

ALKALINE WATER ELECTROLYSIS

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Contents

1. Introduction
 2. Structure of Alkaline Water Electrolyzers
 - 2.1 Unipolar Electrolyzer
 - 2.2 Bipolar Water Electrolyzer
 - 2.3 High Pressure Water Electrolyzer
 3. Advanced Water Electrolyzers
 4. High Temperature, High Pressure Operation
 5. Structural Materials
 - 5.1 Diaphragm Materials
 - 5.2 Electrode Materials
 6. System Design
 - 6.1 Operating Temperature
 - 6.2 Operating Pressure
 - 6.3 Current Density
 - 6.4 Total System Flow
 - 6.5 Gas–Liquid Separator
 7. Control System
 - 7.1 Pressure Control System
 - 7.1.1 The Combination of Pressure Control and Pressure Difference Control
 - 7.1.2 Bottom Connection of the Gas–Liquid Separators
 - 7.2 Other Controls
 - 7.2.1 Electrolyte Flow Control
 - 7.2.2 Temperature Control
 - 7.2.3 Other Safety Measures
 8. Examples of Advanced Electrolyzers
 - 8.1 Sunshine Electrolyzer
 - 8.2 IME Technology Water Electrolyzer
 - 8.3 GHW Water Electrolyzer
 - 8.4 EI-250 Water Electrolyzer
 9. Cost of Alkaline Water Electrolysis
 - 9.1 Plant Cost
 - 9.2 Cost of Electrolytic Hydrogen Production
 10. Conclusion
- Glossary
Bibliography
Biographical Sketch

Summary

Alkaline water electrolysis has a long history in the chemical industry. Its application for energy conversion in the hydrogen energy system is attracting attention, and advanced electrolyzers have been developed. The direction of development is towards higher efficiency by applying high temperature and high pressure operation. Although some successful results have been reported so far, whether this system can be actually used or not depends on the development of its competitors, solid polymer electrolyte (SPE) water electrolysis or high temperature steam electrolysis (HTE).

1. Introduction

The principle of water electrolysis is rather simple. Applying direct current to water causes electrolysis, splitting water into hydrogen and oxygen through the reaction shown in shown in Eqs. 1–3.



Through this reaction, two molecules of water are decomposed and hydrogen evolves in the cathode. In the anode, oxygen evolves and at the same time one molecule of water is regenerated. As a result, one molecule of water is decomposed and another molecule of water moves to the anode.

In industrial alkaline water electrolysis, 20–40% sodium hydroxide or potassium hydroxide aqueous solution is used for electrolyte instead of pure water, since pure water is highly resistive to electricity.

E_r , the reversible potential (equilibrium potential, namely theoretical voltage of electrolysis) is given by following equation.

$$E_r = E_0 - \frac{RT}{2F} \ln \frac{P}{P_0} \quad (4)$$

where E_0 is standard equilibrium potential, R is gas constant, T is absolute temperature, P_0 and P are vapor pressure of pure water and electrolyte respectively. E_0 is given by $\Delta G_0/2F$, ΔG_0 is increment of Gibbs free energy and F is Faraday constant (96519.4 coulomb), which is 1.226 V under 298 K and 1 atm. This is slightly higher than the decomposition voltage of pure water under the same condition. Electricity required to produce 1 N m³ of hydrogen is, from Faraday's law, 2393 Ah (Ampere hours). As this reaction proceeds almost quantitatively, the minimum energy required is 2.94 kWh for 1 cubic meter of hydrogen. Since E_r is theoretical equilibrium potential, actual cell voltage needed to continue the reaction is higher with the addition of ohmic loss of electrolyte and diaphragm and overvoltage (overpotential) by electrode reaction.

Actual cell voltage E is calculated according to the following equation.

$$E = E_r + E_{ir} + E_{ohm} \quad (5)$$

where E is electrolysis voltage (cell voltage), E_r is reversible potential (reversible voltage, theoretical voltage of electrolysis), E_{ir} is overvoltage (overpotential), and E_{ohm} is ohmic loss.

Reversible potential is theoretically decided according to the reaction condition, but overvoltage and ohmic loss vary with activity of electrodes and cell design. Overvoltage is loss due to “resistance” by the chemical reaction rate. To drive the chemical reaction of electrolysis, extra energy is required in addition to the reversible potential which corresponds to a zero reaction rate. In water electrolysis, overvoltage is decided by the reaction rate at the electrodes. Therefore electrodes with highly active electrocatalysts can reduce the overvoltage. Ohmic loss is mainly caused by electric resistance of electrolyte, which can be reduced by shortening the distance between anode and cathode. Ohmic loss is also caused by electric resistance of circuitry. Both overvoltage and ohmic loss increase with the increasing current density (current per unit area of electrode), hence increase of cell voltage and, therefore, increase of electric power to make hydrogen.

The water electrolyzers currently used in industry work at a cell voltage of 1.8–2.2 volts corresponding to 4.3–5.3 kWh per $N\ m^3$ hydrogen. “N” stand for “normal condition” that means the volume at 0°C and 1atm. pressure.

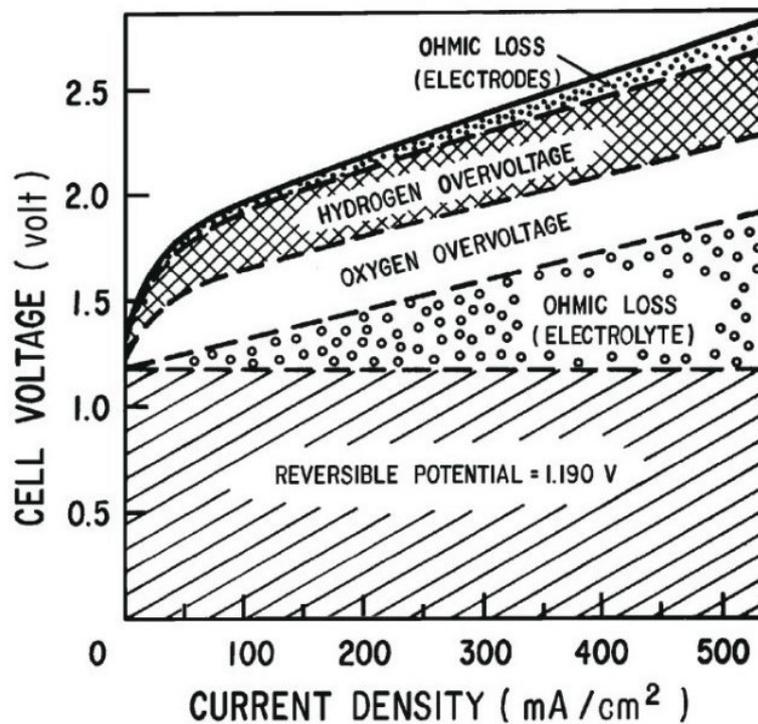


Figure 1. Distribution of cell voltage.

Figure 1 shows an example of distribution of cell voltage to its component.

The enthalpy change, ΔH , to electrolyze water is shown as follows:

$$\Delta H = \Delta G + T\Delta S \quad (6)$$

The decomposition reaction of water by electrolysis is an endothermic reaction, where energy corresponding to ΔG must be supplied in the form of electricity and the rest, $T\Delta S$, by heat. Cell voltage corresponding to ΔG is reversible voltage, about 1.2 V, and $T\Delta S$, heat absorption potential, about 0.28 V. In actual electrolysis, cell voltage is higher than reversible potential and the difference is converted into heat. Since the reaction is endothermic, heat thus caused is absorbed by the reaction until total cell voltage exceeds 1.48 V, the sum of reversible voltage and heat absorption potential.

At this cell voltage, all heat generated by overvoltage and ohmic loss is used by the reaction and there is no heat generation or absorption to and from outside of the system. Therefore, this voltage is called “thermoneutral voltage” where all electric energy used for electrolysis is converted into heat content of evolved hydrogen gas. This voltage is used for the standard of 100% efficiency. Since current efficiency is almost 100% in water electrolysis, dividing 1.48 by cell voltage gives energy efficiency of electrolysis.

No electrolysis is possible at cell voltage under reversible voltage, but it is possible, at least theoretically, to electrolyze water under thermoneutral voltage. High temperature steam electrolysis uses this principle and by supplying part of the energy with heat, it reduces cell voltage. As for alkaline water electrolysis, it is not practical to expect an electrolyzer to work below the thermoneutral voltage.

The thermoneutral voltage is very important in designing electrolyzers, since all electricity supplied beyond this point is converted into heat, which must be removed to maintain the temperature of cells. It is desirable to design the heat balance of electrolyzers so that the heat generated at the operating cell voltage is equal to the heat loss at the operating temperature. Figure 2 shows the change of these voltages versus temperature.

The reversible voltage decreases with increased temperature, but thermoneutral voltage does not show much change, since this corresponds to the energy of hydrogen generated.

The energy efficiency of a water electrolyzer is defined as the quotient of higher heat value of generated hydrogen by electric energy supplied to the system. Since electric energy is proportional to voltage under a constant current, the efficiency is calculated from cell voltage as mentioned before.

In water electrolysis, the current efficiency is usually very high, more than 95%, and therefore the energy efficiency is almost equal to the voltage efficiency.

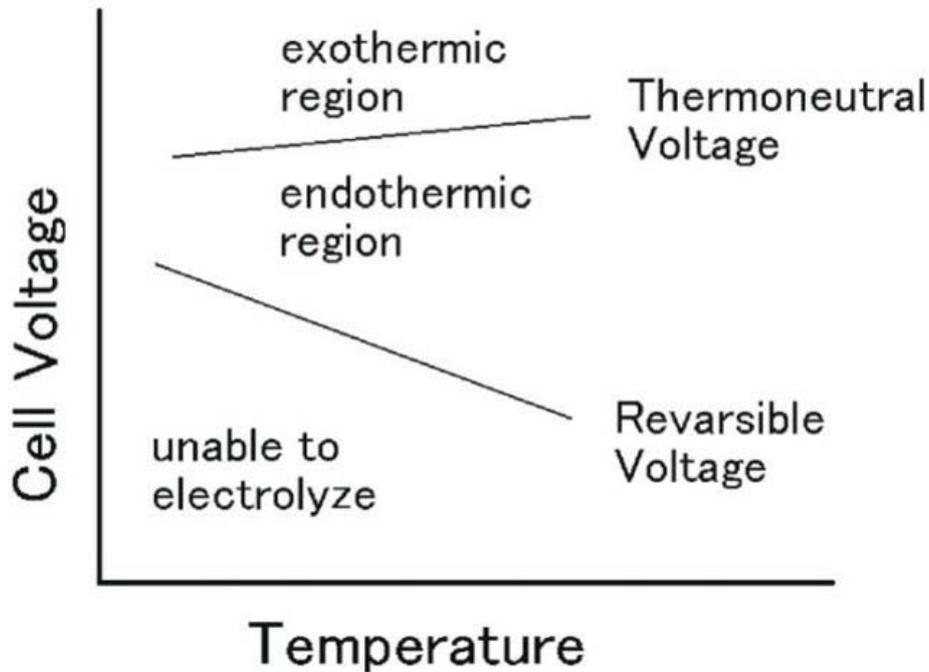


Figure 2. Change of cell voltage by temperature.

2. Structure of Alkaline Water Electrolyzers

There are two kinds of electrolyzer, unipolar and bipolar. These names come from the electrochemical function of the electrode in each type, and the two types are different in structure.

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Biographical Sketch

Isao Abe, born September 16, 1939, in Osaka, Japan, received his Bachelor of Engineering degree from the Department of Fuel Engineering, Faculty of Engineering, University of Tokyo (1963), and Master of Engineering from the Department of Reaction Chemistry of the same faculty, the same university (1966). He worked for Showa Denko K.K. as a chemical engineer (1966–1999), and was involved in development of the advanced alkaline water electrolyzer under the Sunshine Project of the Japanese government as the director of technical development (1974–1984); during that period, he worked as formal alternate representative of Japan to the IEA Task IV (water electrolysis) workshop. He has been editor-in-chief of *Journal of the Hydrogen Energy System Society of Japan* since 1998.