

Efficiency and Gas-water Balance Condition of Solar Energy $\text{H}_2\text{O} \rightleftharpoons \text{H}_2 + \frac{1}{2}\text{O}_2$ power Cycle

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Abstract: In this paper, the principle and concept of $\text{H}_2\text{O} \rightleftharpoons \text{H}_2 + \frac{1}{2}\text{O}_2$ ideal cycle were proposed firstly, which prove the existence of theoretical efficiency limits and why it is irreversible, as well as the essential of theoretical efficiency. Discussed impact factor of the working cycle efficiency and Gas-water Balance Condition, analysis method and design computation equation were showed, which build the theoretical foundation of the application of the power cycle.

Keywords: principle, Efficiency, Gas-water Balance, $\text{H}_2\text{O} \rightleftharpoons \text{H}_2 + \frac{1}{2}\text{O}_2$ power Cycle

Introduction: the principle of solar energy $\text{H}_2\text{O} \rightleftharpoons \text{H}_2 + \frac{1}{2}\text{O}_2$ power cycle is to collect and transfer the solar energy into electrical energy with photovoltaic effect of semiconductor, and into chemical energy of hydrogen and oxygen through water electrolyzing, with which the solar energy is stored. And the chemical energy can be transferred into electrical energy through hydrogen and oxygen fuel cell. And the $\text{H}_2\text{O} \rightleftharpoons \text{H}_2 + \frac{1}{2}\text{O}_2$ power cycle is finished when the hydrogen and oxygen are composed as water finally. With this new power cycle, the unstable, intermittent, scattered, uncontrolled, and low-grade solar energy are collected, transferred and stored as stable and high-grade energy. It could be supposed as a engine which could independently run using sunlight as fuel, which could be used as power source for architecture on earth or space, which is the important advanced technology for renewable energy. In this paper, we will begin with the ideal cycle theory and enthalpy-entropy graphic, and then introduce the irreversible reason, as well as the concept and analysis methods for efficiency limit, working cycle efficiency and the Gas-water balance condition.

1. $\text{H}_2\text{O} \rightleftharpoons \text{H}_2 + \frac{1}{2}\text{O}_2$ ideal cycle

Supposing that water electrolyte process $\text{H}_2\text{O} \rightarrow \text{H}_2 + \frac{1}{2}\text{O}_2$ and fuel cell process $\text{H}_2 + \frac{1}{2}\text{O}_2 \rightarrow \text{H}_2\text{O}$ are carrying with infinity slow speed in constant temperature and pressure, they can be considered as reversible processes. Then the electrolyte process $\text{H}_2\text{O} \rightarrow \text{H}_2 + \frac{1}{2}\text{O}_2$ will translate all the input electrical power W_i into Thermodynamic Potentials energy ΔG_H of $\text{H}_2 + \frac{1}{2}\text{O}_2$, fuel cell process $\text{H}_2 + \frac{1}{2}\text{O}_2 \rightarrow \text{H}_2\text{O}$ will turn all the Thermodynamic Potential energy ΔG_L into output electrical power W_o , which because that the water electrolyte process turn the H^+ and OH^- of liquid H_2O into $\text{H}_2 + \frac{1}{2}\text{O}_2$ directly, while fuel battery process turn $\text{H}_2 + \frac{1}{2}\text{O}_2$ into free H_2O molecule (correspond to gaseity water), the coagulation of water does not attend the electrochemical process, as shows in figure1.

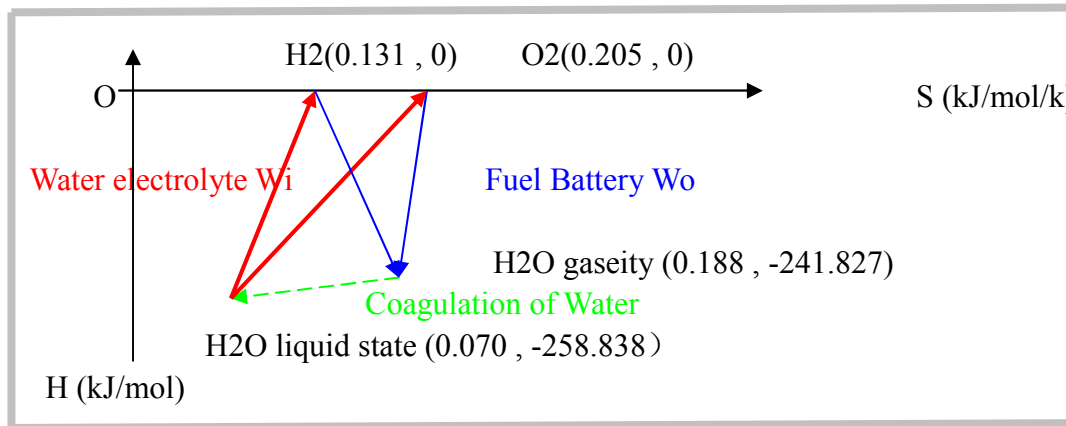
So, $\eta_{\max}$, the efficiency of ideal cycle $\text{H}_2\text{O} \rightleftharpoons \text{H}_2 + \frac{1}{2}\text{O}_2$, can be described as:

$$\eta_{\max} = W_o / W_i = \Delta G_L / \Delta G_H.$$

ΔG_H is the Gibbs free energy of liquid state H_2O ;

ΔG_L is the Gibbs free energy of gaseity H_2O .

Fig1: STP $\text{H}_2\text{O} \rightleftharpoons \text{H}_2 + \frac{1}{2}\text{O}_2$ Ideal Cycle enthalpy-entropy Graphic



As Gibbs function $G = H - TS$

Water electrolyte process in constant temperature and pressure: $\text{H}_2\text{O} \rightarrow \text{H}_2 + \frac{1}{2}\text{O}_2$

The change of Gibbs free energy per mol outcome to reactant: $\Delta \hat{g}_f H = \Delta \hat{h}_f - T \Delta \hat{s}$

$$\text{Here: } \Delta \hat{h}_f = (\hat{h}_f)_{\text{H}_2} + \frac{1}{2}(\hat{h}_f)_{\text{O}_2} - (\hat{h}_f)_{\text{H}_2\text{O liquid state}}$$

$$\Delta \hat{s} = (\hat{s})_{\text{H}_2} + \frac{1}{2}(\hat{s})_{\text{O}_2} - (\hat{s})_{\text{H}_2\text{O liquid state}}$$

Fuel cell process in constant temperature and pressure: $\text{H}_2 + \frac{1}{2}\text{O}_2 \rightarrow \text{H}_2\text{O}$

The change of Gibbs free energy per mol outcome to reactant: $\Delta \hat{g}_f L = \Delta \hat{h}_f - T \Delta \hat{s}$

$$\text{Here: } \Delta \hat{h}_f = (\hat{h}_f)_{\text{H}_2\text{O gaseity}} - ((\hat{h}_f)_{\text{H}_2} + \frac{1}{2}(\hat{h}_f)_{\text{O}_2})$$

$$\Delta \hat{s} = (\hat{s})_{\text{H}_2\text{O gaseity}} - ((\hat{s})_{\text{H}_2} + \frac{1}{2}(\hat{s})_{\text{O}_2})$$

Note: $(\hat{h}f)_{H_2}$, $(\hat{h}f)_{O_2}$, $(\hat{h}f)_{H_2O}$ and $(\hat{s})_{H_2}$, $(\hat{s})_{O_2}$, $(\hat{s})_{H_2O}$ are mol enthalpy and entropy of hydrogen, oxygen, water

Gibbs Free energy loss of $H_2O \rightleftharpoons H_2 + \frac{1}{2}O_2$ ideal cycle

$$\Delta\hat{G}_c = \Delta\hat{g}_fH - (-\Delta\hat{g}_fL) \\ = [(\hat{h}f)_{H_2O \text{ gaseity}} - (\hat{h}f)_{H_2O \text{ liquid state}}] - T[(\hat{s})_{H_2O \text{ gaseity}} - (\hat{s})_{H_2O \text{ liquid state}}]$$

Note: Gibbs Free energy loss of Ideal cycle has no correlation with process of water electrolyte or fuel battery process, which only is correlative to enthalpy and entropy of liquid state or gaseity water on the run state (temperature, pressure).

In STP condition (298.15K, 0.1MPa): $\Delta\hat{g}_fH = 237.21$ [kJ/mol], $\Delta\hat{g}_fL = -228.64$ [kJ/mol]
 Loss of idea cycle is: $\Delta\hat{G}_c = [-241.827 - (-285.838)] - 298.15 * [0.18883 - 0.07005]$
 $= 8.6$ [kJ/mol]

Efficiency of the ideal cycle is: $\eta_{\max} = \Delta\hat{g}_fL / \Delta\hat{g}_fH = 96\%$

Conclude:

- 1) Although in the ideal cycle $H_2O \rightleftharpoons H_2 + O_2$, that is both the water electrolyte and fuel battery processes are reversible, there are absolute Gibbs free energy loss of as: $\Delta\hat{G}_c = \Delta\hat{g}_fH - (-\Delta\hat{g}_fL)$
- 2) The efficiency limit of ideal cycle $H_2O \rightleftharpoons H_2 + O_2$ is : $\eta_{\max} = \Delta GL / \Delta GH$
- 3) On STP, the efficiency of ideal cycle $H_2O \rightleftharpoons H_2 + O_2$ is : $\eta_{\max} = 96\%$

2. $H_2O \rightleftharpoons H_2 + O_2$ Working Cycle

In fact, the process of water electrolyte $H_2O \rightarrow H_2 + \frac{1}{2}O_2$ and fuel battery process $H_2 + \frac{1}{2}O_2 \rightarrow H_2O$ are both irreversible. Then water electrolyte process $H_2O \rightarrow H_2 + \frac{1}{2}O_2$ can turn part of the input power W_i as $\eta_e W_i$ into Thermodynamic Potential energy $\Delta GH = \eta_e W_i$ of $H_2 + \frac{1}{2}O_2$, while fuel cell process can only turn part of Thermodynamic Potential energy ΔGL as $\eta_f \Delta GL$ into output electrical power $W_o = \eta_f \Delta GL$.

Thus, the working cycle efficiency is:

$$\eta_C = W_o / W_i = \eta_e \eta_f \Delta GL / \Delta GH = \eta_e \eta_f \eta_{\max} = 1.18 (V_{fc} / V_{ec}) \eta_{\max}$$

Here: $\eta_e = 1.48 / V_{ec}$ is the electrolyte efficiency,

$V_{ec} = 1.6 - 2.0V$ is the electrolyte monopole volt.

$\eta_f = V_{fc} / 1.25$ is the fuel cell efficiency,

$V_{fc} = 0.85 - 1.15V$ is the fuel cell monopole volt.

η_e, η_f is from Faraday Law

When the working current is less than 500mA/cm², it can come to $\eta_e > 85\%$, $\eta_f > 75\%$; the working cycle efficiency is $\eta_C > 60\%$ at present

H₂O $\rightleftharpoons$ H₂+O₂ Working Cycle's Gas-water Balance

Pe is the Water electrolyte power;

H₂O $\rightarrow$ H₂+1/2O₂ water consuming speed and hydrogen Oxygen producing speed:

Speed of water consuming: $\eta_e P_e / V_{ec} / 2F$ [molH₂O/s], F is the Faraday constant

Speed of hydrogen producing: $\eta_e P_e / V_{ec} / 2F$ [mol H₂/s]

Speed of oxygen producing: $\eta_e P_e / V_{ec} / 4F$ [mol O₂/s]

Fuel cell power is Pf:

H₂+1/2O₂ $\rightarrow$ H₂O hydrogen Oxygen consuming speed and water producing speed:

Speed of water producing: $P_f / \eta_f / V_{fc} / 2F$ [molH₂O/s]

Speed of hydrogen consuming: $P_f / \eta_f / V_{fc} / 2F$ [mol H₂/s]

Speed of Oxygen consuming: $P_f / \eta_f / V_{fc} / 4F$ [mol O₂/s]

Synchronous Gas-water Balance condition of working Cycle:

$$P_f / P_e = \eta_e \eta_f V_{fc} / V_{ec} = 1.18 (V_{fc} / V_{ec})^2$$

Suppose that water electrolyte process works Ne hour/day; Fuel battery process works Nf hour/day,

Asynchronous Gas-water balance condition of working Cycle :

$$P_f / P_e = \eta_e \eta_f V_{fc} / V_{ec} = 1.18 (N_e / N_f) (V_{fc} / V_{ec})^2$$

Conclude:

1) Practical working cycle efficiency is: $\eta_C = 1.18 (V_{fc} / V_{ec}) \eta_{max}$

2) Synchronous Gas-water balance condition is: $P_f / P_e = 1.18 (V_{fc} / V_{ec})^2$

3) Asynchronous Gas-water balance condition is: $P_f / P_e = 1.18 (N_e / N_f) (V_{fc} / V_{ec})^2$

4) Efficiency of fuel cell is more reasonable to be calculated by low-heat value:

$$\eta_f = V_{fc}/1.25$$

3. Solar Energy $H_2O \rightleftharpoons H_2 + O_2$ working cycle

If: The efficiency of PV is η_s , the area S_k [m²] is placed horizontally;
the local annual average solar radiation is E_s [W/m²],
sunshine time is H_a [h/a],
the maximum of continue cloudy is D_{cax} ,
the maximum of transient radiation is E_{smax} [W/ m²]

Then: the average input power of water electrolyte is: $P_e = \eta_s S_k E_s$ [W],
the max input power of water electrolyte is: $P_{emax} = \eta_s S_k E_{smax}$ [W],
The hydrogen production is: $3600 H_a \eta_e P_e / V_{ec} / 2F$ [mol H₂/a]
the max transient hydrogen production is: $\eta_e \eta_s S_k E_{smax} / V_{ec} / 2F$ [mol H₂/s]

If: Output power of fuel cell is P_f , the efficiency is η_f ,
Design annual working hour is N_a ,
the max transient output is P_{fmax} [W]

Then:

Annual hydrogen consuming is $3600 N_a P_f / \eta_f / V_{fc} / 2F$ [mol H₂/a]
Cycle least hydrogen reserves is $24 * 3600 D_{cax} P_f / \eta_f / V_{fc} / 2F$ [mol H₂]
Max transient hydrogen consuming is $P_{fmax} / \eta_f / V_{fc} / 2F$ [mol H₂/s]

Annual asynchronous Gas-water balance condition of Working Cycle is :

$$P_f / P_e = \eta_e \eta_f (H_a / N_a) V_{fc} / V_{ec} = 1.18 (V_{fc} / V_{ec})^2 (H_a / N_a)$$

Or: $P_f / S_k = \eta_s \eta_e \eta_f (H_a / N_a) V_{fc} / V_{ec} = 1.18 (V_{fc} / V_{ec})^2 (H_a / N_a) \eta_s E_s$ [W / m²]

Annual utilization efficiency of solar energy is:

$$\eta_{CS} = P_f N_a / E_s S_k H_a = \eta_s \eta_e \eta_f V_{fc} / V_{ec} = 1.18 \eta_s (V_{fc} / V_{ec})^2$$

Conclusions

1. Annual utilization efficiency of solar energy is: $\eta_{CS} = 1.18 \eta_s (V_{fc} / V_{ec})^2$
2. Annual asynchronous Gas-water balance condition of Working Cycle is:
 $P_f / P_e = 1.18 (V_{fc} / V_{ec})^2 (H_a / N_a)$
3. Cycle least hydrogen reserves is: $24 * 3600 D_{cax} P_f / \eta_f / V_{fc} / 2F$ [mol H₂]
4. the maximum of transient in/output power and flux are design parameter correlative to circuit and pipeline.

According to the simple analysis of idea cycle $\text{H}_2\text{O} \rightleftharpoons \text{H}_2 + \text{O}_2$, working cycle efficiency and Gas-water balance condition, the principle and main characters of solar energy $\text{H}_2\text{O} \rightleftharpoons \text{H}_2 + \text{O}_2$ power cycle were introduced, and the synchronous、asynchronous、transient Gas-water condition were pointed out.

References

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