrodic gap width, whereas the Mol electrolyser and the SODETEG electrolysers possess zero-gap configuration. It should be stressed, that the further development of all three versions has been continued beyond the end of the European programme and that the version of Mol is now already offered commercially.

Hydrogen production costs for the three versions were calculated and compared with costs for production by a conventional electrolyser for a production unit of 2 MW. Table 9 compares the costs for the three advanced electrolyser units split into separate costs, for electrolysers, transformer–rectifier units, lye processing units and piping, valves and instrumentation. The costs for the conventional ambient pressure unit amounted to 1.6 million DM (800 DM/kw) in mid-1983. Not surprisingly, the new versions were estimated to be more expensive because of the more sophisticated production procedures of electrolyser components, more expensive materials and higher risks in the use of novel technologies. (The electrolysers of Mol and SODETEG are of small scale, – 100 MW.)

Table 10 summarizes the data of the cell voltage–current density correlation for advanced electrolysers which is the basis for the cost-comparison of UHDE. The evaluation based on conservative calculations which may be compared with an independently published estimation [49] obtains slightly higher costs for electrolysis-hydrogen obtained by the advanced technique than for conventional electrolysis, but predicts some advantage of the advanced over the established technology in the foreseeable future because the energy price is so dominant for hydrogen costs and energy prices are expected to rise faster than equipment costs. There is even a prediction of an advantage of hydrogen produced by water electrolyses (with electricity from nuclear or hydro-power) over hydrogen from natural gas or lignite in 10 to 20 years time (see Fig. 7). It should be stressed that cost competitiveness depends on the scale of production and on the specific use of the hydrogen. It is, particularly, the small scaled use of H_2 for production of specialities, fat hardening, etc., where electrolytic hydrogen is already competitive today and where obviously the better chances for advanced electrolysers exist in the near future. For electrolytic production of hydrogen on a large scale (10 to several 100 MW) the energy price and the specific energy consumption is dominant and there the energy price contributes to between 60 and 80% of the total production costs of hydrogen.

Fig. 7 compares the current–voltage curves of advanced water electrolysers with current–voltage curves of high-temperature steam electrolysis. The figure clearly demonstrates that high-temperature steam electrolysis, although a technology which is still far from technical maturity, will eventually offer the best chances for hydrogen production by electrolytic water decomposition, since it uses remarkably less electrical energy than alkaline water electrolysis (approx. $3\,kWh\,Nm^{-3}\,H_2$), combined with investment costs which are expected to be equal to or lower than for advanced alkaline water electrolysis.

Fig. 8 demonstrates the target of the work performed by Dornier System within the framework of the European hydrogen programme (Nos 38, 118), the development of ultra-thin ($< 50\,\mu m$) zirconia membranes deposited on a porous zirconia support by electrochemical vapour deposition of ZrO_2. Such ultra-thin, ceramic, oxygen-anion conducting membranes are the precondition for a further improvement of the cell voltage–current density characteristics of high-temperature steam electrolysers.

Table 9. Estimated invested costs for 2 MW el. water electrolysis units of advanced and established technologies; costs in 1983 (DM)

Technology	*Mol**	*Lab. de Marcoussis*	*SODETEG*	*Conventional*
Electrolysers	860 000	720 000	930 000	–
Transformer/rectifier	460 000	460 000	460 000	–
Lye processing	280 000	350 000	230 000	–
Piping, valve instrumentation	770 000	1 000 000	730 000	–
Total	2 370 000	2 530 000	2 350 000	1 600 000

* Mol's technology was developed for electrolysers of small scale (typically 100 MW).

Table 10. Current–voltage correlation for advanced and conventional electrolysers used for comparative cost estimation

	Cell voltage (V)			
	4 kA m^{-2}	*6 kA m^{-2}*	*8 kA m^{-2}*	*10 kA m^{-2}*
Advanced electrolyser (V)	1.60	1.65	1.70	1.75
Established electrolyser (V)	–	1.80	(3 kA m^{-2} – fixed current density)	

7. Hydrogen costs with inclusion of storage costs

Investigation of the contribution of storage costs on effective hydrogen costs was the aim of a supplementary study of market chances of advanced water electrolysis in Belgium and France [48]. Both countries were chosen because of their high percentage of nuclear electricity already achieved, which offers access to relative inexpensive electric energy during off-peak hours (0.026 DM kWh^{-1} in 1983). The study evaluated H_2 production costs for 1984 and the year 2000 for three different cases:

(i) small plant/speciality market, 15 Nm^3 H_2 h^{-1} continuous demand; (60–70 kW)

(ii) medium size plant/ammonia market, 20.581 Nm^3 h^{-1} continuous demand; (80–100 MW)

(iii) large plant/ammonia market, 106.692 Nm^3 h^{-1} approx (1.250 NH_3 per day). (400–500 MW)

Table 11. Economic evaluation of H_2 production by different routes. Small plant/speciality market/Belgium 1984 and 2000 [48]

Assumptions[a]

Annual hydrogen demand (Nm^3) = 119 000
Cumulative offpeak power (h per year) = 4215
Industrial power (h per year) = 8760
Maximum consecutive offpeak hours = 57
Maximum consecutive indust. hours = 8760
1984 price of offpeak power (DM kWh^{-1}) = 0.022
1984 price of indust. power (DM kWh^{-1}) = 0.1100
Hydrogen storage required Yes
Underground storage available No
Oxygen byproduct saleable No
1984 natural gas proce (DM/GJ) = 17.41
1984 coal price (DM/GJ) = 6.73

Offpeak operation

Plant output (Nm^3 h^{-1}) = 28
Current density (kA m^{-2}) = 12.5
Cell voltage (V) = 1.81
Liquid storage is preferred

Capital costs (DM)	
Electrolysis	212.879
Storage	38.348
Total	251.226

Unit costs (DM Nm^{-3})	
Power	0.097
Other operating	0.015
Capital (elec.)	0.420
Storage (total)	0.096
Total	0.629

Offpeak operation is more economic

Continuous operation

Plant output (Nm^3 h^{-1}) = 15
Current density (kA m^{-2}) = 11.1
Cell voltage (V) = 1.78
No storage is preferred

Capital costs (DM)	
Electrolysis	127.697
Storage	0
Total	127.697

Unit costs (DM Nm^{-3})	
Power	0.478
Other operating	0.072
Capital (elec.)	0.252
Storage (total)	0.000
Total	0.801

Results – electrolysis versus other processes

1984

	Unit costs (DM Nm^{-3})	*Capital costs (DM)*
Electrolysis	0.629	251.226
Gas reforming	1.266	491.262
Coal gasification	2.838	1 419.077

Most economic process is electrolysis

2000

	Unit costs (DM Nm^{-3})	*Capital costs (DM)*
Electrolysis	0.801	251.226
Gas reforming	1.344	491.262
Coal gasification	2.880	1 419.077

Most economic process is electrolysis

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[a] Investment costs for all three processes and energy costs for the electrolysis route are set constant through the time from 1984 to the year 2000. As most important variable changing costs for coal and natural gas are taken into account and the price of electrical energy, being the reference, is virtually taken to be the same 1984 and 2000. The relative costs for methane and coal are supposed to increase by 23% during those 16 years.

Table 12. Economic evaluation of H_2 production by different routes. Large plant/ammonia market/France 1984 and 2000

Assumptions[a]

Annual hydrogen demand (Nm^3) = 845 000 000
Cumulative offpeak power (h per year) = 5110
Industrial power (h per year) = 8200
Maximum consecutive offpeak hours = 5110
Maximum consecutive indust. hours = 8200
1984 price of offpeak power (DM kWh^{-1}) = 0.0260
1984 price of indust. power (DM kWh^{-1}) = 0.0585
Hydrogen storage required Yes
Underground storage available Yes
Oxygen byproducts saleable No
1984 natural gas price (DM/GJ) = 16.54
1984 coal price (DM/GJ) = 6.73

Offpeak operation		*Continuous operation*	
Plant output ($Nm^3 h^{-1}$)	= 165 362	Plant output ($Nm^3 h^{-1}$)	= 106 692
Current density ($kA\,m^{-2}$)	= 12.5	Current density ($kA\,m^{-2}$)	= 8.6
Cell voltage (V)	= 1.81	Cell voltage (V)	= 1.71
Underground storage is preferred		No storage is preferred	
Capital costs (DM)		*Capital costs (DM)*	
Electrolysis	403 663 103	Electrolysis	315 392 333
Storage	191 979 650	Storage	0
Total	595 642 752	Total	315 392 333
Unit costs (DM Nm^{-3})		*Unit costs (DM Nm^{-3})*	
Power	0.115	Power	0.245
Other operating	0.017	Other operating	0.037
Capital (elec.)	0.112	Capital (elec.)	0.088
Storage (total)	0.058	Storage (total)	0.000
Total	0.303	Total	0.369
Offpeak operation is more economic			

Results – electrolysis versus other processes

1984	*Unit costs (DM Nm^{-3})*	*Capital costs (DM)*	*2000*	*Unit costs (DM Nm^{-3})*	*Capital costs (DM)*
Electrolysis	0.303	595 642 752	Electrolysis	0.369	595 642 752
Gas reforming	0.324	171 071 590	Gas reforming	0.398	171 071 590
Coal gasification	0.287	494 163 169	Coal gasification	0.328	494 163 169
Most economic process is coal gasification			Most economic process is electrolysis		

[a] Investment costs for all three processes and energy costs for the electrolysis route are set constant through the time from 1984 to the year 2000. As most important variable changing costs for coal and natural gas are taken into account and the price of electrical energy, being the reference, is virtually taken to be the same 1984 and 2000. The relative costs for methane and coal are supposed to increase by 23% during those 16 years.

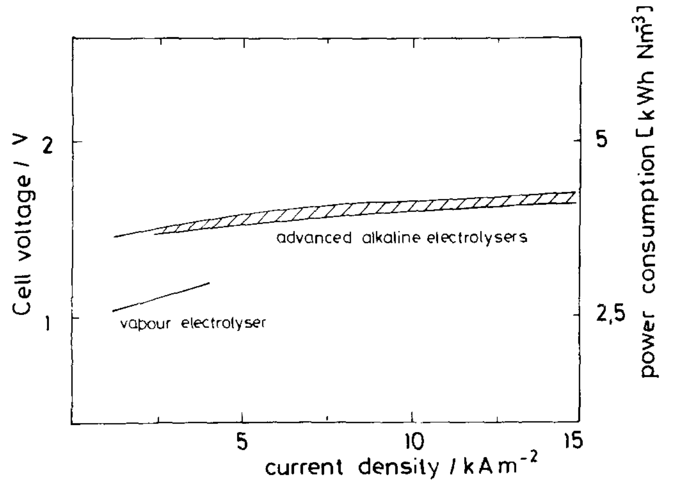

Fig. 7. Comparison of current density–cell voltage correlation for advanced alkaline water electrolysers and high-temperature steam electrolysis.

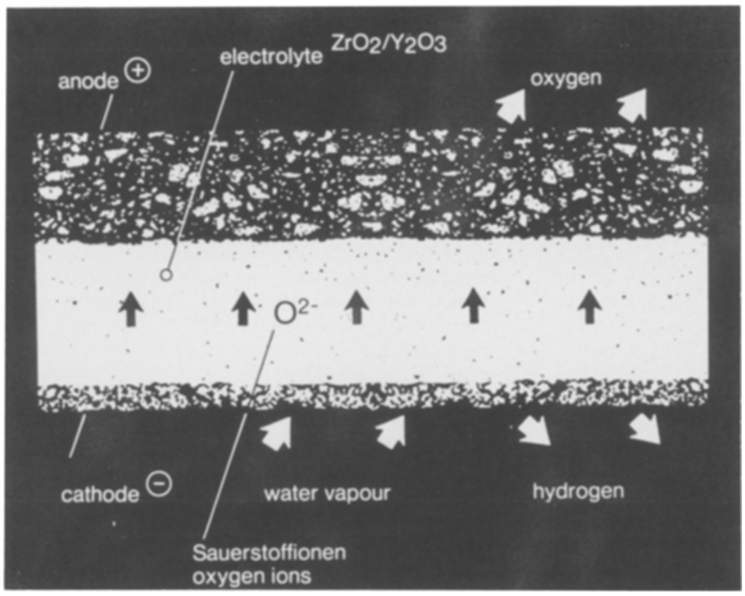

Fig. 8. Cross section of a unit comprising solid electrolyte (ZrO_2) together with porous anode and cathode for high-temperature steam electrolysis.

The study compares hydrogen production costs by electrolysis with H_2 generation by gas reforming and coal gasification and includes storage costs (for instance for small-scale use it is liquid H_2, whereas for very large production it is stored underground) into the calculation. As an example, Table 11 compiles the calculated costs for a small plant (case i) for 1984 and the year 2000 with the result that, already, H_2 production by electrolysis is the most cost-efficient method.

In Table 12 the data for a large ammonia plant are given which demonstrate that, at present, coal gasification would be more advantageous, but which predict an advantage for electrolytic hydrogen at the turn of the century. A sensitivity study shows that the electrolysis would be rendered uneconomic if any of the following events were to occur separately:

(i) higher basic costs for electrolysis cells,
(ii) less favourable scale-up behaviour than anticipated,
(iii) all equity funding by the developer,
(iv) lower price for natural gas,
(v) higher electricity costs.

8. General terms of programme and dissemination of knowledge

During the performance of the two research and development programmes on hydrogen electrolysis the Commission emphasized the free exchange of information between the contractors by contractors meetings and the dissemination of the results achieved by printed communications and public seminars. It was always the aim to transmit important achievements to interested laboratories, firms and industries. The success of this policy is reflected by observable advances in established hydrolysis techniques and the emergence of new technologies and products.

9. Concluding remarks

The R & D programme of the Commission of the European Communities has already made an observable impact on industrial innovation in the field of water electrolysis. Moreover, it is expected to influence the technology for off-peak electricity use planned by EdF and GdF in France for the coming decade.

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