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The Analysis of Energy Efficiency of Water Electrolysis

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---***ABSTRACT***---

This work analyzed the energy efficiency of water electrolysis under high pressure and high temperature by current-voltage diagram. Four different kinds of reaction mechanisms namely reversible voltage, activation polarization, ohmic polarization and concentration polarization are investigated in details. At the standard temperature, the concentration overpotential increase with temperature increasing, and can be neglected while current density is lower than 1A/cm^2.

The whole consumption of electric energy at 500bar/370^o*Cis saved about 17% compared with that at 1bar/80*^{o}*C. If the power consumption of compressing the gas from 1bar to 500bar is considered, then the water electrolysis at 500bar/370*^{o}*C saves about 22% of the power consumption.*

KEYWORDS: *water electrolysis, activation overpotential, hydrogen production, overpotential*

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I. INTRODUCTION

The focal point of this article is water electrolysis, so the other methods of hydrogen production will not investigate in this article. The purity of hydrogen produced by water electrolysis is higher than other methods. The method of water electrolysis will not produce the carbon monoxide, so there is no platinum-poison problem, and water electrolyzer can be small, and it is the advantage of the method.

II. FUNDAMENTAL THEORY

The cation moves to the cathode of electrode, and the anion moves to the anode when current passes electric potential. Thus electrolysis is a term that we define broadly to include chemical changes accompanying faradaic reactions at electrodes in contact with electrolytes. The process of water electrolysis is the reverse reaction of the reaction of hydrogen and oxygen react into water. Therefore, as long as enough energy is offered, water can be deformed. Pollution-free is simple for the process of water electrolysis, but the electric consumption is great. The electricity consumption is even up to 73% of total cost in hydrogen production in Ivy [1].

Under Standard Temperature and Pressure conditions, the reversible voltage is 1.23V, reversible voltage is the minimum voltage needed under water electrolysis process. The electric energy is equal to the Gibbs free energy of water electrolysis, so we can obtain reversible voltage from the relation between Gibbs free energy and reversible voltage, investigated as below:

$$\Delta G = -nEF \qquad (1)$$

where ΔG is Gibbs free energy, n is the number of electrons passed during reaction, E is cell emf, F is the Faraday constant.

when 1 mol water changed into 1 mol hydrogen and 0.5 mol oxygen, under standard temperature and pressure conditions, the difference of Gibbs free energy (the difference of free energy between reactant and product) is 237.2kJ, the charge requirement is one Faraday (26.8A・h) , n=2, so E can be calculated:

$$-E = \frac{\Delta G}{nF} = \frac{237.2 \times 1000}{2 \times 96485} = 1.23V \qquad (2)$$

The reaction of water electrolysis is:

$$H_2O \leftrightarrow H_2 + \frac{1}{2}O_2 \qquad (3)$$

It is a reversible reaction. The reaction spontaneously react from right to left and produce a reversible voltage (emf) if we don't offer electric potential under standard temperature and pressure conditions. The reversible voltage is 1.23V, if we apply a -1.23V reverse voltage that means current direction is opposite to current direction forced by reversible, and then the reaction approach balance. There is no macro mass change between two sides of equation, this is called chemical equilibrium.

When electric current passes through an electrochemical battery, there exists a potential difference between electrode and electrode in chemical equilibrium, this phenomenon is called electrode polarization as Koryta [2]. The degree of electrode polarization is represented by overpotential which is defined by

$$\eta = E - E_e \qquad (4)$$

where η is overpotential, E is electrode potential, E_e is reversible voltage. Three different kinds of polarization mechanisms, namely: 1.concentration polarization 2.activation polarization 3.ohmic polarization.

The hydroxyl produced in cathode as reaction (1) when current pass through alkaline electrolyte in water electrolysis will transport to anode by net electric force. If the velocity of transportation is not fast enough or the quantity of ions flow is not great enough will results in decreasing of hydroxyl concentration not enough near anode, and is unfavorable to reaction on anode, Because for anode, hydroxyl is reactant , so if concentration of hydroxyl near anode is not enough , will cause the hindrance of reaction. So if we want to maintain certain electric current, we must strengthen electric potential, this phenomenon is called concentration polarization. The adding electric potential due to concentration polarization, is called concentration overpotential.

There is a diffusion layer on the surface of electrode, that is to say there exist a concentration difference from the surface of electrode to the edge of diffusion layer. In the steady state electrolyte without fluid flow field, the thickness of the layer (δ) is 0.05 cm. The thickness of the layer is reduced to 0.001 cm in fast-stirring solution. The stirring vibration of electrolyte or the rotation of electrode can be lower concentration overpotential.

In the electrolysis reaction, when the ion thickness near the electrode surface approach to zero, the total overpotential of water electrolysis reaction will suddenly increase, the electric current is called the limit current. No matter how to increase voltage, electric current density will not increase and the current is limit current density. The relation between limit current density and electrolyte is

$$(5) \qquad i_L = \frac{D_j a_j F Z}{(1 - t_j)\delta}$$

Where i_L is limit current density and a_j is activity of ion j, D_j is diffusion coefficient of ion j, δ is thickness of diffusion layer, t_j is transition coefficient of ion j. The relationship between concentration overpotential and electric current is:

$$\eta_0 = \frac{RT}{ZF} \ln \frac{i_L}{i_L - i} \qquad (6)$$

Where η_0 is concentration overpotential and i is electric current.

All chemical reaction is needed to cross over an energy obstacle, so we need to increase electric potential difference to electrolyze water. This kind of electric potential difference added is called the activation overpotential.

We can use Butler-Volmer equation to obtain the relation between activation overpotential and electric current. Butler-Volmer equation is:

$$(7) \qquad i = i_o[\exp(\frac{\alpha z F \eta}{RT}) - \exp(\frac{-(1-\alpha) z F \eta}{RT})]$$

Where , η is activation overpotential, i_o is exchange current density, directly relate to the material of electrode , α is fraction of overpotential or called transfer coefficient, in the electrolysis reaction, α is probably equal to 0.5.

The relationship between reaction rates to Gibbs free energy can be obtained by Maxwell distribution as below:

$$V = k\exp(-\Delta G/RT) \qquad (8)$$

Where V is reaction rate, the meaning is equal to exchange current density in the experiment of water electrolysis. The k is reaction constant, ΔG is differences of Gibbs free energy, and the physical meaning is activation energy in electrolysis reaction. Due to all kinds of experiment, we know the differences of Gibbs free energy varies with temperature, thus we know exchange current density change as temperature change.

It can be divided into ohmic polarization due to electrode line segment and ohmic polarization due to bubbles. Ohmic polarization due to electrode line segment is simply considered by the ohmic resistance and the line segment of electrode (electric wire), ohmic resistance due to bubble is due to hydrogen generated by cathode, oxygen generated by anode, and the bubbles will obstruct the ion transportation, thus the ohmic resistance is occurred.

III. COMPUTING METHOD AND DISCUSSION

In the article we will explain the computing method and discuss the different of reaction mechanisms. Four different kinds of reaction mechanisms is namely reversible voltage, activation polarization, ohmic polarization and concentration polarization are investigated in details.

Then we add all potential of four kinds of mechanisms, and compare the electric energy consumption at 1bar/80^{o}C with that at 500bar/370^{o}C. Finally, we will consider adding to the energy of compress hydrogen into 500bar, and then compare the electric energy consumption under 1bar /80^{o}C plus energy consumption of compress hydrogen into 500bar, to energy consumption under 500bar / 370^{o}C.

The data of the reversible voltage is according to the Gibbs free energy of the liquid water, and the value of reversible voltage varies with different temperature and pressure is calculated by the Gibbs free energy using formula (1).

The calculation result of reversible voltage showed in fig.1 shows: 1.The higher temperature have lower reversible voltage. 2. The higher pressure has lower reversible voltage. That is to say, the efficiency of water electrolysis will be improved when we raise the temperature and pressure if only considering the reversible voltage, but the effect of changing pressure to reversible voltage is actually very small. There are still many advantages for electrolyzing water in high pressure condition. For example, water can still maintain the liquid state under high pressure even when temperature is high.

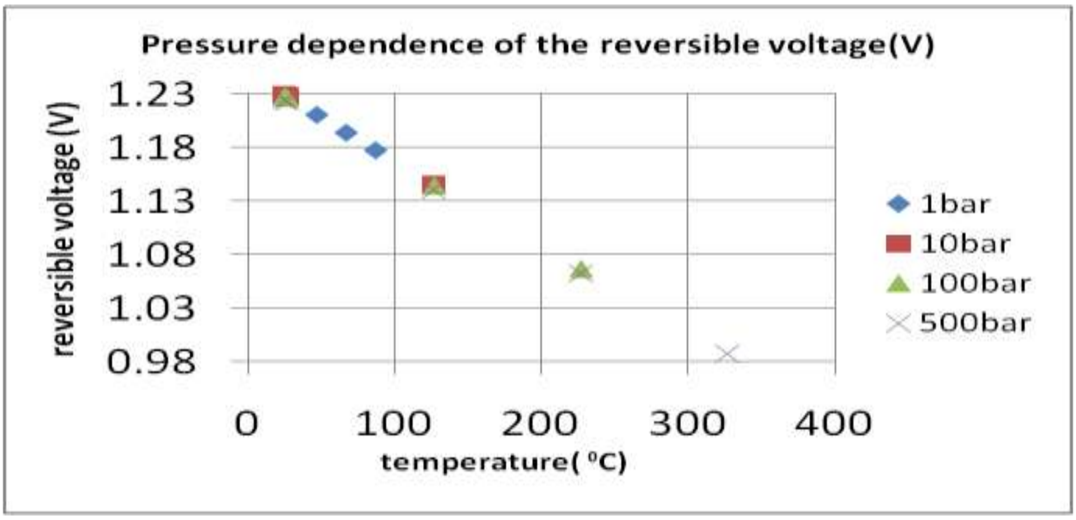

Fig. 1 diagram of reversible voltage via temperature and pressure

To raise temperature can significantly improve the efficiency of water electrolysis in all of reaction mechanism. To compress hydrogen in the electrolyzer can also save the energy consume of compressing hydrogen if we need to compress hydrogen into hydrogen storage,

To consult the research of proton exchange membrane fuel cell (PEM fuel cell) found the activation polarization is the same between proton exchange membrane fuel cell and electrolysis without proton exchange membrane fuel cell. So we quoted the research of the proton exchange membrane fuel cell in Thampan [3], the relationship between current density and temperature is:

(9)

$$i_0 = \gamma_M \exp[-\frac{E}{R}(\frac{1}{T} - \frac{1}{T_{ref}})] i_{0.ref}$$

If we consider the anode, the formula is:

(10)

$$i_{A.0} = \gamma_M \exp[-\frac{E_A}{R}(\frac{1}{T} - \frac{1}{T_{ref}})] i_{A.0.ref}$$

If we consider the cathode, the formula is:

(11)

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

Where $i_{A.0}$ and $i_{C.0}$ are exchange current density of anode and cathode respectively, $i_{A.0.ref}$ and $i_{C.0.ref}$ are reference exchange current density of anode and cathode respectively. The value of platinum electrode of that are 10^{-3}A/cm^2 and 10^{-11}A/cm^2 respectively. r_M is roughness factor, it's value is about 1.8 for platinum electrode in Wang[4].

Regarding to the influence of pressure to activation overpotential, owing to ionic bond energy is almost not influence by pressure in Hamann [5]. Furthermore, rate determining step of activation polarization reaction is desorption between hydrogen ion and electrode. This is metal -nonmetal bonding, is typical ionic bond, and the bonding energy determine the rate of desorption, according to statement in Hamann [5], thus we can conclude that activation overpotential is not influenced by pressure. So activation overpotential is not considered in this article.

Fig. 2 shows that when we fix exchange current density, we found activation overpotential increase when temperature increases. The result is not compatible with experimental result. On the experiment, when temperature is the higher, the supply voltage is lower. The phenomenon can be observed under low current density like 100mA/cm^2. Activation overpotential plus reversible voltage are almost equal to total supply voltage under the low current density like 100mA/cm^2. And we know reversible voltage do not change with temperature that much than that of supply voltage. So we can make a conclusion, that is, when temperature is higher, the activation overpotential becomes lower. As fig. 3, we can see the result of correcting current density varied with temperature, when temperature rises, activation voltage decreases, it is qualitatively correspond to the result of experiment.

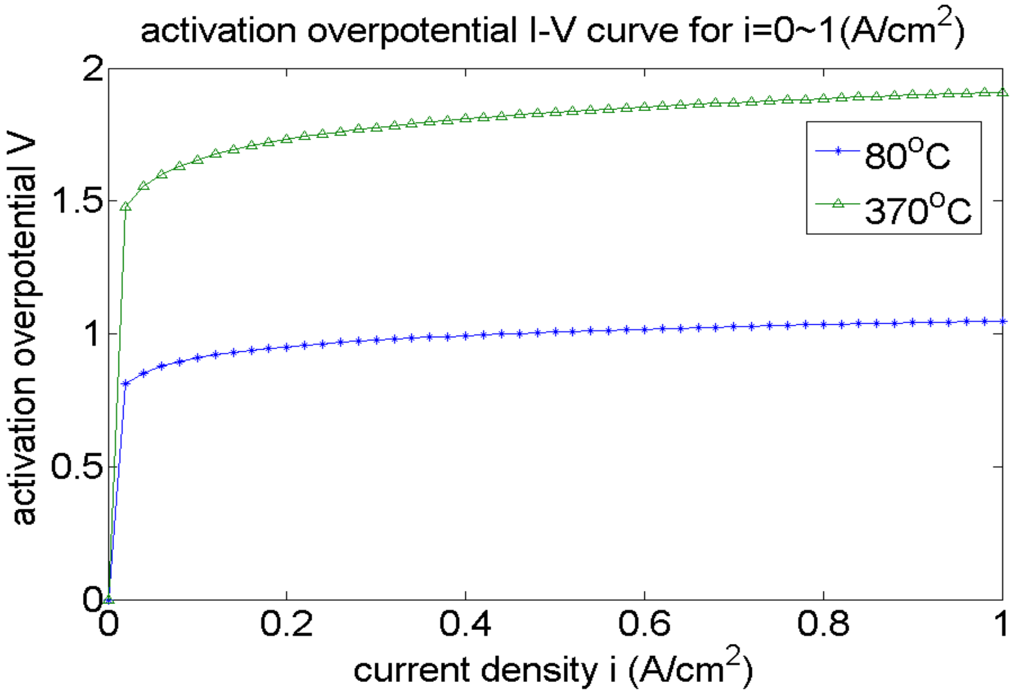

Fig. 2 relation between activation overpotential and current under 80°C, 370°C while the effect of temperature to exchange current density is not considered

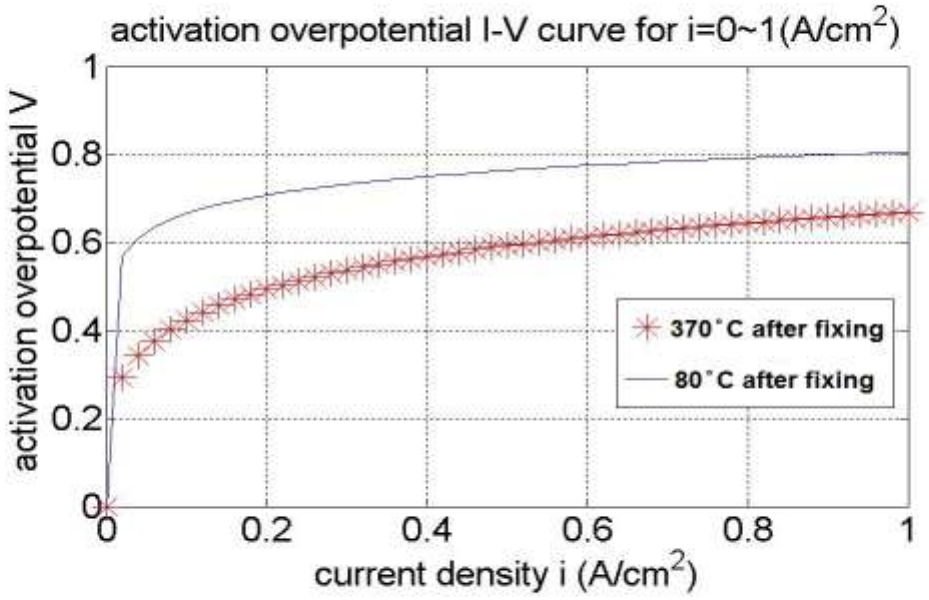

Fig. 3 polarization curve of activation overpotential, after considering the effect of temperature to exchange current density

Line segment of electrodes means the wire which joins the electrode slice to supply the electric current, and the part have same temperature with electrode. Because this article must consider the high temperature, metal ohmic resistance will increase in this condition, this article has discussed about this. We only consider the line segment ohmic resistance without electrode resistance to calculate ohmic overpotential. Because electrode slice is very thin and compared with the area of line segment, the area of electrode is wilder. So the resistance of electrode slice, compared with resistance of line segment is very small and can be neglected.

We have compared the experimental value of ohmic overpotential made by Kuhn [6], which used proton exchange membrane not added electrolyzer. The calculated result of empirical equation of ohmic overpotential had made by Roy [7]. We found the electrolyte not added in proton exchange membrane has better performance only considering the effect of bubble. The reason should be the interference that the bubbles cause between two electrodes become significant when the interval of electrodes is very small. Because of void fraction rising seriously interfere in the transportation of the ion between two electrodes. But this article considers the no added proton membrane electrolyte with proper interval between electrodes. In view of the experimental result of Kuhn [6]., we can make a conclusion the ohmic overpotential due to bubbles can be neglected under the current density smaller than 1A/cm^2.

There is no theory to calculate concentration overpotential varies with temperature, pressure and current. We investigate the diffusion of ion with standard pressure and temperature as table 1.

We substitute the data in table 1 into Eq. (6), which is the relationship between concentration overpotential and current. The concentration overpotential can be neglected when the current density is below 1A/cm^2. The concentration overpotential should be lower under the high temperature which we discussed. Because the equivalent conductivity and ionic mobility increase with temperature increasing causes ions more easy to transport, then decrease the resistance shown as table 2.

Table 1 some properties of 0.5m electrolyte NaOH under standard temperature and pressure

Comments	**Parameters**	**Dimensions**	**values**
The activation of ion j	α_j	mol/ml	0.693
The diffusion coefficent of ion j	D_j	none	2.632x10^{-9}
The transport number of ion j	t_j	none	0.798
diffusion layer thickness	d	m	0.0005

The mobility of ion j	u_j	m^2/s V	$20.5x10^{-8}$
∗in alkaline electrolyte, ion j is OH^-			

Table 2 the effect of temperature on ions [6], [16]

OH^-	Dimensions	18°C	25 °C
equivalent conductivity	cm^2/Ω	171	198.3
mobility of ion	m^2/V s	$17.7x10^{-8}$	$20.5x10^{-8}$

In addition, the effect of pressure to ionic transportation is limited found by Hamann [5]. We neglect the effect of pressure to calculate concentration overpotential.

We only consider the relationship of voltage and current below $1A/cm^2$, and then we can neglect ohmic overpotential due to bubble and concentration overpotential under the situation. The supply voltage is added by the three mechanisms which is reversible voltage, activation of overpotential and Ohmic overpotential owing to the electrode of segment of line.

The influence of temperature for supply voltage is shown in fig. 4. The supply voltage is lower when temperature is higher. This is the reason why we want to electrolyte water under the high temperature. We can get the energy efficiency difference between large and small line segment area from fig. 5 and fig. 6 while the ohmic overpotential due to line segment is about 23% of supply voltage under high temperature as fig. 5, thus the ohmic overpotential due to line segment should be considered. But in general we have to save equipment funds, often using $1mm^2$ cross-sectional area of the line segment, in fact, result in the loss of power on.

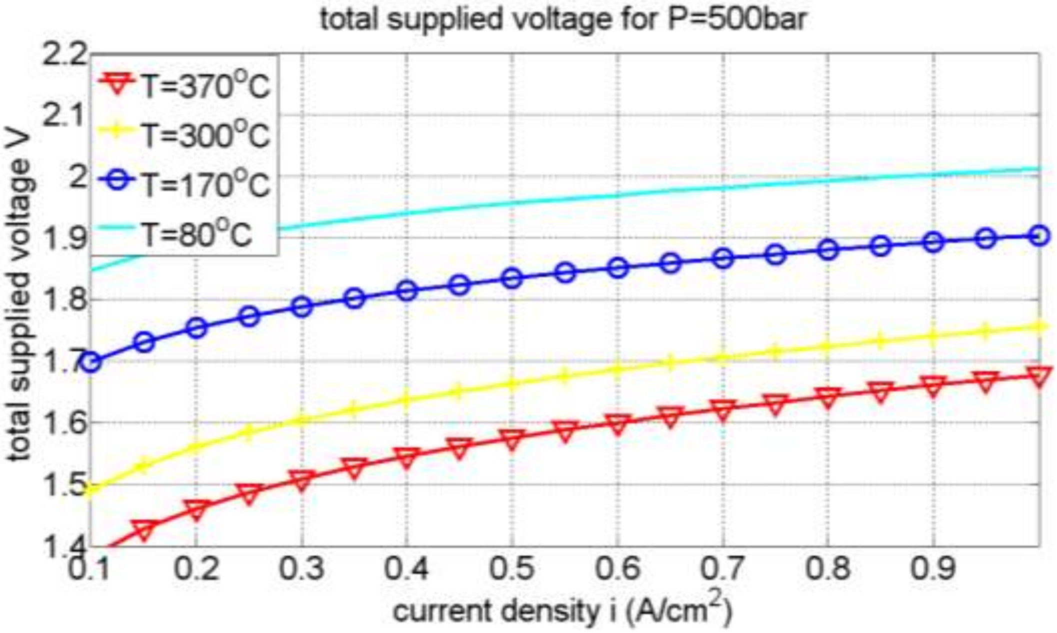

Fig. 4 polarization curve of supply voltage under 500bar

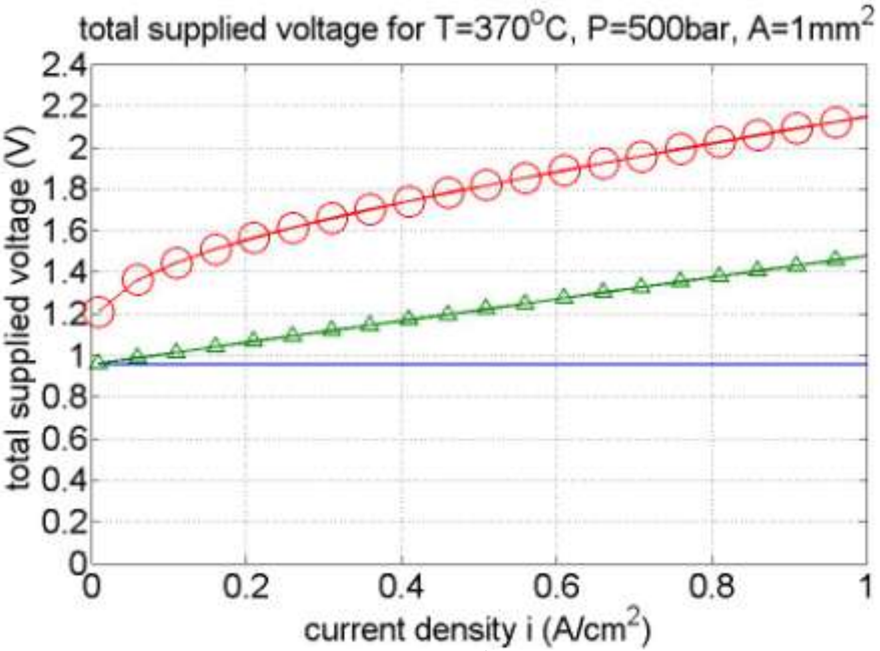

Fig. 5 comparison of three mechanism under 370^0C/500bar，the area of line segment is 1mm^2, line=reversible overpotential, triangle=ohmic overpotential plus reversible overpotential, circle=total supplied voltage=ohmic overpotential plus reversible overpotential plus activation overpotential

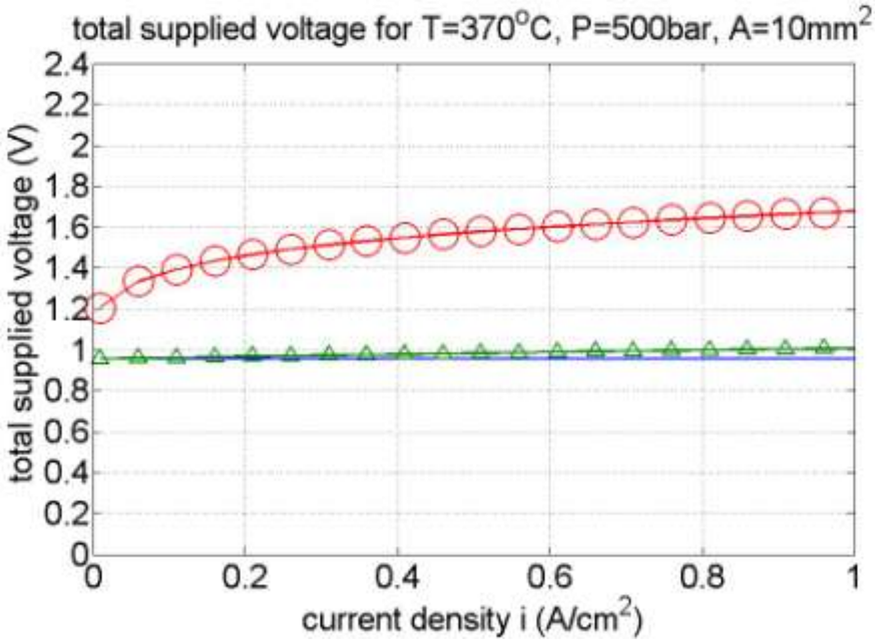

Fig. 6 comparison of three mechanism under 370^0C/500bar，the area of line segment is 10mm^2, line=reversible overpotential, triangle=ohmic overpotential plus reversible overpotential, circle=total supplied voltage=ohmic overpotential plus reversible overpotential plus activation overpotential

The efficiency comparison of electrolysis under high temperature and high pressure and standard temperature and pressure are obtained by comparing fig. 6 and fig. 7. Under high temperature and pressure, electrolysis efficiency is better. Because the supply voltage is 1.678V under 500bar/370^{o}C, 1A/cm^2 and is 2.016V under 1bar/80^{o}C, 1A/cm^2, then we can obtain the efficiency increased about 17 %. Because while using the hydrogen commercially, mostly use the high-pressure hydrogen, and we need it be compressed while transporting it, so it is necessary to let hydrogen be high pressure condition.

The calculation of energy consumption is from Roy [7], and we change the hydrogen production rate unit into 1mole/s, then the power for compressing hydrogen form standard pressure into 500bar is 28.06 kW. If we fix current density to 1A/cm^2, the supply voltage is 1.678V under 500bar/370^{o}C. Increase the electrode area so the hydrogen producing rate is 1mole/s. After calculating, under 500bar/370^{o}C and the hydrogen generation rate is 1mole/s, the power of water electrolysis is 323.803kW.With the same method, we can obtain the power of water electrolysis is 389.027kW under 1bar/80oC and the hydrogen generation rate is 1mole/s.

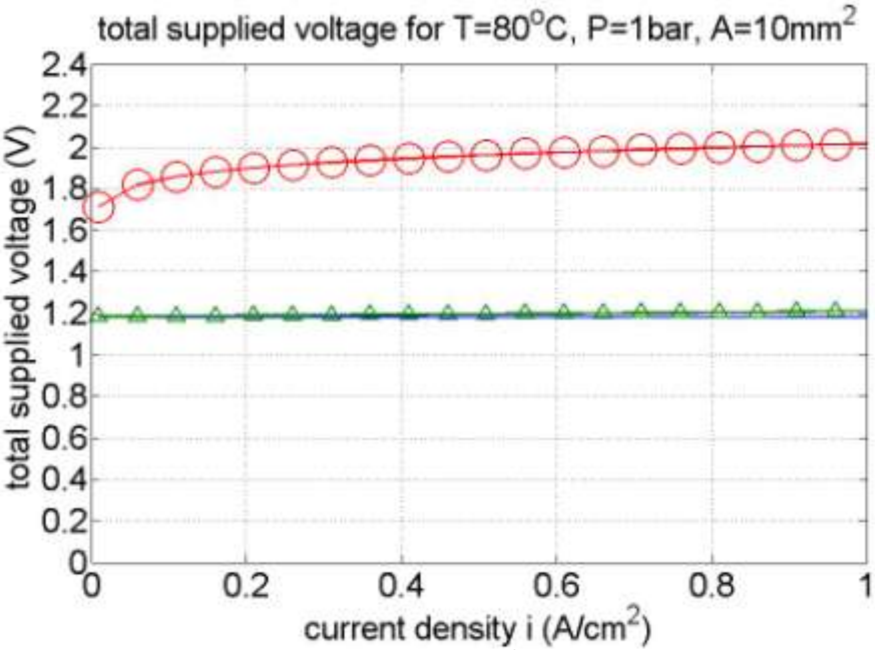

Fig. 7 the comparison of three mechanism under 80^{0}C/1bar, the area of line segment is 10mm^{2}, line=reversible overpotential, triangle=ohmic overpotential plus reversible overpotential and circle=total supplied voltage=ohmic overpotential plus reversible overpotential plus activation overpotential.

Then we add the hydrogen compressing energy 2.78kW and the power of water electrolysis 389.027kW. And 500bar/370^{o}C is originally high pressure, the hydrogen do not need to be compressed. Thus, The hydrogen producing efficiency at 500bar/370^{o}C, compared with that at 1bar/80^{o}C, is increased about 17%.The result of this article shows, electrolyze water under high pressure is more efficient then that under standard pressure, and the result hold the same position with the experimental result of Marangio [8].

IV. CONCLUSION

1. As temperature or pressure rises, the reversible voltage is decreases.
2. The activation overpotential decrease as the temperature increases, but almost without pressure.
3. In the high temperature of 370^{o}C, the ohmic overpotential of the line segment should be subject to consideration, but we can reduce it by increasing the area of line segment or reducing the length of line segment.
4. The ohmic overpotential due to bubbles increased with temperature increasing, and decrease with pressure increasing, but it can be neglected while current density is lower than 1A/cm^{2}.
5. At the standard temperature, the concentration overpotential increase with temperature increasing, and can be neglected while current density is lower than 1A/cm^{2}.
6. When the consumption of compressing gas in high temperature and high pressure condition is not considered, the efficiency of water electrolysis is increased about 17%. When the consumption of compressing gas in high temperature and pressure condition is considered, the efficiency of water electrolysis is increased about 22%.

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