

protons. With the formation of ${}^4\text{He}$, each neutron is bound to a proton, bringing the helium abundance to 24% against 76% for hydrogen. The correspondence is impressive.

All these phenomena developed in the primordial Universe over a very short time scale, as shown in Table 1.

The best expression for dating the successive temperatures $T(t)$, seems to be: $R(t_0)/R(t)$ where t_0 is the present age of the Universe, since from the relation $RT = cte$, we obtain:

$$T(t)/T(t_0) = R(t_0)/R(t)$$

where $T(t_0) = 3 \text{ K}$.

The age itself, in seconds or in years, is obtained by the choice of the function $R(t)$, according to a Friedmann model or with the help of the total density of the Universe at this moment — a function of the temperature $T(t)$. Moreover, the well known relation for cosmological redshift z :

$$1 + z = R(t_0)/R(t)$$

shows finally that, for large values of $R(t_0)/R(t)$, the value of $T(t)$ is a good approximation for the redshift of a cosmic object which could be hypothetically observed in that phase of the Universe. As an example, it may be considered that matter condensation has a redshift of 10^{13} , whereas the largest redshifts observed today (in quasars) are three or four only!

Are the fascinating phenomena of the primaeval Universe observable? Perhaps, if to-morrow, astrophysicists develop a neutrino astronomy or a graviton astronomy. But today, the answer is unfortunately negative, as optically, a physical horizon exists at $z = 1000$ and $T = 3000 \text{ K}$, the photon opacity of the Universe.

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Johannes Kepler University Linz

In the Faculty of Technical and Natural Sciences (Technisch-Naturwissenschaftliche Fakultät) of the Johannes Kepler University, Linz, Austria, the position is vacant for a

Full Professor in Biophysics

The candidate for this post will be expected to devote his research activities to experimental membrane biophysics as his main effort. His teaching should be focused on courses which enable graduate students in physics, chemistry, computer sciences and mathematics to acquire knowledge in biophysics. He should be proficient in German.

Applications including a curriculum and a list of publications should be sent before 30 October 1981, to:

Prof. Dr. Bruno Buchberger
Dean (Dekan) of the Faculty,
Altenbergerstr. 69, A-4040 Linz

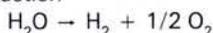
Hydrogen Production by Water Electrolysis

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Hydrogen gas is used in large quantities as a raw material in chemical industries. The present need of $\sim 25 \text{ Mt/a}$ is almost entirely extracted from hydrocarbon fuels by reaction with water. The driving force for the reaction in the steam reforming process which liberates four moles of H_2 from one mole of CH_4 and two moles of H_2O , is part of the energy stored in the natural gas. With the increasing cost of fossil fuels, processes will become competitive which produce hydrogen from water using nuclear or solar energy as the driving force.

The enthalpy change ΔH for the water splitting reaction



equals 270 KJ/mol at room temperature. This high energy input for the production of 1 mol of hydrogen (2 g) is one reason why hydrogen has been discussed as a potential synthetic fuel for future energy systems: hydrogen has the highest energy storage density by weight achievable with a chemical fuel. Moreover hydrogen, burnt to form water is an environmentally clean fuel.

Physicochemical Background

According to chemical thermodynamics, the enthalpy ΔH is composed of a free enthalpy term ΔG and an entropy term $T\Delta S$:

$$\Delta H_{(T)} = \Delta G_{(T)} + T\Delta S_{(T)}$$

$\Delta G_{(T)}$ and $T\Delta S$ denominate the relative amounts of work and heat that are thermodynamically necessary for the reaction to proceed at a given temperature T . Fig. 1 shows how ΔH and ΔG depend upon temperature; the energy scale is in electron volts and corresponds to the electrochemical potential scale. The free enthalpy

decreases with temperature, indicating that at temperatures high enough ($> 3000 \text{ K}$) ΔG becomes negative and direct thermal water splitting would be possible, provided resistant materials and a high temperature energy source were available.

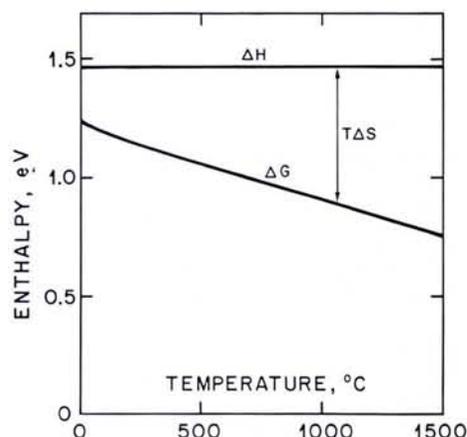
The most straightforward way to overcome the positive ΔG at reasonable temperatures is by driving the reaction in an electrochemical cell, consisting of two electrodes immersed in an aqueous electrolyte (Fig. 2). A current flowing in the direction indicated in Fig. 2 produces oxygen at the anode and hydrogen at the cathode. The cell voltage is a function of the current density

$$U = U^0 + \eta_a(i) + \eta_c(i) + Ri$$

where η_a , η_c are overvoltages due to reactions at the electrodes. Extrapolation to zero current yields the reversible cell voltage U^0 which gives the free enthalpy ΔG of the reaction. U^0 at room temperature for the water splitting reaction is 1.23 V (see Fig. 1).

Electrolysis is thermodynamically possible at cell voltages above 1.23 V at room temperature. The rate of electrolysis depends on the functions η_a and η_c describing the kinetics of the electrode reaction at the anode and cathode, and on the ohmic resistance R of the cell. The difference between the actual and reversible cell voltages multiplied by the current i gives the amount of electricity which is transformed into heat. As the process itself consumes heat ($T\Delta S$), some of the waste

Fig. 1 — Dependence on temperature of the thermodynamic functions ΔH , ΔG , and $T\Delta S$ for the water splitting reaction.



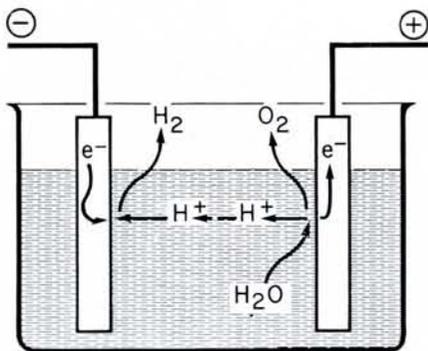


Fig. 2 — Schematic representation of the electrochemical process involved in a water electrolysis cell.

heat is stored in the hydrogen produced and thus not actually wasted. The voltage corresponding to ΔH is 1.47 V at room temperature and is called the thermoneutral voltage. At higher voltages heat has to be removed from the cell.

In electrochemical kinetics, the overvoltages η_i are related to the current density by an expression (Tafel's equation) which may be written in simplified form as

$$\eta = a + b \log i$$

where a and b are characteristic parameters for the kinetics of a given electrode reaction. They depend on the structure of the electric double layer, the solvation of the reacting species in the electrolyte phase and, if more than one electron is transferred in the reaction, on the adsorptive properties of the electrode surface for intermediate species. In the latter case, i.e. when the overall reaction rate is mainly governed by the activation energy of adsorbed intermediates, we become concerned with heterogeneous catalysis, or more specifically, with electrocatalysis. Electrocatalysis is involved in both the hydrogen and oxygen evolution reactions, the formation of H_2 requiring two and the formation of O_2 four consecutive electron transfers. This means that the current-voltage characteristics of a water electrolysis cell depend strongly on the electrode materials. The overvoltage of the hydrogen evolution reaction at a current density of 1 mA/cm² may vary from 0.02 V for platinum to 1.0 V for mercury. Platinum is the best known catalyst for the hydrogen evolution reaction.

The search for a good electrocatalyst for the oxygen evolution reaction is complicated by the fact that no metals are stable at the electrode potentials involved. Oxides, which fulfil the following conditions have to be used: electronic conductivity, preferably metallic, and stability against anodic corrosion. The best known catalysts are RuO_2 , IrO_2 in acid and Ni-based mixed oxides in base. RuO_2 shows an overvoltage of ~ 200 mV at 1 mA/cm² at room temperature, which is considerably higher than the values for the best hydrogen electrodes. It is questionable whether better catalysts can be found, since the irrever-

sibilities associated with oxygen reactions are almost intrinsic (transfer of four electrons!).

At high current densities the ohmic resistance R of the cell determines the slope of the current-voltage curve. R depends on the bulk conductivity of the cell components, especially the electrolyte, and can be influenced by optimizing the cell design. Increasing temperature decreases the overvoltages as well as the ohmic resistance of the electrolyte.

Present Situation

Hydrogen production by water electrolysis has been an industrially established technology for 70 years. Today water electrolysis is used only in special cases, i.e. when either the cost of electricity is very low (remote hydropower) or is not decisive for small scale applications.

Electrolytic hydrogen production is at present only about 1% of the overall hydrogen needs. The future share produced by water electrolysis will be determined by the relative economics of the fossil fuel competitors, that is, steam reforming and coal gasification. The economics of established water electrolysis technology can be improved considerably as is shown below.

The traditional technique uses an aqueous solution of KOH as electrolyte. The electrodes are made from steel (cathode) and Ni plated steel (anode) and to keep the gases separate an asbestos diaphragm is introduced between anode and cathode. An electrolyzer is formed by a stack of up to 80 cells connected electrically in series. The largest units have an output of 300 m³/h of hydrogen gas. The cells have electrode areas of the order of 1 - 4 m² and are operated at a current density of 2 kA/m², at a temperature of 80°C and with a specific energy consumption of ~ 4.9 kWh/m³ of hydrogen. This corresponds to a cell voltage around 2.0 - 2.1 V. Comparing these values with the reversible cell voltage of 1.23 V or the thermoneutral voltage of 1.47 V, shows that there must be considerable losses associated with the process.

Development Goals

A number of so-called advanced water electrolysis systems are under development at different laboratories. The work concentrates on systems operating at elevated temperature, on improved cell designs including the use of solid electrolytes and on electrocatalysis, with the goal of producing lower cell voltages. The optimum current density, which determines the cell voltage of a given system, is governed by an economic balance of investment cost vs. energy cost. For sufficiently large units, the investment cost is roughly proportional to the overall electrode surface of the system. Reducing investment cost thus means increasing the current density. As any advanced electrolysis system needs a more

complex design and more expensive materials than the present technology to attain the efficiency goals, increased current density is a precondition for meeting the economic goals. The systems under development aim at current densities of 10 kA/m² or more, i.e. more than five times the current density of today's techniques.

Three technically different main development routes have been followed in recent years. They are generally classified by the choice of electrolyte:

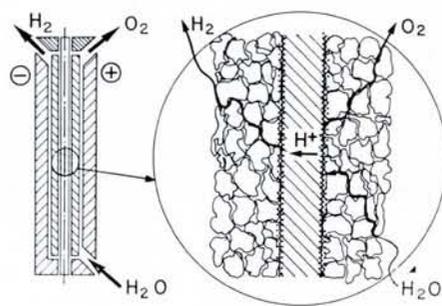
- Advanced alkaline electrolysis
- Solid polymer electrolyte (SPE) electrolysis
- High temperature electrolysis using a ceramic solid electrolyte.

Advanced Alkaline Water Electrolysis

The most obvious way to decrease the specific power consumption of the traditional KOH technology is to raise the temperature of operation, because both activation and ohmic losses decrease with temperature. Without any additional catalyst on the Ni-electrodes, temperatures of 200°C in a pressurized system are sufficient to achieve a specific power consumption of 4.3 kWh/m³ at a current density of 15 kA/m². Asbestos and Ni-plated steel are not stable against caustic corrosion at temperatures above 120°C. The problem in running an electrolysis at 200°C is mainly to find corrosion resistant materials for the electrolyzer and peripheral apparatus as a whole. Only bulk nickel has been shown to meet stability requirements at 200°C in 30% KOH. Porous nickel sheets have been proposed as separators in such cells, the stability of porous structures in this environment being still somewhat questionable.

The choice of usable materials increases with decreasing operating temperature, but the cell performance has then to be improved by catalyst-covered electrodes to meet efficiency goals. Most actual work on advanced alkaline electrolysis concentrates on systems in the temperature range of 120-150°C. Separator materials based on K_2TiO_3 or K_2TiO_3 -hydrophilized PTFE seem to be suitable substitutes for asbestos. Ohmic loss can be reduced by more compact cell design. The most promising electrocatalysts for alkaline systems are all bas-

Fig. 3 — SPE cell, principle of operation.



ed on nickel. For the anode reaction mixed oxides of nickel with Co or La, are reported to show high activity and for the cathode, Raney nickel, nickel sulphide and nickel boride are suggested. The most critical problems with these catalysts are a marked decrease in activity with time of operation and, in some systems, instability under open circuit conditions. Catalyst ageing and the loss of activity may have several causes:

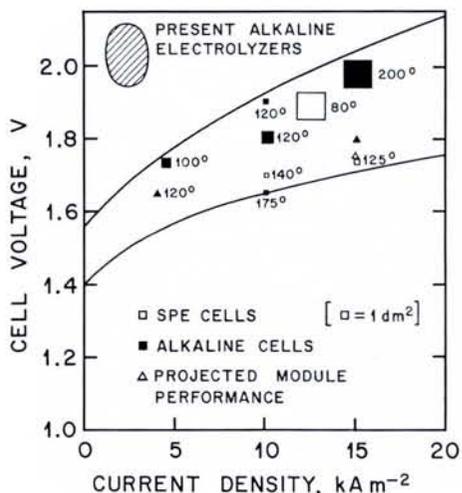
- 1) Poisoning by impurities of the feed water and/or corrosion products. The cathode is particularly sensitive to poisoning.
- 2) An intrinsic deactivation due probably to reconstruction of surface defects.
- 3) A loss of active surface area owing to the sintering of catalyst particles.
- 4) Mechanical loss of catalyst particles caused by gas bubbles and/or electrolyte flow.

Solid Polymer Electrolyte (SPE) Electrolysis

A new type of ion exchanging membrane based on a chemically stable fluorocarbon polymer is at the origin of a recent electrolysis development, known as the solid polymer electrolyte (SPE) technique. The membrane consists of a PTFE backbone polymer with sulphonic acid groups attached to side-chains. Contacted on both sides by suitable porous electrodes, the membrane immersed in pure water acts as electrolyte and separator for the gases (Fig. 3). The process established on this membrane concept offers a number of technical advantages:

— The direct bonding of the electrode materials to the solid electrolyte defines a small and uniform electrolyte gap of 0.1-0.2 mm thickness which minimizes ohmic resistance and hence is favourable to high current density operation.

Fig. 4 — Performance of alkaline and SPE electrolysis systems. Shaded area: present alkaline technique. The size of the squares symbolizes the size of the cells for which data were reported in 1980 (compiled from Refs. 1 and 2).



— Gas bubbles evolve on the back of the electrodes, and cause no increase in electrolyte resistance at high current densities.

— The peripheral apparatus (gas-liquid separators, tubing, pumps, etc.) is operating with deionized water, rather than strong alkali.

— Catalysts are embedded in the polymer matrix and are shielded from mechanical wear and poisoning.

SPE membranes can be used at temperatures up to 150°C on permanent load in a pressurized system.

The main problems with SPE technology arise from the acidity of the membrane which restricts the choice of materials directly in contact with it. The catalysts used are noble metal based. In order to obtain optimal use of the catalysts, preparation techniques of the catalyst-polymer-interface are of prime importance.

High Temperature Electrolysis

Like the SPE technique the high temperature electrolysis uses a solid electrolyte (both techniques come from fuel cell technology developed during the sixties). The electrolyte is an oxygen ion conducting zirconia ceramic tube in contact with porous electrodes. The cell operates with a feed of superheated water vapour at temperatures around 1000°C. At these temperatures, the reversible cell potential (i.e. ΔG) is considerably reduced (from 1.23 V at room temperature to about 0.9 V at 1000°C). Activation overvoltages are practically non-existent. Losses are predominantly ohmic, given by the bulk resistance of the oxygen conductor.

The main problems with this technique are related to scaling up to production or even semi-production size: thermal stability, interconnection materials etc. In contrast to the advanced alkaline or SPE methods, it is still considered to be far from technical realisation.

Development Status of Advanced Water Electrolysis

From the presentations that were made at the 3rd World Hydrogen Energy Conference in Tokyo 1980¹, it could be deduced that advanced alkaline and SPE electrolysis have both reached a state of development beyond the research and laboratory scale. Units of up to some 100 kW of output are under test in facilities in Europe, US and Japan. Fig. 4 shows a collection of reported data of projected, laboratory scale ($\leq 1 \text{ dm}^2$) and scaled-up cell performances. There is still quite a gap between the demonstrated performance of laboratory cells and that reported for 100 kW units.

Generally it seems that the performance of the first generation of advanced electrolyzers will be in the order of 4.3 kWh/m³ H₂ at current densities of 10 - 15 kA/m². SPE cells are expected to be slightly superior in performance compared to alkaline systems.



PROFESSORSHIP IN THEORETICAL PHYSICS

The University of Zurich (Switzerland) announces a vacancy for a Professor of Theoretical Physics. The appointee is expected to work in an important field of research (e.g. astrophysics, particle physics, statistical physics or solid state/condensed matter physics). He should have a broad knowledge of general physics which allows him to participate in the task of teaching theoretical physics to students of experimental and theoretical physics. Candidates who are not older than 40 are preferred.

Letters of application, together with a curriculum vitae and a list of publications should be addressed to:

Prof. Dr. K. Ströbel,
Dekan der Phil. Fakultät II,
Universität Zürich,
Rämistrasse 71,
CH-8006 Zürich.

Applications should arrive not later than 31 December 1981.

Those wishing to draw the faculty's attention to potential candidates are invited to write to the same address.

Efforts are still required in the following areas: engineering of large cells to overcome scaling up effects, long term stability of all components, further research in electrocatalysis.

As was stated above, the break-even point of the cost of electrolytic hydrogen with that of hydrogen from fossil sources will depend on a set of economic factors, but it is expected that advanced electrolysis will become available on a technical and commercial scale in the second half of this decade. An efficient electrolysis process will be a powerful instrument for the increasingly important substitution of fossil energy resources.

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