Optimum Temperature for an Alkaline Water Electrolysis Cell*¹

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Abstract

An alkaline water electrolysis cell equipped with liquid-gas separators on both anode and cathode sides is studied in view of minimizing the total energy consumption. Irreversible voltage or the sum of overvoltages and solution IR drops, and hence heat generation, is reduced at high temperatures. There is an optimum temperature at which heat generation is just compensated by heat loss from the system, since the heat losses increase with increasing temperature. The effects of reduction of solution IR drops and overvoltages on the optimum temperature are also discussed.

1 INTRODUCTION

A significant saving of electric energy is anticipated when an electrolysis cell is operated at high temperatures under pressure since the terminal voltage decreases with the rise in temperature. On the other hand, the heat losses from the structure increase with the operating temperature. As a result, the balance of these two factors gives rise to an optimum operating temperature under given electrolysis conditions.

Practical electrolyzers with aqueous solutions are normally operated under ambient pressure, and the operating temperature is limited to the boiling point of the solution in the cell. In such a case, no optimum temperature exists because a rise in the operating temperature continues to reduce the energy consumption up to the boiling temperature. In contrast, a possibility of energy saving for electrolysis through the pressurized and high temperature operation has been surveyed: an example is a paper by Torikai and

co-workers¹⁾. Quantitative analysis and knowledges on the cell performance at high temperatures are required to evaluate the optimum temperature since the optimum point can be lower than the boiling temperature of electrolyte.

An equation of heat balance with appropriate parameters has to be established to evaluate the optimum temperature. In fact, the heat balance is represented by a relatively simple equation, but the selection of adequate parameters is troublesome. Although the thermal analysis of industrial cells has been discussed by several authors^{2~7)}, these articles have still contained inconsistencies to some extent. The present authors have proposed the analysis of heat balance in combination with temperature measurements⁶⁾, which has been applicable to evaluate the cell performance at high temperatures.

The overvoltages and the solution conductivity of concentrated NaOH solutions were measured in the temperature range of 50 to 200°C to conduct numerical calculation at 200°C^{8,9)}. Combination of these with thermodynamics of water electrolysis¹⁰⁾, and water vapor pressure on alkaline solutions¹¹⁾ facilitated the analysis, which then was applied to examining the effects of the operating pressure on the energy consump-

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tion¹²⁾. This paper extends the analysis to the effects of the operating temperature.

A simple model of alkaline water electrolyzer having liquid-gas separators on both anode and cathode sides¹²⁾ was considered. Table 1 shows the specification of the system and the operating conditions assumed.

Table 1 Operating conditions of a water electrolyzer considered

Electrolyzer:	Plate-and-frame type structure with bipolar connection equipped with 20 pairs of the electrodes. 1.5 m diam., 1.1 m deep, fabricated with Type 304 stainless steel of 50 mm thick. For 304 SS, thermal conductivity $k_p = 14$ kcal/m-h-K and emissivity $\epsilon = 0.8$
Electrode:	Area = 1.0 m ²
Electrode spacing	= 10 mm
Electrolyte:	10m NaOH (28.6%)
Temperature:	Feed water, t_i 30°C
	Liquid-gas separators, t_c 40°C
	Ambiance, t_a 30°C

2 ENERGY REQUIREMENTS

The total energy E_{total} consists of electricity for electrolysis IV , heats from or to an external source Q_{EX} , and heat dissipated in liquid-gas separators, Q_C , where I is amperage and V terminal voltage. Of these, Q_{EX} is given by

$$Q_{\text{EX}} = Q_V + Q_S + Q_L - Q_E \quad [1]$$

where Q_V = heat loss caused by water vaporization or the latent heat

Q_S = heat loss accompanying with water flow or the sensible heat

Q_L = heat loss from the cell wall

Q_E = heat generation or the Joule heat in the electrolyzer.

The details of these factors are as follows¹²⁾:

$$Q_V = 3.36 \times 10^{-4} a_1 \gamma_w I \quad [2]$$

$$Q_S = 3.36 \times 10^{-4} I ((a_1 - a_2) C_{pw} (t_s - t_c) + (1 + a_2) C_{pw'} (t_s - t_i)) \quad [3]$$

$$Q_L = \Sigma UA (t_s - t_a) \quad [4]$$

$$\text{and } Q_E = 0.86 I (V - E_H) \quad [5]$$

where $a_1 = 1.5p_w / (p - p_w)$ at t_s
 $a_2 = 1.5p_w' / (p - p_w')$ at t_c
 γ_w = latent heat for water vaporization at t_s
 C_{pw} = specific heat of water at $(t_s - t_c) / 2$
 $C_{pw'}$ = specific heat of water at $(t_s - t_i) / 2$
 U = overall heat transfer coefficient from the cell wall
 A = surface area of the cell wall
 E_H = enthalpic voltage¹⁰⁾
 t_s = solution temperature
 p = operating pressure
 p_w = water vapor pressure on the solution
 p_w' = water vapor pressure at t_c .

Q_C is represented by

$$Q_C = 3.36 \times 10^{-4} I (a_1 - a_2) (\gamma_w' + C_{pw} (t_s - t_c)) + 1.87 \times 10^{-2} I (a_2 C_{pv} + C_{pH} + 0.5 C_{pO}) (t_s - t_c) \quad [6]$$

where

γ_w' = latent heat for water vaporization at t_c

C_{pv} = specific heat of water vapor at $(t_s - t_c) / 2$

C_{pH} = specific heat of hydrogen at $(t_s - t_c) / 2$

C_{pO} = specific heat of oxygen at $(t_s - t_c) / 2$

These parameters have been correlated with temperature, concentration of solution, pressure, and current density^{6, 12)}.

Figure 1 illustrates the results of the components of total energy (IV , Q_{EX} , and Q_C) as a function of temperature under the following conditions:

Solution composition	10m NaOH (m = molality)
Current density	5 kA / m ²
Pressure	100 atm.

Fig. 1 Breakdown of total energy requirement as a function of temperature

The positive side shows the requirement of heating and the negative side cooling. Two lines IV and Q_{EX} labeled $V - E_d = 0$ (V) are electric energy and external heat, respectively, with no generation of the Joule heat in the cell or electrolysis at the theoretical decomposition voltage E_d where $(V - E_d)$ is an irreversible voltage. The requirement of external heat Q_{EX} decreases with increasing irreversible voltage which causes the increase in heat generation Q_E or the Joule heat as illustrated by arrows. As a result, the system must be cooled. At $V - E_d = 0.7$ V, the external heat is negative up to around 210°C, in other words, the system must be cooled to keep the operating temperature (see the bottom line).

Now we may consider a critical condition that a heat exchanger recovers the entirety of excess heat and utilizes to warm up the system under discussion. Total energy E_{total} is given by

$$E_{total} = 0.86 IV + Q_{EX} + Q_C \quad [7]$$

where a coefficient 0.86 is a conversion factor for the heat in kcal/h.

Substituting Eqs. 1 and 5 into Eqs 7, we have

$$E_{total} = 0.86 IE_H + Q_V + Q_S + Q_L + Q_C \quad [8]$$

This equation does not contain irreversible voltage, and E_{total} is a function of the operating temperature as shown by the dotted line in Fig. 2. The higher the temperature the higher is the total energy requirement, and it is impractical. Of course, recovery of a part of the Joule heat generated by electrolysis is possible if an adequate usage is available in the outside of the cell room area, depending on the quality of generated heat. This is beyond the scope of the present discussion.

The solid lines show the energy *vs.* temperature curves when all the excess heat is wasted. A concave line illustrates the energy requirement or E_{total} when electrolysis is conducted under the thermodynamic decomposition voltage E_d . As is shown in Fig. 1, Q_{EX} is always positive, and hence, E_{total} is increased monotonically with temperature (see label 0 V), while it is impractical. At a given value of irreversible voltage (see curves at 0.7 V in Figs. 1 and 2, for example), excess heat is dissipated at low temperatures (up to 210°C), and it consumes only electricity for electrolysis. The larger the irreversible voltage the larger is the waste

Fig. 2 Total energy as a function of temperature

Broken line: total energy when excessive heat is utilized.
Solid lines: total energy when excessive heat is wasted.

heat and the total energy. The total energy is decreased somewhat with the rise in temperature since the decomposition voltage E_d decreases.

The waste heat decreases with the rise in temperature as illustrated by the bottom line in Fig. 1 and tends toward zero, at which temperature, t_{op} , an electrolyzer consumes a minimum energy E_{total} as shown in Fig. 2. The electrolyzer requires extra heat when the operating temperature is higher than t_{op} . Its energy requirement is represented by a curve labeled 0 V at such high temperatures. t_{op} is an optimum temperature where the energy consumption of the system is minimized under given conditions of irreversible voltage. That is,

$$E_{total} = 0.86 IV \text{ at } t < t_{op} \quad [9]$$

$$\begin{aligned} \text{and } E_{total} &= 0.86 IV + Q_{EX} \\ &= 0.86 IE_H + Q_V + Q_S + Q_L \\ &\quad \text{at } t > t_{op} \quad [10] \end{aligned}$$

The energy consumption depends on the operating pressure since water vaporization varies with pressure and temperature¹²⁾ and hence t_{op} also changes. Figure 3 illustrates t_{op} as a function of the irreversible overvoltage and the operating pressure. The curves are convex with large slopes at low overvoltages. t_{op} is low at low pressures: 89°C at 0.4 V and 5 atm, for example. The total energy requirement increases with temperature when the temperature exceeds 89°C, and the excess heat is wasted. Water vaporization and heat dissipation are minimized if the cell is pressurized. At 100 atm, for example, t_{op} is as high as 140°C. In other words, pressurization makes it possible that the reduction of E_{total} with temperature is effective up to high temperatures.

3 OVERVOLTAGE VS. TEMPERATURE

The irreversible voltage was assumed to be independent of the operating temperature as the first approximation in the preceded section and hence the effects of the temperature on the total energy was underestimated in the temperature range lower than t_{op} . In fact, the overvoltages and the solution conductivity are the function of the solution

Fig. 3 Temperature at which total energy becomes minimum, t_{op} , as a function of irreversible voltage under various pressures

temperature^{8,9)}. With these data, we may evaluate the energy consumption of water electrolyzer to eliminate or minimize these inconsistencies with practical conditions.

The anodic and the cathodic overvoltages of iron, nickel, and platinum in 10m NaOH at 5 kA/m² are shown in Fig. 4^{8,9)}. A solid Pt anode showed relatively low oxygen overvoltages even at low temperatures and was almost unchanged with solution temperature. The oxygen overvoltage of Ni anode was decreased greatly with the increase in operating temperature, and became almost the same level as of the Pt anode at 200°C. Iron was not examined since it was inadequate as anode under such conditions. The hydrogen overvoltage of Pt was decreased considerably by increasing solution temperature, and was some 0.3 V lower than that of Ni cathode at 150 and 200°C. Iron cathode showed relatively low overvoltages while its corrosion was still remarkable even under cathodic polarization⁸⁾.

We may compare the irreversible voltages of a water electrolyzer equipped with a pair of Pt anode and cathode to that of a cell having a Ni anode and cathode pair. The

Fig. 4 Decrease in hydrogen and oxygen overvoltages of some electrodes at 5 kA/m² in 10 m NaOH solution with temperature

anode-to-cathode gap is 10 mm. A concave curve in Fig. 5 represents the voltage with minimum consumption of energy. The voltage V_m is calculated from the external heat with no irreversible voltage Q_{EX}' since Q_{EX}' is the heat which is compensated by the Joule heat at the optimum temperature.

$$V_m = Q_{EX}' / 0.86I$$

$$= E_H - E_d + (Q_V + Q_S + Q_L) / 0.86I \quad [11]$$

The cross points on this curve with the irreversible voltage vs. temperature curves indicate the optimum temperatures of these cells.

If the irreversible voltage is greater than V_m at a given temperature, the cell is to be cooled to maintain the temperature, and the energy requirement is equivalent to IV . The reduction of the irreversible voltage is related directly to the reduction of the energy requirement. On the other hand, the cell

Fig. 5 Irreversible voltages as a function of temperature

See text for the concave line. Electrolyte=10 m NaOH. Current density = 5 kA/m². Pressure=20 atm. Anode-to-cathode gap = 10 mm

must be heated and the energy requirement becomes $IV + Q_{EX}$ if the irreversible voltage is lower than V_m . The energy requirement is not minimized at all under such conditions while the terminal voltage is reduced by increasing the operating temperature.

The operating temperature can be lowered considerably by using low overvoltage electrodes, and hence the operating pressure could also be reduced, which enables to select the structural materials for an electrolyzer and to design the hardware easy. On the other hand, the optimum temperature t_{op} is lowered with the decrease in irreversible voltage or overvoltage. As a result, the energy saving through the rise in the operating temperature is not anticipated when t_{op} is too low. The total energy is larger than the minimum requirement under such conditions.

Further reduction of the cell voltage with no consumption of extra energy is anticipated by increasing temperature and pressure since water vaporization and the related heat losses are decreased. Improvement

of thermal insulation is also of the great importance. Of course the cell must be designed to endure these conditions and hence the fixed charge must be increased.

4 CONCLUSION

The effects of the operating temperature on the energy consumption of alkaline water electrolyzer has been discussed. The energy consumption is minimized at the optimum temperature t_{op} , at which the Joule heat compensates for the heat losses from the entire system. Although the cell voltage can be reduced by increasing the temperature, the energy saving is not anticipated when the temperature is higher than t_{op} . It is possible to rise the optimum temperature by pressurization.

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