

REVIEW

# *Advances in water electrolysis technology with emphasis on use of the solid polymer electrolyte\**

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Efforts to improve water electrolysis technology are being made using three promising approaches: (a) development of solid polymer electrolyte (SPE) water electrolyzers, (b) increasing the operating temperature of alkaline water electrolyzers from 80°C to a temperature in the range 120–150°C, and (c) investigation of advanced concepts. The research and development efforts on SPE water electrolyzers are aimed at (a) low cost current collectors, (b) high-activity electrocatalysts, (c) high temperature capability, (d) low cost SPE, and (e) design and construction of scaled-up cell stacks. Attempts are being made to find materials for cells and auxiliaries which are stable in an alkaline environment at elevated temperatures. Advanced concepts for electrolytic hydrogen production, including (a) finding better reversible electrocatalysts, (b) use of anode depolarizers, (c) water vapour electrolysis in molten or solid electrolytes, (d) development of hydroxyl ion transporting membranes, (e) investigation of thermochemical–electrochemical hybrid cycles, and (f) photoelectrolysis of water, are still at a preliminary research stage.

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## 1. Introduction

### 1.1. *Present status and the need for research and development on advanced water electrolyzers*

Water electrolysis, the simplest method for producing pure hydrogen on a large or small scale, is a well-developed technology, particularly in Europe. Conventional water electrolyzers are constructed with a bipolar configuration in which a series of electrodes is arranged, vertical and parallel to one another. A gas separator is incorporated between two adjacent electrodes to form a hydrogen chamber on one side and an oxygen chamber on the other [1]. The electrolyte is circulated through each electrode-separator space. By applying a voltage across the two end electrodes, each intermediate electrode becomes bipolar, evolving hydrogen on one side and oxygen on the other.

At the present time, only the Lurgi water electrolyzers operate at elevated pressure (about 30 atm), with Ni as the electrocatalyst for hydrogen and oxygen electrodes. The gases evolved in pressurized cells are convenient for direct storage or utilization for some chemical processes (e.g.,  $\text{NH}_3$  production). With increasing pressure, the size and number of ascending gas bubbles in the electrolyte decrease. Thus, ohmic losses (i.e.,  $IR$ -drop) in the solution are reduced. As a result of the reduction of ohmic losses, higher voltage efficiencies are obtained in pressure electrolyzers. In addition, pressure electrolysis cells provide the capability to operate at a temperature in the range of 120–150° C, where a voltage efficiency (based on  $\Delta H$ ) close to 100% can be achieved at the desired operating current density of about 200  $\text{mA cm}^{-2}$  [2]. The thermoneutral potential of a pressure electrolysis cell is slightly higher than 1.48 V because the  $\int PdV$  term increases the reversible potential of water electrolysis under elevated pressure conditions. In an electrolyser operating at 35 atm gas pressure and at 120° C, for example, the thermoneutral potential of water electrolysis is about 1.56 V [3].

In spite of the advantages previously mentioned, commercial pressure water electrolyzers, operating in concentrated (25–35 wt%) alkaline solution at 70–90° C, exhibit voltage efficiencies ranging from 65–75% at practical current densities of about 200

$\text{mA cm}^{-2}$ . The poor efficiency and low operating current density are the reasons for the high capital costs of water electrolyzers and the high production costs of electrolytic hydrogen, as compared to the cost of hydrogen directly derived from natural gas or oil. With a view of minimizing the cost of hydrogen produced by water electrolysis, it is essential to improve this well-developed technology with respect to energy efficiency and capital costs [3–5].

### 1.2. *Uses of hydrogen*

The large-scale hydrogen market is mainly in the fertilizer, metallurgical, petrochemical, semiconductor, and pharmaceutical industries, where an energy equivalent of  $1 \times 10^{15}$  Btu of hydrogen is being used annually in the USA. Due to the much higher production cost of electrolytic hydrogen in comparison to hydrogen derived from fossil sources, electrolytic hydrogen is primarily used in only a few areas, such as food processing and semiconductor manufacture, which require highly pure hydrogen gas. Water electrolyzers are currently employed as oxygen generators for life-support systems in submarines and spacecrafts and as a small-scale hydrogen supplier for gas chromatographs and other laboratory apparatus. Commercial electrolysis cells are also used to provide hydrogen for cooling electricity generators. According to recent estimates, the highly expanding hydrogen market in industry will result in a demand for hydrogen to a level of  $3 \times 10^{15}$  Btu at the end of the century in the USA. However, if one takes into account the strong possibility of using hydrogen, in large quantities, as a clean fuel for fuel cells, gas turbines, and for providing thermal energy (e.g., supplementation of natural gas), this estimate will have to be significantly increased.

### 1.3. *Rationale for advanced water electrolyzers*

In order to meet the anticipated enhancement in demands for hydrogen as a chemical feedstock, as a process gas and as a clean fuel, the development of alternative techniques for bulk hydrogen generation is of crucial importance. With the continued increase in costs and dwindling availability of natural gas and oil, which are the major sources of present hydrogen, the production of hydrogen

from coal or by water electrolysis, using electricity derived from nuclear, solar, or geothermal energy, will become quite attractive in the near future. From an environmental viewpoint, hydrogen fuel derived from coal needs to be purified prior to utility application, and its cost of purification will raise its cost to approximately the same level as that of electrolytic hydrogen. In certain cases where relatively small quantities of hydrogen or oxygen are required, on-site electrolysis of water will again be more economical than the production by other methods at a central site, if the cost for the storage and transport to the site of application is included.

At present, all commercially available water electrolyzers are designed and constructed to meet quite different specifications of the small market of electrolytic hydrogen. The small-scale water electrolyzers are not economical and practical, if a large quantity of hydrogen is required. The scale-up of present electrolyzers to a level of megawatts in power inputs, without sacrificing energy efficiency and reliability of operation, will significantly lower the production cost of electrolytic hydrogen. The electrolyser depreciation raises this cost. To minimize production costs of electrolytic hydrogen, water electrolyzers should demonstrate a lifetime of at least 10 years with minimum maintenance, particularly for large-scale electrolysis systems.

#### 1.4. *Research and development activities on advanced water electrolyzers*

Aiming at the goals of increased energy efficiency, reduced capital costs and prolonged lifetime of water electrolyzers, intensive work is being carried out in the United States and Europe. The promising approaches for the improvement of electrolysis technology are mainly in three different areas: (a) development of solid polymer electrolyte (SPE) water electrolyzers, capable of operation at high current density ( $1 \text{ A cm}^{-2}$ ) and cell voltage ( $1.6 \text{ V}$ ) close to the thermoneutral potential; (b) increasing the operating temperature of conventional alkaline water electrolyzers from  $80^\circ \text{C}$  to a temperature in the range of  $120\text{--}150^\circ \text{C}$ ; and (c) investigation of advanced concepts for hydrogen production. The progress made until the present time and the needed research and development

activities in each of these areas, with the aim of making the cost of electrolytic hydrogen comparable with that of the presently used methods, are briefly presented in the following sections.

## 2. Development of solid polymer electrolyte water electrolyzers

### 2.1. *Design of cell and performance characteristics*

The development of highly efficient solid polymer electrolyte (SPE) water electrolyzers is being actively conducted at General Electric Co. More recently it has also been initiated at Brown Boveri Research Center, Baden, Switzerland. The General Electric SPE water electrolysis cells are designed and fabricated closely following the technology originally developed for space fuel cells, which were used to provide electrical power for the Gemini spacecraft in the 1960's. At present, small-scale SPE water electrolyzers are commercially available for providing oxygen in spacecrafts and submarines or as hydrogen generators for laboratory uses (e.g., for gas chromatographs). However, the present costs of SPE cells are considerably higher than those of conventional alkaline water electrolyzers.

In SPE cells, a solid sheet of perfluorocarbon sulphonate cation exchange membrane (i.e., Nafion) of 10–12 mil\* in thickness is used as the electrolyte (see Fig. 1). Charge carriers in the membrane are hydrated hydrogen ions ( $\text{H}^+ \cdot x\text{H}_2\text{O}$ ) which move through the solid electrolyte by passing from one fixed sulphonic acid group to the adjacent one. Teflon bonded Pt black (for the cathode) and noble metal alloy (for the anode), in the form of fine particles are pressed, using a proprietary procedure, onto each face of the SPE membrane. A stable conductive material, used as a separator between the anode chamber of one cell and the cathode chamber of the adjacent cell, also serves as a current collector in a bipolar configuration.

While operating an SPE water electrolyser, deionized pure water is circulated, at a sufficiently high flow rate to remove the waste heat, through the anode chamber where it is decomposed electrochemically, producing oxygen gas, hydrogen

\*1 mil = 0.001 in.

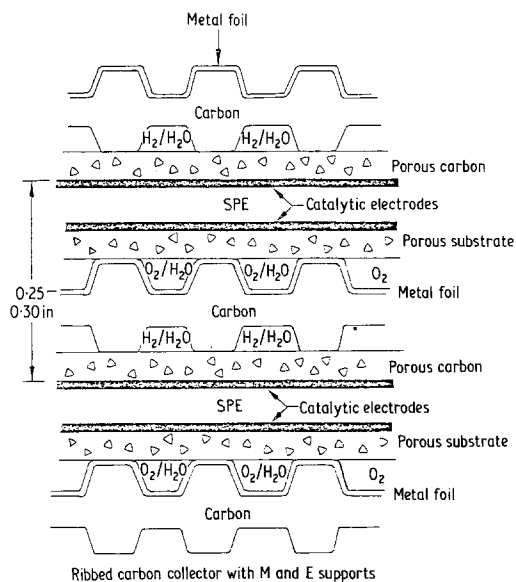


Fig. 1. Schematic representation of two SPE single cells, connected in series. (M = membrane, E = electrode)

ions, and electrons. The hydrogen ions move through the SPE and recombine electrochemically with electrons, which pass via the external circuit, to form hydrogen gas in the cathode chamber. Due to the maximization of active surface areas of the electrodes and the minimization of inter-electrode spacing, the General Electric SPE water electrolyzers are capable of operation at current densities of over  $1 \text{ A cm}^{-2}$ , which is at least five times higher than the production rate of hydrogen in conventional alkaline water electrolyzers, using a voltage input of 1.9–2.0 V at  $80^\circ \text{C}$  and of about 1.6 V at  $150^\circ \text{C}$ . Fig. 2 illustrates a comparison of

the performances of a General Electric SPE cell and of commercial alkaline water electrolyzers [6].

## 2.2. Economic considerations

The estimated capital cost of SPE water electrolyzers has been reduced from about \$260 to \$90 per square foot of active electrode area in the past two years [6]. The hydrated SPE, used in the water electrolyzers, is highly acidic with a pH equivalent to a 10 wt%  $\text{H}_2\text{SO}_4$  solution [7]. Thus, noble metal electrocatalysts and current collector materials with high corrosion resistance are required. At present, more than 90% of the capital cost of an SPE water electrolyzer is for Nafion membranes, electrocatalysts, and current collectors.

The ultimate goals for the development of SPE water electrolysis systems at the General Electric Company are to achieve, within the next five years, an overall system efficiency of  $\sim 90\%$  and a capital cost of about \$80/kW, including costs of electrolysis cells, installation, power conditioner, and accessory components. The SPE water electrolyzers, operating at a temperature of  $\sim 150^\circ \text{C}$  and a pressure of  $\sim 40 \text{ atm}$  are expected to exhibit a cell voltage of  $\sim 1.58 \text{ V}$  (i.e. a voltage efficiency of  $\sim 93\%$ ) at a current density of  $\sim 1 \text{ A cm}^{-2}$ . It is projected that a 500 kW electrolysis system will be completed in 1981 and a 5 MW system in 1982. To achieve further reduction in capital costs and improvement in the performance of SPE water electrolyzers, major

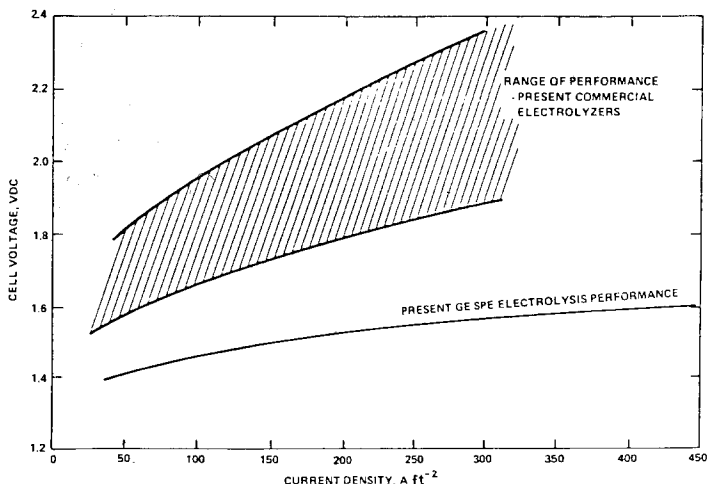


Fig. 2. A comparison between the performance of an SPE cell and that of present commercial water electrolyzers.

efforts are necessary for the development of (a) highly active and stable electrocatalysts, (b) low cost current collectors, (c) high temperature/high pressure capability, (d) low cost SPE, and (e) optimum cell configuration.

### 2.3. Investigation on electrocatalysts for SPE water electrolyzers

The slowness of the oxygen evolution reaction results in a significant efficiency loss in water electrolyzers. Attempts have been extensively made in finding more reversible oxygen catalysts. With a view to lowering the capital costs of SPE cells, advanced techniques are being developed to reduce the loading of noble metals from the present  $4 \text{ mg cm}^{-2}$  to a desired goal of  $0.18 \text{ mg cm}^{-2}$  on the anode and of  $0.02 \text{ mg cm}^{-2}$  on the cathode with minimum loss in the cell performance. Binary and ternary alloys of Pt, Ir, Ru, and other transition metals (e.g., Ti, Ta, Nb, Zr, W), as well as the electrocatalysts prepared by the reduction of mixed oxides of noble metals, have been investigated for oxygen evolution in SPE water electrolyzers. A proprietary catalyst of reduced mixed oxide (designated as E-50 at General Electric), having a BET surface area in the range of  $40\text{--}160 \text{ m}^2 \text{ g}^{-1}$ , shows an oxygen overpotential of approximately  $400 \text{ mV}$  less than that on Pt black at a current density of  $\sim 200 \text{ mA cm}^{-2}$  and at  $49^\circ \text{ C}$  [7].

For the oxygen evolution reaction from acidic media, Ir exhibits higher electrocatalytic activity

than Pt. The optical and electrochemical analysis of oxide films formed on Ir have been carried out in  $1 \text{ N H}_2\text{SO}_4$  solution using combined ellipsometric and reflectometric measurements [8]. An oxide film of thickness over  $200 \text{ nm}$  can be grown on Ir by potential multicycling between  $0.0\text{--}1.5 \text{ V}$  versus RHE. By increasing the polarization potential into the region for oxygen evolution, the thick oxide film shows an absorption coefficient typical for semiconductors ( $\hat{n}_f = 1.43 - 0.10i$  at  $1.50 \text{ V}$ ). As illustrated in Fig. 3, this thick semiconducting oxide film on the Ir electrode exhibits a lower Tafel slope and a lower oxygen overpotential, as compared to the electrode which is not covered by an oxide film. (The oxide film on Ir can be completely removed by anodic polarization at potentials above  $1.65 \text{ V}$ , as detected by the ellipsometric measurements.)

In acidic media, Ru is superior to Ir as an  $\text{O}_2$  electrocatalyst. As seen from Fig. 4, the overpotential for oxygen evolution at  $1 \text{ mA cm}^{-2}$  from  $1 \text{ N H}_2\text{SO}_4$  solution at  $20^\circ \text{ C}$  is only  $\sim 210 \text{ mV}$  on Ru, while at the same current density, Pt and Ir show oxygen overpotentials of  $\sim 640$  and  $\sim 360 \text{ mV}$ , respectively. Ellipsometric studies [9] revealed that the oxide film formed on Ru during the oxygen evolution, is highly light-absorbing and is thus an excellent electronic conductor. At constant potentials below  $1.43 \text{ V}$ , the current densities for oxygen evolution on the Ru electrode are practically stable after a polarization time of  $\sim 15 \text{ min}$ , yielding a Tafel slope of  $\sim RT/2F$ . However, it was observed that ruthenium oxide ( $\text{RuO}_x$ ) film dissolves at potentials above  $1.44 \text{ V}$ .

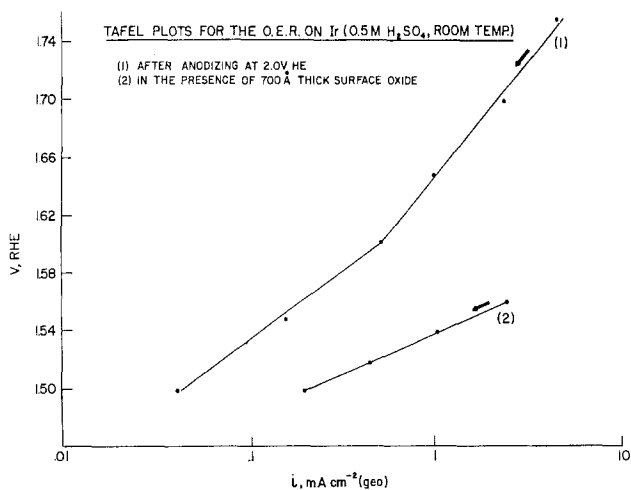


Fig. 3. Effect of pre-treatment of Ir electrodes on Tafel plots for oxygen evolution.

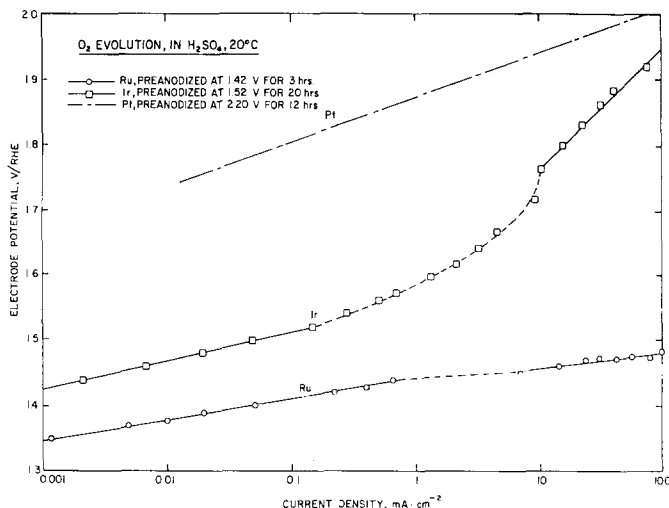


Fig. 4. Tafel plots for oxygen evolution on pre-anodized Pt, Ir, and Ru electrodes in 1 N H<sub>2</sub>SO<sub>4</sub> solution.

Preliminary studies on the electrocatalytic activities of Ru alloys indicate that binary alloys, consisting of Ru and transition metals, show significant improvement in the initial performance for oxygen evolution, but the oxygen overpotentials on these alloys increases rapidly with the polarization time, essentially due to the anodic dissolution of the Ru component. Since RuO<sub>x</sub> is less expensive than the mixed oxide of Pt and Ir, techniques for the stabilization of RuO<sub>x</sub> are being developed to achieve low cost and high-activity anode catalysts for SPE water electrolyzers.

In the research and development of hydrogen catalysts for SPE cells, focus has been mainly on the reduction of noble metal loadings through use of graphite or transition metal silicide supports. Prior to being fabricated into an electrode structure, graphite or silicide in the form of powder is sputtered with platinum to increase both the electronic conductivity and the electrocatalytic activity. Two SPE water electrolysis cells, which were made using platinum sputtered on graphite of loading 0.25 and 1.0 mg cm<sup>-2</sup>, respectively, as the cathodes, showed a cell voltage only 30 mV higher than the baseline cell with a cathode, composed of pure Pt black of loading 2 mg cm<sup>-2</sup>, at ~ 1 A cm<sup>-2</sup> and at 80°C [7]. However, the SPE cell, using silicide as a diluent of noble metal on the cathode, exhibited an extremely poor performance, possibly due to the high impedance of this material.

#### 2.4. Current collector development

In the SPE water electrolyzers, a bipolar current collector serves mainly as (a) a conductor for the electron transfer from the oxygen electrode of one cell to the hydrogen electrode of the adjacent one, (b) a separator of the hydrogen and oxygen gases evolved in the cathode and anode chamber, respectively, and (c) a mechanical supporting plate of the SPE membrane under operational differential pressures. At the present time, about 34% of the capital costs of SPE water electrolyzers is for the fabrication of current collectors. The criteria for the selection and evaluation of reliable and economical current collector materials include (a) high electric conductivity, (b) low contact resistance with the electrocatalysts on both sides, (c) sufficient corrosion resistance under operating conditions, (d) capability of being impervious to hydrogen and oxygen, (e) low fabrication costs, and (f) prolonged lifetime.

In the earlier studies on anode current collectors, emphasis was on the reduction of contact resistance of some transition metals or alloys, which show extremely high corrosion resistance in acidic media. Niobium and Ti-0.2 wt% Pd, coated with a thin layer of Pt, exhibit contact resistances as low as that of gold [10]. In the hydrogen chamber, a small fraction of hydrogen evolved on the electrode may diffuse into the crystal lattice of the collector materials. Thus, hydrogen embrittle-

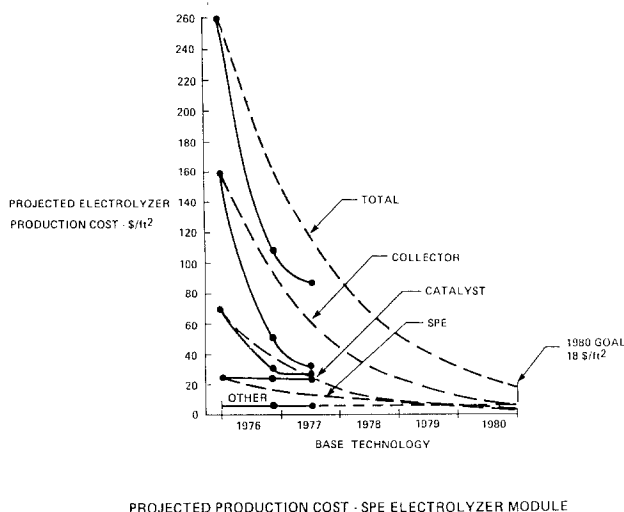
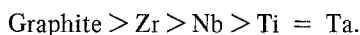


Fig. 5. Projected (dashed lines) and actual (solid lines) fabrication costs of GE SPE water electrolyser and its components.

ment takes place on cathode current collectors and then results in the performance degradation of SPE water electrolyzers. According to the work of Laconti, Fragala, and Boyack [7], the resistance to hydrogen embrittlement of some potential candidate materials, which have been investigated as cathode current collectors in SPE cells, is in the following order:



At present, moulded carbon current collectors are of particular interest, substantially due to the low cost of this material [6]. More specifically, the application of carbon current collectors on both cathode and anode sides has considerably reduced the costs of current collectors to less than 1/5 of the costs of 1975 (see Fig. 5). With a view to improving corrosion resistance, electronic conductivity, mechanical strength, and fabrication costs, more efforts are being made in developing advanced techniques for the fabrication of moulded current collectors.

### 2.5. High-temperature capability

Most of the commercial SPE water electrolyzers operate at  $\sim 80^\circ\text{C}$ . It has been reported [7] that, at a current density of  $\sim 1\text{ A cm}^{-2}$ , an increase of the operating temperature from  $80^\circ\text{C}$  to  $\sim 150^\circ\text{C}$  results in an improvement of 150 mV in the cell voltage. In association with the increase of operation temperature, the anticipated drawbacks or disadvantages mainly include: (a) increased para-

sitic loss arising from the diffusion of product gases through the SPE membrane, (b) additional SPE support required to prevent the membrane creeping, (c) difficulties in finding chemically and mechanically stable materials for use as gaskets, sealants, and cell frames, and (d) an enhancement of hydrogen embrittlement effect on the cathode current collectors.

According to some estimates, the diffusion loss of hydrogen generated in the cathode chamber is  $\sim 8\%$  if an SPE cell operates at a temperature of  $\sim 150^\circ\text{C}$  and a pressure of  $\sim 40\text{ atm}$ . Some promising materials such as fluorosilicones, fluorocarbons, fluorochlorocarbons, lexan, polysulphone, and silicones are being evaluated as gaskets at various temperatures up to  $\sim 150^\circ\text{C}$ . A 'gasketless' sealing technique, in which the SPE membrane serves directly as a gasket-type seal, capable of withstanding a pressure of over 34 atm at elevated temperatures, has been developed at General Electric. This sealing technique is being utilized to construct a 120-cell water electrolysis system. Furthermore, an SPE water electrolyser, which operates at a constant current density of  $\sim 1\text{ A cm}^{-2}$  and at  $\sim 150^\circ\text{C}$ , has been successfully tested for more than 5000 hours; it shows a voltage efficiency over 85% and a slight degradation in the cell performance.

### 2.6. Advanced studies on SPE

In order to optimize the performance and lifetime of SPE water electrolyzers, each Nafion membrane

is pre-treated, prior to being impregnated with electrocatalysts on each face, by introducing a small quantity of catalysts into the membrane. Hydrogen peroxide and certain ions such as  $\text{Fe}^{2+}$ , which are possibly present in the circulating water, have been confirmed [7] to attack Nafion structure, and consequently cause a considerable degradation of the membrane performance, particularly at elevated temperatures. Therefore, techniques for the deionization and the contamination control of feed water need be further improved. In addition, an intentional reduction of the membrane thickness in a SPE cell from conventional 12 mil to the order of 5–6 mil, results in a significant improvement of  $\sim 250$  mV in the cell voltage, while the cell operates at  $\sim 2 \text{ A cm}^{-2}$  [7]. However, the parasitic losses arising from the gas permeation through the SPE increases with the diminution of the Nafion thickness.

The present cost (about  $\$30/\text{ft}^2$ ) of Nafion membranes is too expensive for the solid polymer electrolyte water electrolysis systems to be feasible and economical for industrial and utility applications. According to some reports, the production cost of Nafion will not be lower than  $\$20/\text{ft}^2$  in the near future. Present efforts are essentially concentrated on the investigations and development of low cost SPE membranes. Some promising polymer films such as trifluorostyrene and fluorocarbon are being evaluated systematically as SPE membranes in water electrolysis. It is noted that a perfluorocarboxylic acid membrane, recently developed in Asahi Chemical, Tokyo, Japan, appears to be competitive with Nafion for use as a separator in the chlor-alkali cells. Essentially, the goal in the development of a promising alternative cation exchange membrane for SPE water electrolysis systems is to reduce the cost of SPE membranes to about 1/10 of the current price of Nafion.

### 2.7. Scale-up of SPE water electrolysis systems

Commercial SPE water electrolysis systems, available to date, consist of stacks of single cells with an active electrode area of  $0.05 \text{ ft}^2$ . For the large-scale production of electrolytic hydrogen, water electrolysis with such small electrodes are not practical and economical. Initial efforts are being made to scale-up the cell area from  $0.05 \text{ ft}^2$  to

$2.5 \text{ ft}^2$ . At the present time, the projected voltage efficiency of SPE water electrolysis is in the range of 80–85% at  $\sim 1 \text{ A cm}^{-2}$ . Major problems connected with the scale-up of active cell area are being investigated. The development of alternative techniques, used to impregnate the electrocatalysts on the surfaces of SPE membranes, and to fabricate large-size current collectors is underway. This scaling-up programme is essentially aimed at the construction of large SPE water electrolysis systems with an active cell area of about  $10 \text{ ft}^2$  (with power inputs ranging from 0.5–5 MW), which operate at temperatures of  $\sim 150^\circ \text{C}$  and pressures of  $\sim 40$  atm, generating hydrogen at an energy efficiency of  $\sim 90\%$  and capital costs of about  $\$80/\text{kW}$ .

## 3. Development of advanced alkaline water electrolysis systems

### 3.1. Proposed improvements in technology

It has been demonstrated [2] that a voltage efficiency close to 100% is attainable if the operating temperature of alkaline water electrolysis is increased from  $80^\circ \text{C}$  to about  $150^\circ \text{C}$ . More recently, the work by Appleby and Crepy [3] and by Braun [11] has confirmed that an increase of the operating temperature of advanced water electrolysis systems to temperatures in the range of  $120$ – $150^\circ \text{C}$  is advantageous from the point of view of improving the energy efficiency and lowering hydrogen production costs. The major drawback, associated with increasing the operating temperature, is in finding stable materials for use as separators, gaskets, sealants, and cell frames. As far as the severe problems of corrosion of cell construction materials in strong alkaline environments under the operating conditions are concerned, it appears most profitable to develop alkaline water electrolysis systems, which will operate at  $120^\circ \text{C}$  rather than  $150^\circ \text{C}$ .

Efforts, towards the development of advanced alkaline water electrolysis systems, have been made in four different areas: (a) operational evaluation of suitable materials for cell construction, (b) development of better electrocatalysts for the hydrogen and oxygen electrodes, (c) determination of reasons for the time variation of performance of water electrolysis systems and of methods to inhibit it,



and (d) optimization of cell configurations to minimize the ohmic losses.

### 3.2. Evaluation of cell construction materials

With raising the operating temperature to over 100° C, one of the most significant problems is in finding a substitute for asbestos as the gas separator in water electrolyzers. More than 50 materials, including ion exchange membranes, porous membranes, woven materials, polypropylene felts, etc., have been evaluated as separator materials in alkaline water electrolyzers at temperatures ranging from 80° C to ~ 150° C [12]. Nafion and Teflon-bonded potassium titanate paper are the most promising. The ohmic losses across Nafion membranes are less in NaOH solution than in KOH solution of the same concentration. It is generally accepted that the failure of asbestos separators at temperatures over 100° C is essentially due to an enhancement of the dissolution rate of asbestos in the strong alkaline environment. It has been suggested [13] that a pre-saturation of the electrolyte by dissolving silicates is effective in reducing the dissolution rate. However, sodium silicate added to the electrolyte to stabilize asbestos, was observed to show a considerable negative effect on the performance of electrolysis cells, possibly due to the catalyst poisoning. Asbestos separators, pre-treated with tin hydrosol for stabilization, are being tested for long-term stability at elevated temperatures [14]. In addition, polysulphone which is processed into a thin fibre form has been shown to be stable in a strong alkaline solution at temperatures up to 125° C [15].

Evaluation of various materials for cell construction revealed that polysulphone is suitable for cell frames, if the operating temperature is about 120° C. This material has to be pre-annealed, otherwise stress cracking occurs. Viton gaskets are unstable at temperatures above 100° C, while ethylene-propylene seals are satisfactory at temperatures up to 120° C [12].

### 3.3. Development of novel electrocatalysts

In the past two to three years, there has been considerable progress in the development of electrocatalysts for both the hydrogen and oxygen evolution

reactions from alkaline media. For use as a hydrogen electrode in alkaline electrolytes, nickel boride shows an electrocatalytic activity superior to that of the conventional nickel cathode, particularly for long-term operation [16]. Evaluation of nickel boride hydrogen electrodes, developed at Deutsche Automobile Gesellschaft Forschungs Laboratorium, Esslingen, Germany, has been carried out in single cells using 30 wt% KOH at 90° C for over 500 hours [17]. In comparison with a nickel screen electrode, the improvement of hydrogen overpotential on this electrode is about 400 mV at a current density of ~ 330 mA cm<sup>-2</sup>. In addition, sintered nickel electrodes, impregnated with non-stoichiometric amounts of cobalt molybdate, have been investigated for hydrogen evolution from concentrated KOH solution and show higher electrocatalytic activities than nickel and even platinized platinum [3]. At a current density of 400 mA cm<sup>-2</sup>, for example, the hydrogen overpotential on this electrode is about 50 mV less than one platinized platinum at 90° C.

As to the development of alternative electrocatalysts for oxygen evolution from alkaline media, recent emphasis has been on oxide catalysts with high surface areas. Semiconducting oxides with the spinel or perovskite structure such as NiCo<sub>2</sub>O<sub>4</sub> and Ba<sub>2</sub>MnReO<sub>6</sub> are of special interest for use as oxygen electrodes. Long-term tests for the oxygen evolution reaction in 5 N KOH at 80° C revealed that the Teflon-bonded NiCo<sub>2</sub>O<sub>4</sub> electrode has a much higher catalytic activity for this reaction, as compared to nickel screen electrodes [18]. Evaluation of Teflon bonded NiCo<sub>2</sub>O<sub>4</sub> electrodes for oxygen evolution in alkaline single cells showed that, at a current density of ~ 330 mA cm<sup>-2</sup>, a decrease of at least 150 mV in overpotential is achievable as compared with Ni electrodes [17]. Unfortunately, the structural stability of Teflon-bonded electrodes is rather poor, particularly at temperatures above 100° C and at current densities over 200 mA cm<sup>-2</sup>. Efforts are being made to develop alternative techniques (i.e., other than the Teflon-bonded type) for preparing porous oxide electrodes with sufficient mechanical stability.

More recently, sintered nickel electrodes impregnated with nickel hydroxide, which are developed and broadly utilized in the battery industry, have been investigated for use as oxygen electrodes in

concentrated KOH solutions [3]. These impregnated electrodes also show considerably higher catalytic activities for the oxygen evolution reaction than smooth nickel and sintered nickel electrodes. According to the work of Gras and Pernot [19], the alloy 50 wt% Ni–50 wt% Fe, which exhibits high corrosion resistance in the strong alkaline environment, is better than the commercial Ni 200 for the evolution of oxygen. The improvement in the electrocatalytic activity of this alloy is attributed to the *in situ* formation of a complex oxide film  $\text{Ni}_x\text{Fe}_y\text{O}_z\text{K}_t$ , which was identified using secondary ion mass spectroscopy (SIMS).

### 3.4. Mechanism of time variation of oxygen overpotential on nickel

One of the significant factors contributing to the performance degradation with time in commercial water electrolyzers, is ascribed to the gradual increase of the overpotential for oxygen evolution. In general, the continuing increase of the cell voltage of a water electrolyser, at a constant operating current density, takes place for a period of at least two years. The performance decay on oxygen evolving electrodes was first observed on platinum in the potential range of 1.6–2.0 V [20]. It also occurs on iridium [21] and on nickel [18] anodes. The mechanism of the performance degradation on nickel has been investigated using ellipsometry to analyse the nature of anodic oxide films [22].

Fig. 6 shows that nickel oxide films, formed potentiostatically at 1.5 V versus RHE are more active than untreated (i.e., freshly prepared) nickel for oxygen evolution at a constant potential of 1.8 V. The *in situ* ellipsometric analysis revealed that the oxide film, formed on Ni at 1.5 V, is mainly composed of  $\beta\text{-NiOOH}$ , which is presumably ‘the right type of nickel oxide’ for this reaction. Further anodization of  $\beta\text{-NiOOH}$  films results in the chemical transformation of  $\text{Ni}^{3+}$  to  $\text{Ni}^{4+}$  ions, which are inactive for this reaction. The ratio of  $\text{Ni}^{3+}$  to  $\text{Ni}^{4+}$  ions in the non-stoichiometric oxide film is strongly dependent on the anodization potential [23] and the polarization time [24]. Therefore, the time variation of current density, for oxygen evolution at constant potentials (above 1.56 V), as demonstrated in Fig. 6, is interpreted as being due to the gradual conversion of  $\text{Ni}^{3+}$  to  $\text{Ni}^{4+}$  ions in the oxide film on the surface of nickel electrodes.

In general, higher oxides such as  $\text{NiO}_2$  are less stable at elevated temperature. The rate of the conversion of  $\text{Ni}^{3+}$  to  $\text{Ni}^{4+}$  ions in oxide films also increases with increasing temperature. Thus, as seen from Fig. 7, the higher the electrolyte temperature, the shorter the period of time for approaching a stable current density. The electrocatalytic activities of aged electrodes are regained by ‘rejuvenating’ the electrodes at 1.5 V. Ellipsometric investigations revealed that the ‘rejuvenation’ of aged oxide films is essentially attributed to the recovery of active sites (i.e.,  $\text{Ni}^{3+}$  ions) on

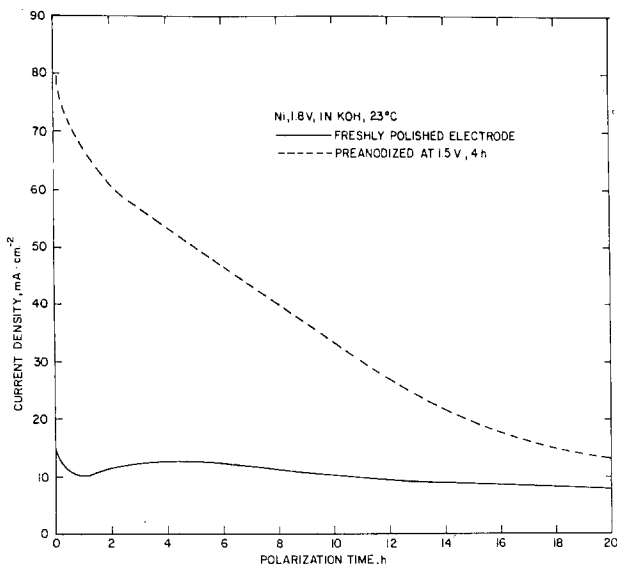


Fig. 6. Effect of pre-anodization, at 1.5 V versus RHE on the current density for oxygen evolution of nickel electrodes (at a constant potential of 1.8 V) in 1 N KOH at 23°C.

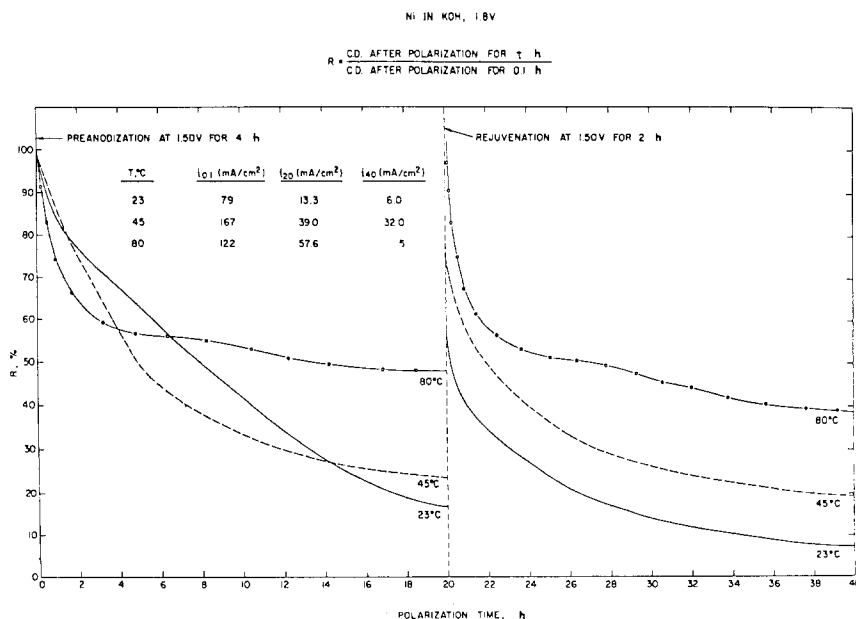


Fig. 7. Effect of temperature on the rate of current decay for the oxygen evolution reaction of pre-anodized and rejuvenated nickel electrodes.

the very top layers of the films, rather than the diminution of the film thickness. Fig. 7 also shows that, with increasing temperature, there is a more significant improvement of the electrocatalytic activity by 'rejuvenation' on aged electrodes.

Effects of electrochemical pre-treatment of oxide films on nickel electrodes on the kinetics of the oxygen evolution reaction have also been investigated. Tafel plots for this reaction on nickel, pre-anodized or 'rejuvenated' at 1.5 V, exhibit only one linear region with  $b \approx 170$  mV at high  $\eta$ , where  $b$  and  $\eta$  represent the Tafel slope and oxygen overpotential, respectively. As illustrated in Table 1, the thickness of oxide film on nickel electrodes plays a less important role than its chemical identity in determining the kinetic parameters of the oxygen evolution reaction.

From the practical point of view, the performance degradation of nickel anodes can be prevented or, at least, retarded by (a) increasing the operating temperature to lower the equilibrium ratio of  $\text{Ni}^{4+}$  to  $\text{Ni}^{3+}$  ions in the oxide film, (b) using high surface area electrodes to maintain the polarization potential below the initial value of 1.56 V at desired current densities, and (c) introducing a secondary cation into the nickel oxide film (e.g.,  $\text{NiCo}_2\text{O}_4$ ).

### 3.5. Optimization of cell configurations

At present, the Lurgi pressure water electrolyzers are constructed of single cells of thickness  $\sim 1$  cm, using smooth nickel electrodes and asbestos separators. A fine nickel mesh, serving as a pre-electrode

Table 1. Kinetic parameters for oxygen evolution on pre-treated nickel electrodes

Pre-treatment	$d_f$ , (nm)*	Tafel slope, b(mV)		Exchange current density, $i_0$ (A cm <sup>-2</sup> )	
		high $\eta$	low $\eta$	high $\eta$	low $\eta$
Pre-anodization at 1.5 V, 2 h	$\sim 23$	—	39	—	$3.8 \times 10^{-12}$
Pre-anodization at 1.8 V, 24 h	$\sim 62$	170	43	$4.2 \times 10^{-6}$	$1.1 \times 10^{-11}$
Pre-anodization at 2.0 V, 6 h	$\sim 140$	167	40	$6.2 \times 10^{-7}$	$2.2 \times 10^{-12}$
Rejuvenation at 1.5 V, 2 h	$\sim 62$	—	38	—	$1.1 \times 10^{-12}$

\* oxide film thickness.

is placed in each electrode-separator spacing. This configuration causes a considerable ohmic loss of  $\sim 150$  mV at a current density of  $\sim 200$  mA cm $^{-2}$  and at about 80°C, because a rather thick asbestos separator ( $\sim 4$  mm) is incorporated. A modified cell configuration, in which a thinner separator ( $\sim 0.3$  mm) of Teflon-bonded potassium titanate is used and thus the inter-electrode spacing is minimized, has been suggested in the work of Appleby and Crepy [3]. The overall thickness of an improved single cell is about 2.5 mm; an ohmic drop of only  $\sim 100$  mV is predicted at 400 mA cm $^{-2}$ .

More recently, a thin cell water electrolyser has also been proposed by Exxon on the basis of their fuel cell technology. With this novel concept, one is able to foresee a significant improvement in the voltage efficiency of an electrolyser and therefore, reduce the cost for hydrogen production.

#### 4. Advanced concepts for hydrogen production

##### 4.1. Investigation and development of reversible oxygen electrodes

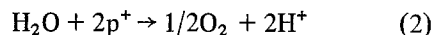
As stated previously, the irreversibility of the oxygen evolution reaction is one of the major drawbacks which limit the energy efficiency of water electrolyzers and secondary metal/air batteries. Since this reaction always occurs on electrode surfaces covered with oxide films, the most promising candidates for reversible oxygen electrodes are semiconducting oxides or compound oxides [4, 18]. It has been reported that NiCo $_2$ O $_4$  spinel and TiO $_2$ -based RuO $_2$  show higher electrocatalytic activities for oxygen evolution than smooth nickel [25, 26]. More efforts are being made in the investigation of oxides with spinel or perovskite structures for oxygen electrodes and in the stabilization of RuO $_x$  for use in acidic media. In the selection and evaluation of oxides for use as oxygen electrocatalysts, essential criteria include: (a) reversible potential of metal/metal oxide or the lower metal oxide/higher metal oxide couple being lower than or similar to the reversible potential for oxygen evolution, (b) corrosion resistance under operating conditions, (c) low electric resistivity, and (d) high electrocatalytic activities [18].

##### 4.2. Photoelectrolysis of water

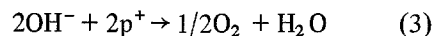
The photoelectrochemical production of hydrogen was initially demonstrated by Fujishima and Honda [27], who used single-crystal TiO $_2$  as the working anode coupled with a platinum cathode. Polycrystalline TiO $_2$  has also been investigated for use as the oxygen electrode [28], exhibiting electrocatalytic activity comparable to TiO $_2$  single crystal. During operation, photons of energy  $h\nu$  higher than the energy gap ( $E_g$ ) of the working electrode excite hole-electron pairs, that is



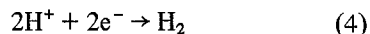
The electrons pass through an external circuit to the cathode, while the holes move to the anode surface, where the electrochemical reactions occurring are



and



in acidic and alkaline solutions, respectively. The corresponding reactions on the cathode are



and



It has been reported [28] that, using TiO $_2$  of  $E_g \approx 2$  eV, the maximum quantum efficiency for the photoelectrolytic process is only 1–2% at  $h\nu \approx 4$  eV. Theoretical analysis on the photoelectrolysis of water has been carried out by Bockris and Uosaki [29]. Depending on the properties of the semiconductor anodes, the calculated quantum efficiencies of photoelectrolysis cells vary from 10 $^{-2}$ –10%. Furthermore, Mavroides and co-workers [30] have pointed out that the quantum efficiency of a photoelectrolysis cell using SrTiO $_3$  anode, a semiconductor with an electron affinity being 0.2 eV less than that of TiO $_2$ , is higher by at least a factor of ten than that of the cell using TiO $_2$  anode.

According to the work of Bockris [31], if a quantum efficiency of  $\sim 5\%$  for the solar spectrum (not at specific wavelengths) can be practically attained, the production cost of photoelectrolytic hydrogen may be lower than by other methods. (The present quantum efficiency of photoelectrolysis cells is only  $\sim 0.2\%$ .) However, the energy gaps of existing semiconductor anodes such as TiO $_2$  (3 eV) and SrTiO $_3$  (3.2 eV) are too high for

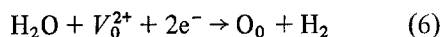
efficient solar-energy conversion. It is of crucial importance to examine other semiconducting materials, which exhibit more favourable characteristics than  $\text{TiO}_2$  and  $\text{SrTiO}_3$ .

#### 4.3. Water vapour electrolysis

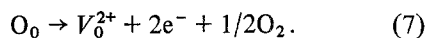
At the present time, over 80% of the production cost of electrolytic hydrogen is due to electricity costs. With the increase of operating temperature, the reversible potential for water electrolysis decreases and thus the electric power input for hydrogen production can be significantly reduced. In water vapour electrolysis, the energy requirements for water decomposition are provided by electricity and heat. From an economic viewpoint, the development of solid oxide water vapour electrolyzers, operating at temperatures of  $\sim 1000^\circ\text{C}$ , turns out to be attractive, because the thermal energy required to carry out the reaction is derived from a fusion reactor at an estimated cost of  $\sim 1/3$  to  $\sim 1/2$  of the present cost of electrical energy.

In 1968, some pioneering work in the development of solid oxide electrolyte water electrolyzers was carried out at the General Electric Company [32]. In the GE solid oxide electrolysis cells, yttria stabilized zirconia was used as the electrolyte.

The oxygen electrode was either lanthanum or praseodymium cobaltite and the hydrogen electrode was porous nickel containing 10 wt%  $\text{ZrO}_2$  as sintering inhibitor. Water vapour is decomposed electrochemically to form hydrogen gas on the cathode, according to the following reaction:



where  $V_0^{2+}$  designates an oxygen ion vacancy and  $\text{O}_0$  represents an oxygen ion in the electrolyte. The anodic reaction on the oxygen electrode is

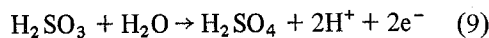
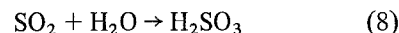


One of the major drawbacks, encountered in the development of solid oxide water electrolyzers was to find a suitable material to connect the cells in series. This material must have high electronic conductivity and capability to withstand differential pressure of up to 15–20 orders of magnitude, and be thermally compatible with other cell components. More recently, Westinghouse Research Laboratories in the United States [33] and

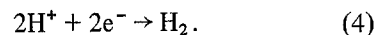
Dornier System in Germany [34] have been interested in the investigation and development of high temperature water vapour electrolyzers.

#### 4.4. Use of anode depolarizers

The reversible potential for the conventional electrolysis of water (1.23 V) is rather high. Recently, the Westinghouse Electric Corporation has proposed a hydrogen generation process based on the electrolysis of sulphurous acid, in which the thermodynamic voltage of the cell is only 0.17 V [35]. Theoretically, this process, through the use of the oxidation of  $\text{H}_2\text{SO}_3$  to  $\text{H}_2\text{SO}_4$  (in place of the anodic evolution of oxygen), utilizes considerably less electricity than the conventional method for the electrolytic production of hydrogen. The chemical and electrochemical reactions in the cell are



and



In general, sulphurous acid tends to migrate from the anode to the cathode with a subsequent reduction to sulphur. In order to prevent the migration of sulphurous acid, a membrane is needed to separate the anodic and the cathodic compartments. Sulphur dioxide ( $\text{SO}_2$ ) is produced by the thermal decomposition of  $\text{H}_2\text{SO}_4$  at  $\sim 870^\circ\text{C}$ , using heat from nuclear reactors.

Because of the irreversibility of the anodic reaction and the incorporation of a membrane, the overall voltage of  $\text{SO}_2$ – $\text{H}_2$  electrolysis cell is generally as high as 0.8–1.0 V at practical current densities (e.g.,  $> 100\text{ mA cm}^{-2}$ ). At present, efforts are being made to find (a) more reversible electrocatalysts, (b) stable and suitable membranes for use as separators, and (c) materials for the construction of chambers for sulphuric acid decomposition.

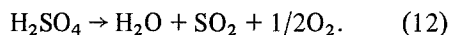
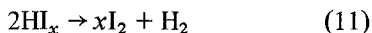
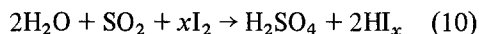
#### 4.5. Development of hydroxyl ion transporting membrane

The hydrated Nafion membrane currently used in SPE cells provides a highly acidic environment, equivalent to a 10 wt%  $\text{H}_2\text{SO}_4$  solution [7]. Thus, noble metals or noble metal oxides of high cor-

rosion resistance have to be used as electro-catalysts or as coating materials on moulded carbon current collectors. It is of particular interest to develop hydroxyl ion transporting membranes, which will enable the substitution of these expensive materials with less expensive ones. It is suggested [4] to incorporate quaternary ammonium or phosphonium functional groups into the solid polymer electrolyte for it to transport hydroxyl ions. More efforts should be made to improve the stabilities and ionic conductivities of these membranes.

#### 4.6. Investigation of thermochemical-electrochemical hybrid cycles

In the past few years, many thermochemical cycles have been proposed to produce hydrogen. Of all the thermochemical cycles proposed, the Westinghouse sulphur-iodine water splitting cycle is the most promising [36]. The electrochemical and chemical reactions involved in this hybrid cycle are



In the development of this technology, one of the difficulties is in finding construction materials which are capable of withstanding boiling sulphuric acid at pressures up to  $\sim 20$  atmospheres and at temperatures up to  $\sim 450^\circ\text{C}$ .

### 5. Conclusions

At General Electric Company, advances in the investigation and development of SPE water electrolysis technology will lead to the fabrication of 5 MW hydrogen generators in 1982 at an estimated cost of \$80/kW. Operating at a temperature of  $\sim 150^\circ\text{C}$  and a pressure of  $\sim 40$  atmospheres, the projected energy efficiency of the SPE water electrolysis systems is 90% at a current density of  $1\text{ A cm}^{-2}$ . Teledyne Energy Systems has projected to build an advanced alkaline water electrolysis system of input power of about 5 MW within five years. This system, operating at about  $120\text{--}150^\circ\text{C}$  and 40 atmospheres, will exhibit an energy efficiency of over 90%. Regarding advanced concepts for electrolytic production of hydrogen,

the more promising techniques are still at an early research stage.

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