

The analysis of energy efficiency in water electrolysis under high temperature and high pressure

L W Hourng^{1,3}, T T Tsai¹ and M Y Lin²

¹Department of Mechanical Engineering, National Central University, Taoyuan, Taiwan

²Department of Mechanical Engineering, Army Academy, Taoyuan, Taiwan

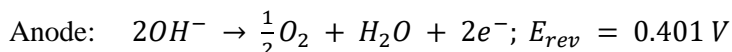
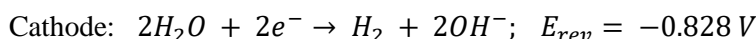
E-mail: lwhong@cc.ncu.edu.tw

Abstract. This paper aims to analyze the energy efficiency of water electrolysis under high pressure and high temperature conditions. The effects of temperature and pressure on four different kinds of reaction mechanisms, namely, reversible voltage, activation polarization, ohmic polarization, and concentration polarization, are investigated in details. Results show that the ohmic and concentration over-potentials are increased as temperature is increased, however, the reversible and activation over-potentials are decreased as temperature is increased. Therefore, the net efficiency is enhanced as temperature is increased. The efficiency of water electrolysis at 350°C/100 bars is increased about 17%, compared with that at 80°C/1bar.

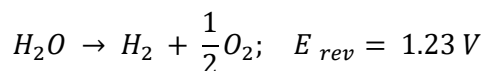
1. Introduction

Hydrogen is considered to be the most promising energy carrier in the future. Most of the hydrogen nowadays is produced through the steam reforming of natural gas. However, the need for hydrogen produced by other processes, which include electrochemical, biomass, biological, and solar hydrogen productions, is increased. Water electrolysis belongs to the electrochemical hydrogen production. The purity of hydrogen produced by water electrolysis is higher than other hydrogen produced methods, and there is no carbon monoxide emitted during the production and consumption processes. Besides, the investment of facility on water electrolysis is rather reasonable. These advantages make water electrolysis being a potential method for hydrogen production.

From electrochemistry and thermodynamics, the semi-reactions on anode and cathode electrodes at 25°C and 1bar are



Therefore, the net reaction in the electrolysis cell is



Under 25°C/1bar, the reversible voltage (E_{rev}) is 1.23 V, which is the minimum voltage needed for water electrolysis process as the reaction occurs ideally. However, when electric current passes through an electrochemical battery, there always exists a potential difference between practical and ideal situations. This phenomenon is called electrode polarization [1], and the degree of electrode



polarization is defined as over-potential.

$$\eta = E - E_{\text{rev}} \quad (1)$$

where η is the over-potential. E is the applied potential, and E_{rev} is the reversible potential or reversible voltage. There are three kinds of polarization, namely, concentration polarization, activation polarization, and ohmic polarization. Basically, the reaction rate and polarizations of water electrolysis depend on the working temperature and pressure. However, there is few researches dealing with this issue, and the present article aims therefore at exploring the influences of temperature and pressure on the water electrolysis theoretically. Three kinds of polarization are described briefly as below.

1.1. Reversible voltage

The relation between the reversible voltage and the Gibbs free energy is

$$E_{\text{rev}} = -\Delta G/nF \quad (2)$$

where E_{rev} is the reversible voltage, ΔG the change of Gibbs free energy, n the equivalent number of material, and F the Faraday's constant. Gibbs free energy of the liquid water at different temperature and pressure can be found in the reference book JANAF [2]. The reversible voltage can thus be obtained by equation (2).

1.2. Activation polarization

All chemical reactions, which occurred on the interface between electrodes and electrolyte, needs extra electric potential in addition to the reversible potential to cross over an energy obstacle. This kind of extra electric potential difference to yield chemical reactions is called the activation over-potential. The relation between activation over-potential and current density is governed by Butler-Volmer equation as below.

$$i = i_0 \left[\exp\left(\frac{\alpha z F \eta_a}{RT}\right) - \exp\left(\frac{-(1-\alpha) z F \eta_a}{RT}\right) \right] \quad (3)$$

η_a is the activation over-potential, and i_0 is the exchange current density. α is the transfer coefficient, which is 0.5 for water electrolysis. R is the universal gas constant and z is electrochemical equivalent. From Thampan, *et al* [3], the relation between exchange current density i_0 and temperature is given as

$$i_0 = g_M \exp\left[-\frac{E}{R} \left(\frac{1}{T} - \frac{1}{T_{\text{ref}}}\right)\right] i_{0,\text{ref}}$$

For anode and cathode, it yields

$$i_{A,0} = g_M \exp\left[-\frac{E_A}{R} \left(\frac{1}{T} - \frac{1}{T_{\text{ref}}}\right)\right] i_{A,0,\text{ref}}$$

$$i_{C,0} = \gamma_M \exp\left[-\frac{E_C}{R} \left(\frac{1}{T} - \frac{1}{T_{\text{ref}}}\right)\right] i_{C,0,\text{ref}}$$

where $i_{A,0}$ and $i_{C,0}$ are exchange current density of anode, and cathode, respectively. $i_{A,0,\text{ref}}$ and $i_{C,0,\text{ref}}$ are reference exchange current density of anode, and cathode respectively. For platinum electrode, the corresponding values are 10^{-3} A/cm² and 10^{-11} A/cm². γ_M is the roughness factor, and taken to be 1.8 for platinum electrode [4].

1.3. Ohmic polarization

Ohmic polarization may be caused by electrode line segment or generated bubbles. Line segment of electrodes is the wire joining the electrode slice to pass the electric current through. Electrode slice is very thin with large cross-sectional area compared with that of line segment. Therefore, the resistance of electrode, compared with resistance of line segment, is very small and can be neglected. In the

present high temperature circumstances, metal ohmic resistance of line segment becomes large and can't be neglected anymore. The ohmic over-potential for line segment obeys the ohmic law as

$$\eta_{ohm} = i\Omega \quad (4)$$

Where η_{ohm} is ohmic over-potential of line segment, and Ω is the resistance of line segment. The resistance is determined by

$$\Omega = \rho l / A \quad (5)$$

Where ρ is the specific resistance, l the length parallel to current direction, and A is the cross-sectional area of the line segment. The relation between specific resistance ρ and temperatures is as below.

$$\rho = \rho_0 (1 + aT) \quad (6)$$

Where ρ_0 is the coefficient of specific resistance and a is the percentage change in resistivity per unit temperature. For platinum, $\rho_0 = 1.1 \times 10^{-7}$ and $a = 0.00392$ [5]. The ohmic resistance due to bubbles will be discussed in more detail later.

1.4. Concentration polarization

For water electrolysis in alkaline electrolyte, the hydroxyl produced in cathode will be transported toward anode by electric force. There is a diffusion layer near the surface of electrode, that is, there exists a concentration gradient from the surface of electrode to the edge of diffusion layer. In a still electrolyte without fluid flow, the thickness of the layer (δ) is about 0.05 cm. The hydroxyl concentration is not high enough near anode, which is unfavourable to reaction on anode. To maintain certain electric current, more electric potential is needed. This phenomenon is called concentration polarization.

In the electrolysis reaction, as the ion thickness near the electrode surface approaches to zero, the over-potential of water electrolysis will be suddenly increased. The corresponding electric current is called the limiting current. As the current reaches its limiting current, no matter how much the applied voltage is added, the electric current will not increase anymore. The limiting current density is related to ion properties as follows.

$$i_L = \frac{D_j a_j F z}{(1 - t_j) \delta}$$

where i_L is the limiting current density, a_j the activity of ion j , D_j the diffusion coefficient of ion j , δ the thickness of diffusion layer, and t_j the transition coefficient of ion j . The relation between concentration over-potential and electric current is

$$\eta_{con} = \frac{RT}{ZF} \ln \frac{i_L}{i_L - i} \quad (7)$$

Where η_{con} is the concentration over-potential and i is the electric current.

2. Results and discussions

Four different kinds of reaction mechanisms, namely, reversible voltage, activation polarization, ohmic polarization, and concentration polarizations, are investigated here in details. Then the electric energy consumption at 1bar/80°C and 500bar/370°C are compared to show the effect of high temperature and pressure on the water electrolysis.

The reversible voltages at different temperatures and pressures are shown in figure 1. It indicates that the higher the temperature and the pressure are, the lower the reversible voltage will be. That is, considering only the reversible voltage, the efficiency of water electrolysis will be improved by raising the operating temperature and pressure. From the figure, it seems that increasing temperature enhances the efficiency of water electrolysis significantly, while the effect of pressure is actually very small. However, the high pressure is still required to maintain water in its liquid phase when the operating

temperature is very high. Furthermore, the hydrogen gas produced with high pressure can be stored in the tank directly, and no compression procedure is required.

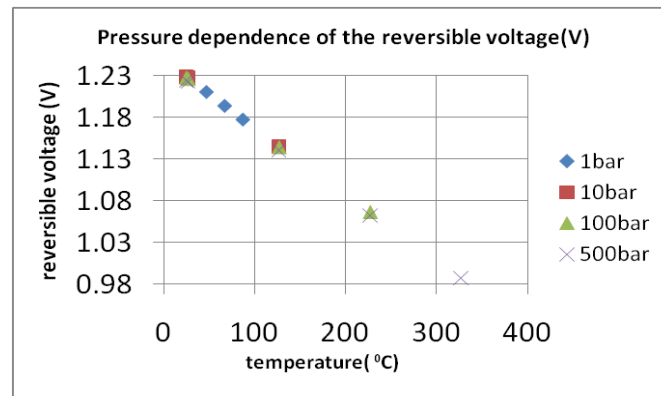


Figure 1. Diagram of reversible voltage via temperature and pressure.

The activation polarization reaction is due to desorption between hydrogen ion and electrode, which is a metal-non-metal bonding or a typical ionic bond. The rate of desorption is determined by ionic bond energy. Since ionic bond energy is almost not influenced by pressure, we can conclude that activation over-potential is also not influenced by pressure. The activation over-potential is thus assumed depending on temperature only in this article.

Figure 2 shows the variation of activation over-potential via temperature as the exchange current density $i_{A,0}$ and $i_{C,0}$ is fixed at certain value. It indicates that the activation over-potential will increase as the current density is increased. It also shows that the activation over-potential increases when temperature increases. This result is not compatible with experimental observation, in which the supplied voltage will decrease as the temperature increases. If the current density is set to be function of temperature, the variation of activation over-potential via temperature is plotted as shown in figure 3. The results show that activation voltage decreases as temperature is increased, which agrees qualitatively with experimental observations. Therefore, low current density and electrolyte temperature is preferred to reduce the activation over-potential during water electrolysis.

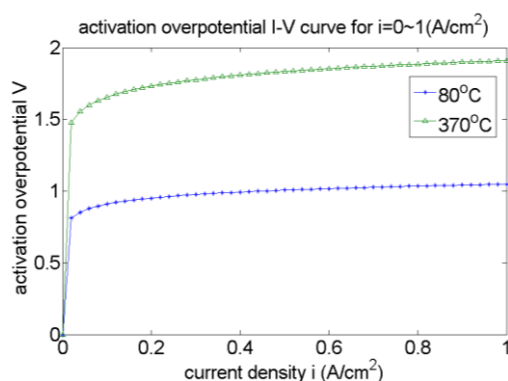


Figure 2. Relation between activation over-potential and current at 80°C and 370°C. The exchange current density is considered to be constants.

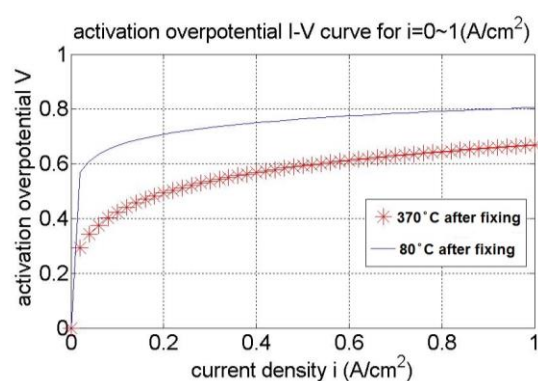


Figure 3. Relation between activation over-potential and current at 80°C and 370°C. The exchange current density is considered to be function of temperature.

The ohmic resistance due to line segment can be calculated based on the ohmic law as described before. The corresponding ohmic resistance is twice higher at 370°C than that at 80°C, thus it should

not be neglected in high temperature water electrolysis. An efficient way to reduce the ohmic resistance is to increase the cross-sectional area of the wire.

Ohmic over-potential due to bubbles in electrolyte made by Kuhn, *et al* [6] is shown in figure 4, and the empirical results of ohmic over-potential due to bubbles in electrolyte immersed with proton exchange membrane made by Roy, *et al* [7] is also shown in figure 5. The former seems to have better performance than the latter. The reason may due to that bubbles are easy to be trapped in the porous media such as proton exchange membrane, and therefore increase the resistance significantly. The water electrolysis in the present study is closer to the experiment of Kuhn, *et al* as shown in figure 4, which indicates that the ohmic over-potential due to bubbles can be neglected when the current density is smaller than 1 A/cm².

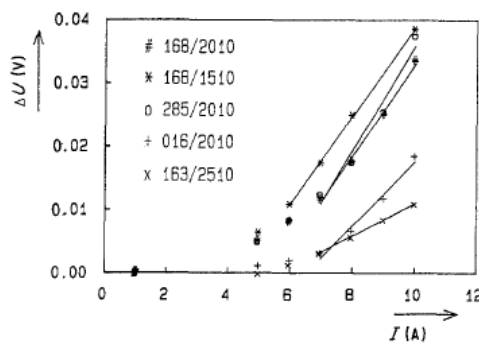


Figure 4. Polarization curve of ohmic over-potential due to bubbles [6].

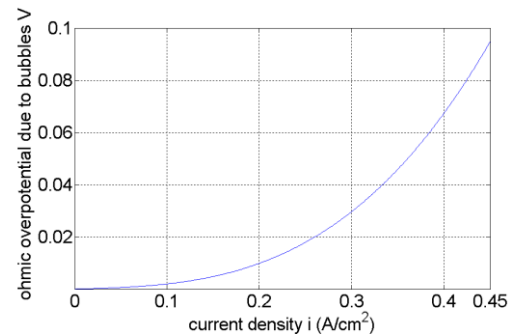


Figure 5. Polarization curve of ohmic over-potential due to bubbles, based on the empirical equation of Roy, *et al* [7].

There is no theory to relate the concentration over-potential with temperature and pressure. However, the diffusion of ions in water electrolysis at standard pressure and temperature can be found in table 1. Substituting the data in table 1 into equation (7), the relation between concentration over-potential and current can be plotted as shown in figure 6. It can be found the concentration over-potential can be neglected when the current density is below then 1 A/cm². At high temperature water electrolysis, as we discuss here, the concentration over-potential should be even less. Because the equivalent conductivity and ionic mobility rise with temperature, ions are more easily to transport and the corresponding resistance will decrease as shown in table 2. In addition, found from [8], the effect of pressure on ionic transportation is limited such that the effect of pressure on concentration over-potential can also be neglected.

Table 1. Properties of 0.5 M NaOH electrolytes at 80°C/1bar.

	Parameters	Dimensions	Values
Activation	α_j	mol/ml	0.693
Diffusion coefficient	D_j	none	2.632×10^{-9}
Transport number	t_j	0.109	0.600
Diffusion layer thickness	d	m	0.0005
Mobility	u_j	m ² /s V	20.5×10^{-8}

Table 2. The effect of temperature on ion properties.

OH ⁻	dimensions	18°C	25°C
Equivalent conductivity	cm ² /Ω	171	198.3
Mobility of ion	m ² /V s	17.7×10^{-8}	20.5×10^{-8}

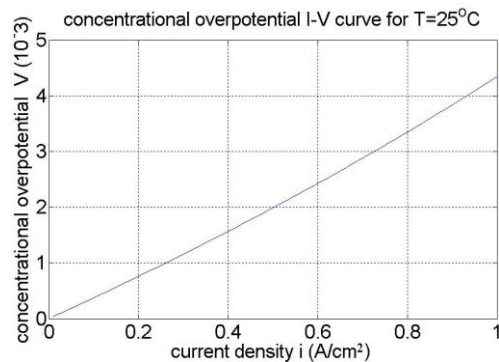


Figure 6. Polarization curve of concentration over-potential at 80°C/1bar.

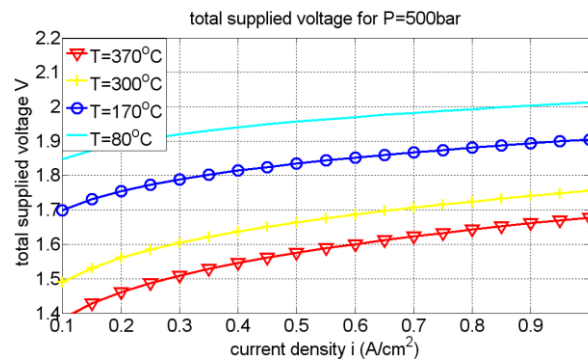


Figure 7. Total supplied voltage for different current density under 500 bar.

Because current density below 1 A/cm² is considered here, the ohmic over-potential due to bubble and concentration over-potential are neglected as mentioned above. The total applied potential thus includes reversible voltage, activation over-potential, and ohmic over-potential due to line segment of electrode. The influence of temperature on the supplied voltage is shown in figure 7. It indicates that the supplied voltage can be reduced as the temperature is increased.

The influence of line segment area on applied voltage is shown in figures 8 and 9. In figure 8, the ohmic over-potential due to line segment with cross-sectional area of 1mm² is about 23% of supplied voltage, and should not be neglected. The percentage of ohmic over-potential may be reduced if a large cross-sectional area is used as shown in figure 9. However, in order to save equipment costs, line segment with cross-sectional area of 1 mm² is generally used.

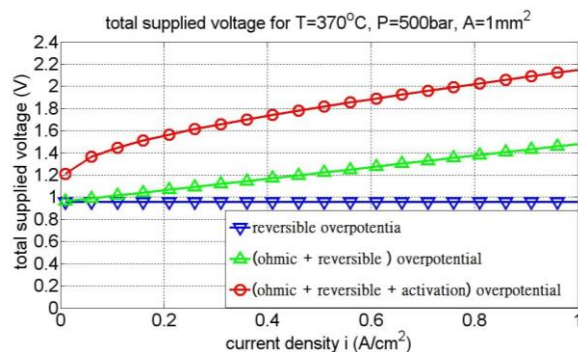


Figure 8. Comparison of over-potentials at 370°C/500 bar. The cross-sectional area of line segment is 1 mm².

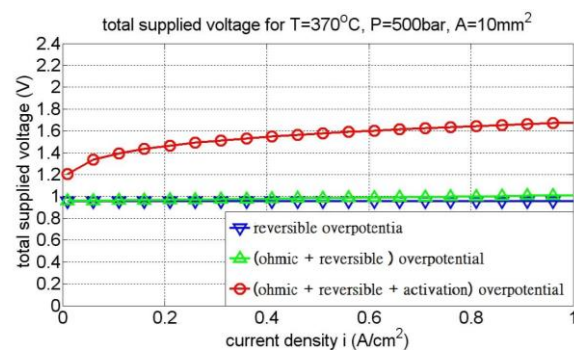


Figure 9. Comparison of over-potentials at 370°C/500 bar. The cross-sectional area of line segment is 10 mm².

The efficiency of electrolysis at 370°C/500 bar and 80°C/1bar are compared in figures 9 and 10. The supplied voltage is 1.678 V at 370°C/500 bar, 1 A/cm² and 2.016 V at 80°C/1 bar, 1 A/cm², thus the efficiency at 370°C/500 bar is increased about 17% for water electrolysis. Furthermore, if the consumption of energy for product hydrogen to elevate pressure from 1 bar to 500 bars is also considered, the efficiency of water electrolysis is increased about 22%. The calculated results are in the consistent trend with the experimental results of Marangio, *et al* [9].

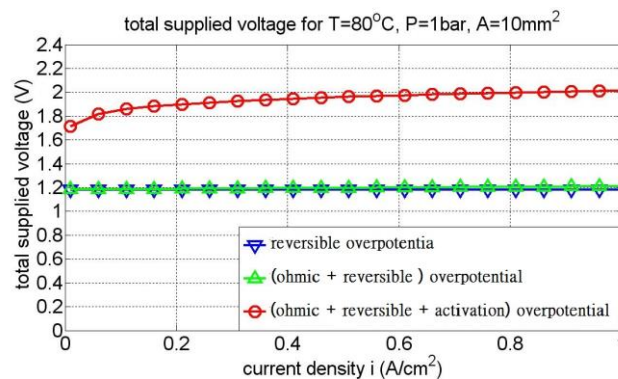


Figure 10. Comparison of over-potentials under 80°C/1bar. The cross-sectional area of line segment is 10 mm².

3. Conclusions

Based on the results and discussions, several conclusions can be drawn as below.

- As temperature or pressure rises, the reversible voltage of water electrolysis is reduced.
- The activation over-potential is reduced as temperature rises, and nearly not affected by pressure.
- Under high temperature of 370°C, the ohmic over-potential of the line segment should be considered. However, it may be reduced by the increase of the cross-sectional area or decrease of the length of line segment.
- The ohmic over-potential due to bubbles is increased with the increase of temperature, as well as the decrease of pressure. However, this effect can be neglected while current density is below 1 A/cm².
- The concentration over-potential is increased with the increase of temperature rise. This effect can be neglected while current density is lower than 1 A/cm².
- The efficiency of water electrolysis at 350°C/100 bars is increased about 17%, compared with that at 80°C/1 bar. If the produced hydrogen is to be used at 1 bar and the expansion work from pressure 500 bars to 1 bar is also fully converted, the efficiency of water electrolysis is increased about 22%.

4. Nomenclatures

a	percentage change in resistivity per unit temperature
a_j	activity of ion j
A	cross-sectional area
D_j	diffusion coefficient of ion j
E	applied potential
E_{rev}	reversible potential
F	Faraday's constant
G	Gibbs free energy
i	electric current
$i_{A.0}$	exchange current density of anode
$i_{C.0}$	exchange current density of cathode
$i_{A.0.ref}$	reference exchange current density of anode and
$i_{C.0.ref}$	reference exchange current density of cathode
i_L	limiting current density
l	length of wire or rod
n	equivalent number of material

R	universal gas constant
T	temperature
t_j	transition coefficient of ion j.
Z	electrochemical equivalent
η	over-potential
η_{act}	activation over-potential
η_{con}	concentration over-potential
η_{ohm}	ohmic over-potential
ρ_o	coefficient of specific resistance
δ	thickness of diffusion layer
Ω	resistance of line segment
ρ	specific resistance
γ_M	roughness factor

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