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ELECTROCHEMICAL ASPECTS
OF THE HYDROGEN ECONOMY

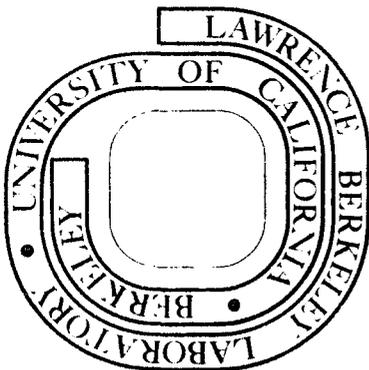
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ELECTROCHEMICAL ASPECTS OF THE HYDROGEN ECONOMY

International Symposium and Workshop on the
Hydrogen Economy, Cornell University, August 20-23, 1973.
Symposium Summary on Electrochemistry

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Water Electrolysis

The generation of hydrogen by electrolysis has been mentioned over and over in the course of this meeting as an important prospect for large-scale hydrogen production. In many ways, electrolysis is ideal for the purposes considered here. Among its attractive features are that no undesirable chemical by-products occur and that no carbonaceous materials are used, provided that they are not employed in the generation of the electrical power.

Undesirable features of electrolytic hydrogen production are low energy efficiency and high capital cost. The low energy efficiency of the process results in high energy cost and increased thermal pollution in the power generation process. The energy efficiency of electrolytic hydrogen generation is manifested by the ratio of the theoretical water decomposition potential, which is 1.23 V at 25°C and 1 atm, and the actual cell voltage. The best presently possible cell voltage¹ (at acceptable current densities i.e., 2000 A/m²) is about 1.8 V which corresponds to an energy efficiency of 68%. Electrolysis cells of the classical design have required 2.2 to 2.5 V.^{1,2} New developments may bring the voltage down to 1.6 V, corresponding to a 77% efficiency.^{3,4} Thus, energy cost represents a large fraction of the cost of electrolytic hydrogen. For instance, at 68% efficiency and with 0.5¢/kWh it is \$2.11/10⁶ BTU.

Plant investment is difficult to assess; a figure of \$100/kW (electric) seems realistic.⁵⁻⁸ With a 100% load factor, and 68% energy efficiency, an investment of \$4.80/10⁶ BTU year is required. At a capital charge rate of 15% per year, this figure results in a capital cost

of $\$0.72/10^6$ BTU. Other operating costs are small compared with power and capital costs and may amount to about $\$0.20/10^6$ BTU.

Fuel Cells

Re-conversion of energy transmitted or stored in the form of hydrogen by use of fuel cells still looks promising. Plant investments^{9,10} of $\$400/\text{kW}$ and conversion efficiencies^{11,12} of about 50% have been mentioned. Since fuel cells have not been discussed specifically during the meeting, they will not be considered in any detail in this summary.

R and D Needs

A 1000 MW water electrolysis plant, operating at 2000 A/m^2 , requires about half a square kilometer of electrode area. The multiplication of present electrolyzer units in very large numbers does not seem to be a rational approach to building such plants; yet, this procedure has to be largely followed because criteria for the scale-up and optimization of electrolyzers, for the most part, still need to be developed.

The energy efficiency of electrolytic hydrogen production needs to be improved by reducing energy losses. The equilibrium potential of water decomposition can be lowered by operating at higher temperatures because the reversible heat of reaction ($T\Delta S$) is endothermic. For instance, at 200°C the reversible potential is 1.08 V, a reduction of 15% over that at room temperature. Increasingly severe materials problems are, however, encountered with increasing temperature. For instance, the relatively inexpensive asbestos cannot be used¹³ for diaphragms above 100°C . Porous polymeric materials and ion exchange membranes need further intensive development for use as diaphragms. Also, metallic diaphragms of the type

employed in the Pechkranz cell may find renewed interest, particularly since new technologies for their production can be borrowed from the electronic industry. At sufficiently high temperatures, the endothermic reversible heat of reaction becomes equal to (or exceeds) the sum of all the exothermic irreversible heats,¹⁴ and a sizeable fraction of the chemical energy of the products is derived from heat. Electrolysis with 100% (or higher) electrical energy efficiency is, therefore, theoretically possible. Taking advantage of this happy prospect, however, presents a major technical challenge, because materials for economical realization do not seem to exist now.--The same thermodynamic arguments favor operation of a hydrogen-consuming fuel cell at low temperature (where the irreversible losses are high).

Irreversible energy losses in water electrolysis (and, similarly, hydrogen-oxygen fuel cells) consist of the kinetic overvoltage, concentration overvoltage and ohmic polarization. The kinetic (or activation) overvoltage of hydrogen and oxygen evolution can be lowered by suitable catalysts. Research efforts continue to be directed toward replacing noble metals. The practical use of Raney nickel catalysts⁴ and double-skeleton porous electrodes according to Justi¹⁵ deserve more attention. Kinetic overvoltages of about 0.3 V at 2000 A/m^2 appear realizable⁴ below 100°C . The use of elevated temperatures also reduces kinetic overvoltages.

Concentration overvoltage is due to the depletion of ions and the supersaturation of hydrogen and oxygen in the electrolyte at the electrode surface. Design criteria to optimize ionic transport with

gas evolution need to be established more firmly. Research on all aspects of gas transport is very much needed. Such work should provide insights into the nucleation, growth, detachment and transport of gas bubbles. At the very least, the direction in which the dynamics of bubble growth should be influenced must be known in order to produce favorable cell designs. Probably another 0.1 V or 8% in energy could be gained from such work.

A further reduction of the ohmic polarization is also connected with an understanding of the dynamics of gas evolution, particularly the growth, detachment and rise of bubbles. Reliable information on these processes will allow us to determine the mixed-phase conductivity and optimize the height of electrodes under natural convection or investigate possibilities for the use of forced convection.--The use of valve electrodes¹⁶ offers the possibility to minimize the effect of gas evolution on electrolyte conductivity, provided that the cost of these electrodes is acceptable.--Elevated pressures have, of course, long been used to decrease the volume of the evolved gas.

Conclusions

1. For the near-term future, electrolytic hydrogen is too expensive for use as a general-utility fuel. There seems to have been general agreement on this point throughout the conference. This conclusion is valid as long as carbonaceous materials, presently in the form of liquid or gaseous hydrocarbons, in the future increasingly in the form of coal, are available for producing hydrogen (or synthetic hydrocarbons).

2. For the long- (and possibly medium) range future, water electrolysis is at present the only feasible, although imperfect, route

to make hydrogen without the use of carbonaceous materials and discharge of carbon dioxide, since no workable schemes for closed-cycle thermochemical hydrogen production with presently-available nuclear reactor temperatures have as yet emerged.

3. For the medium-range future, a likely initial use of electrolytic hydrogen generation lies in the off-peak electrical energy storage. The chemical energy contained in the hydrogen may then be used as a source of heat or re-converted to electrical energy. Electrolytic hydrogen is relatively expensive, however, the only alternative, (if we assume that suitable sites for pumped hydroelectric storage will soon be exhausted), is the use of electrical storage batteries and a considerable effort is still needed for the development of economically attractive batteries.¹⁷

It appears that for a largely nuclear electrical power system there will be great need for off-peak energy storage.

4. Improvements in water electrolysis for the production of hydrogen are necessary and, I think, possible. Except for operation at greatly increased temperatures, the improvements will probably not be of a spectacular kind. However, the R & D effort required and the risks involved are small compared to those for many of the alternatives discussed at this conference.

Referentes

1. A. v. Pichler, Chem. Ing. Techn. 33, 95 (1961).
2. R. Mueller, Allgemeine und technische Elektrochemie nichtmetallischer Stoffe, Springer, Wien 1937, p. 51.
3. R. L. Costa and P. G. Grimes, Chem. Engr. Progress Symp. Series 63, No. 71, p. 45 (1967).
4. W. Vielstich, Chem. Ing. Techn. 33, 75 (1961).
5. F. Salzano, Brookhaven Natl. Lab., this meeting, discussion contribution.
6. J. D. Balcomb, Los Alamos Sci. Lab., this meeting, panel discussion.
7. W. Kincaide, Teledyne Isotopes, this meeting, panel discussion.
8. D. H. Smith, in Industrial Electrochemical Processes, A. T. Kuhn, ed., (Elsevier, 1971), p. 155.
9. A. J. Appleby, Laboratoire d'Electrolyse du CNRS, this meeting, panel discussion.
10. R. A. Wynveen, Life Systems Inc., this meeting, panel discussion.
11. D. P. Gregory, Inst. of Gas Technology, this meeting, talk on "A Hydrogen Economy."
12. J. O'M. Bockris, Flinders University, this meeting, discussion contribution.
13. J. Billiter, Die technische Elektrolyse der Nichtmetalle, Springer, Wien, 1954, p. 34.
14. J. O'M. Bockris, Flinders University, this meeting, talk on "The Electrosynthesis of Hydrogen."
15. E. W. Justi and A. W. Winsel, Kalte Verbrennung, Fuel Cells, Steiner, Wiesbaden, 1962.

16. Reference 14, p. 67.
17. M. L. Kyle, E. J. Cairns and D. S. Webster, Lithium-Sulfur Batteries for Off-Peak Energy Storage: A Preliminary Comparison of Energy Storage and Peak Power Generation Systems, Argonne National Laboratory Report ANL-7958, March 1973.

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