Nernst voltage loss in oxyhydrogen fuel cells

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ABSTRACT

Normally, the Nernst voltage calculated from the concentration of the reaction gas in the flow channel is considered to be the ideal voltage (reversible voltage) of the oxyhydrogen fuel cell, but actually it will cause a concentration gradient when the reaction gas flows from the flow channel through the gas diffusion layer to the catalyst layer. The Nernst voltage loss in fuel cells in most of the current literature is thought to be due to the difference in concentration of reaction gas in the flow channel and concentration of reaction gas on the catalyst layer at the time when the high net current density is generated. Based on the Butler-Volmer equation in oxyhydrogen fuel cell, this paper demonstrates that the Nernst voltage loss is caused by the concentration difference of reaction gas in flow channel and on the catalytic layer at the time when equilibrium potential (Galvanic potential) of each electrode is generated.

Keywords: Nernst voltage; activation overvoltage; concentration loss, equilibrium potential, exchange current density, net current density
1. Introduction

A fuel cell is a chemical device that directly converts the chemical energy contained in fuel into electric energy. It is the fourth power generation technology after hydroelectric, thermal, and atomic power generation. Since the fuel cell converts the Gibbs free energy of the chemical energy of the fuel into electric energy through an electrochemical reaction, it is not limited by the effect of the Carnot cycle, so the efficiency is high [1]. The two parameters closely related to the performance of the fuel cell are the output voltage and current of the battery. Under a certain temperature, pressure, and concentration of the substance, the maximum theoretical voltage that the fuel cell can output is determined by the Nernst equation, which is called reversible voltage. However, there are a series of irreversible processes in actual fuel cells. These irreversible processes lead to a series of corresponding irreversible voltage losses in the fuel cell. There are currently three recognized irreversible voltage losses: 1) Activation overvoltage loss; 2) Ohmic loss; 3) Concentration loss. The activation overvoltage loss is the lost Galvani potential in order to generate a net current. The ohmic loss is due to the voltage loss caused by the ohmic resistance of the internal components of the fuel cell. Obviously, the ohmic loss and the current are linear. The literature considers that concentration loss leads to two different voltage losses: drop of Nernst voltage and increase of activation overvoltage (concentration overvoltage) and in most of literatures it is believed that both of these voltage losses caused by concentration loss are due to the concentration difference between the reaction gas in the flow channel and the reaction gas on the surface of catalytic layer [2, 3]. Based on the Butler-Volmer equation this paper aims to prove that the reduction in Nernst voltage and the increase in activation overvoltage are caused by different concentration effects. This result has important significance, especially in the case of a low exchange current density, because difference in Nernst voltage loss and activation overvoltage loss caused by different concentration differences is very large, therefore, it has a great influence on the prediction of the true output voltage of fuel cells. Using the wrong concentration difference to estimate the concentration loss will seriously affect the judgment of the fuel cell performance.
2. Mathematical analysis

2.1 Galvani potential

When the external circuit of the fuel cell is disconnected, the reaction gas is continuously introduced into the flow channel. At this time, the electrode reaction starts at the catalytic layer. Take the anode reaction as an example:

\[ H_2 \rightleftharpoons 2H^+ + 2e^- \]  \hspace{1cm} (1)

During the reaction, both the forward reaction and the reverse reaction need to overcome certain activation barriers (Fig. 1) [4, 5], even though from the energy point of view the energy of the products is lower than the energy of the reactants (the reaction is spontaneous). However, due to the existence of activation barriers, the reaction rate is still limited. Current density is usually used instead of reaction rate as the basic performance parameter of the fuel cell.

![Fig.1. Energy change of reaction process in anode electrode. \( G_{1a} \) – Gibbs free energy of anode reactants; \( \Delta G_{1a} \) – activation energy of positive reaction in anode; \( G_{2a} \) – Gibbs free energy of anode products; \( \Delta G_{2a} \) – activation energy of reverse reaction in anode.](image)

Forward current density is

\[ j_{1a} = nF c^*_R a f_1 \exp\left(-\frac{\Delta G_{1a}}{RT}\right) \]  \hspace{1cm} (2)

Where

\( j_{1a} \) – The anode current density of the forward electrode reaction, \( \text{A} \cdot \text{cm}^{-2} \);
\( c_{Ra}^* \) – Surface concentration of \( \text{H}_2 \) on anode catalyst layer, \( \text{mol} \cdot \text{cm}^{-2} \);

\( n \) – Number of moles of electrons produced by 1 mol \( \text{H}_2 \);

\( R \) – Ideal gas constant, 8.314472 \( \text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \);

\( F \) – Faraday constant, 96485.33289 \( \text{C} \cdot \text{mol}^{-1} \);

\( T \) – The operating temperature of the fuel cell, K;

\( f_1 \) – The rate of decay from the activated state to the product, \( f_1 = \frac{kT}{h} \), \( k \) – Boltzmann constant; \( h \) – Planck constant. Since the operating process of fuel cell is considered to be a process with constant temperature and pressure [6], the decay rate of each reaction in each electrode is the same. Replace \( f_1 \) by \( f \):

\[
   j_{1a} = nF c_{Ra}^* f \exp\left(-\frac{\Delta G_{1a}}{RT}\right)
\]

(3)

Reverse current density is

\[
   j_{2a} = nF c_{pa}^* f \exp\left(-\frac{\Delta G_{2a}}{RT}\right)
\]

(4)

Where

\( j_{2a} \) – The anode current density of the reverse electrode reaction, \( \text{A} \cdot \text{cm}^{-2} \);

\( c_{pa}^* \) – Surface concentration of product of electrode reaction on anode catalyst layer, \( \text{mol} \cdot \text{cm}^{-2} \).

During the electrode reaction, the reactants are continuously consumed and the products continuously accumulate. The concentration of the reactants is reduced compared to the concentration of the reaction gases in the flow channel. At the same time electrons accumulate at the metal electrodes, \( \text{H}^+ \) accumulate at the surface of catalyst layer, an electric field is formed between the metal electrode and the catalytic layer, the energy of the reaction system increases, the activation barrier of the forward reaction and the reverse reaction both change, the rate of forward reaction decreases, and the rate of reverse reaction increases. When current densities of the forward and reverse reaction are equal, the intensity electric field no longer increases and a stable equilibrium potential difference (Galvani potential) is achieved between the metal electrode and the catalyst layer, at this time between the flow channel and the catalyst layer surface a stable concentration gradient is formed (Figure 2). The activation barriers of the final reaction become as shown in Fig. 3 [2, 3].
Fig. 2. Diagram of the diffusion layer formed at the anode during the operation of the oxyhydrogen fuel cell.

The consumption of $H_2$ gas at the anode-catalyst interface leads to a decrease in concentration of $H_2$. The concentration of $H_2$ gas decreases from the bulk concentration ($c_{H_2}^0$) in the flow channel to a lower concentration in the catalytic layer ($c_{H_2}^{0*}$). The velocity of $H_2$ gas in the flow channel is shown by the size of the flow arrow. At the channel-electrode interface, the velocity of $H_2$ gas drops to 0, which marks the beginning of the gas diffusion layer.

Fig. 3. Energy change of reaction process during equilibrium potential of anode.
As can be seen from the figure, the activation barrier of forward reaction has increased by $\alpha_a nF \Delta \phi_1$, the activation barrier of forward reaction has reduced by $(1 - \alpha_a)nF\Delta \phi_1$. $\alpha$ is called transfer coefficient, $\alpha$ expresses how the change in the electrical potential across the reaction interface changes the sizes of the forward versus reverse activation barriers. The value of $\alpha$ is always between 0 and 1. For “symmetric” reactions, $\alpha = 0.5$. For most electrochemical reactions, $\alpha$ ranges from about 0.2 to 0.5 [2,3,6-8].

At this time current density is

For anode:

$$j_a = nF c_{R_a}^0 f_1 \exp\left(-\frac{\Delta G_{1a}}{RT} + \alpha_a nF \Delta \phi_1\right)$$

(5)

$$j_{2a} = nF c_{p_a}^0 f \exp\left[-\frac{\Delta G_{2a} - (1 - \alpha_a)nF\Delta \phi_1}{RT}\right]$$

(6)

$$j_1 = j_2 = j_{0a}$$

(7)

Where

$\Delta \phi_1$ – Galvanic potential of Anodic, V;

c_{R_a}^0 – Concentration of reactant at equilibrium potential of anode, mol ∙ cm$^{-2}$;

c_{p_a}^0 – Concentration of product at equilibrium potential of anode, mol ∙ cm$^{-2}$;

$\alpha_a$ – Transfer coefficient of Anode electrode reaction;

$j_{0a}$ – Anode exchange current density, A ∙ cm$^{-2}$.

Similarly, the cathode exchange current density is:

$$j_{0c} = nF c_{R_c}^0 f \exp\left(-\frac{\Delta G_{1c} + \alpha_a nF \Delta \phi_2}{RT}\right)$$

(8)

$$= nF c_{p_c}^0 f \exp\left[-\frac{\Delta G_{2c} - (1 - \alpha_a)nF\Delta \phi_2}{RT}\right]$$

where

$\Delta \phi_2$ – Galvanic potential of cathode, V;

c_{R_c}^0 – Concentration of reactant at equilibrium potential of cathode, mol ∙ cm$^{-2}$;

c_{p_c}^0 – Concentration of product at equilibrium potential of cathode, mol ∙ cm$^{-2}$;

$\alpha_c$ – Transfer coefficient of cathode electrode reaction;

$j_{0c}$ – Cathode exchange current density, A ∙ cm$^{-2}$.

From the equations (5), (6), (7), and (8) for exchanging current density, the equilibrium potentials of the anode and cathode can be obtained as:
\[
\Delta \phi_1 = \frac{\Delta G_{2a}-\Delta G_{1a}}{nF} - \frac{RT}{nF} \ln \frac{c_{p,a}^{o*}}{c_{R,a}^{o*}} = \frac{G_{1a}-G_{2a}}{nF} - \frac{RT}{nF} \ln \frac{c_{p,a}^{o*}}{c_{R,a}^{o*}}
\]  
(9)

\[
\Delta \phi_2 = \frac{\Delta G_{2c}-\Delta G_{1c}}{nF} - \frac{RT}{nF} \ln \frac{c_{p,c}^{o*}}{c_{R,c}^{o*}} = \frac{G_{1c}-G_{2c}}{nF} - \frac{RT}{nF} \ln \frac{c_{p,c}^{o*}}{c_{R,c}^{o*}}
\]  
(10)

In fact, \(\Delta \phi_1\) and \(\Delta \phi_2\) are the thermodynamic electrode potential formula [8].

The Nernst voltage of the oxyhydrogen fuel cell is:

\[
E = E_0 - \frac{RT}{nF} \ln \frac{1}{c_{H_2}c_{O_2}^{\frac{1}{2}}}
\]

(11)

Where

\(E_0\) – Standard reversible voltage for oxyhydrogen fuel cell.

Obviously, when the equilibrium potential is reached, the concentration of the reactants at anode and cathode is lower than the concentration of the reactant gas in the corresponding flow channel. The Nernst voltage loss caused by this concentration difference is:

\[
v_{Nernst} = E(c_{R,a}^{0}, c_{R,c}^{0}) - E(c_{R,a}^{0*}, c_{R,c}^{0*})
\]

\[
= (E_0 - \frac{RT}{nF} \ln \frac{1}{c_{R,a}^{0}c_{R,c}^{\frac{1}{2}}} - (E_0 - \frac{RT}{nF} \ln \frac{1}{c_{R,a}^{0*}c_{R,c}^{\frac{1}{2}}})
\]

\[
= \frac{RT}{nF} \ln \frac{c_{R,a}^{0}}{c_{R,a}^{0*}c_{R,c}^{\frac{1}{2}}} + \frac{RT}{nF} \ln \frac{c_{R,c}^{0}}{c_{R,c}^{0*}c_{R,c}^{\frac{1}{2}}}
\]  
(12)

Where

\(c_{R,a}^{0}\) – Concentration of reactant in flow channel of anode, mol \(\cdot\) cm\(^{-2}\);

\(c_{R,c}^{0}\) – Concentration of reactant in flow channel of cathode, mol \(\cdot\) cm\(^{-2}\);

So, the anode Nernst voltage loss is:

\[
v_{Nernst,a} = \frac{RT}{nF} \ln \frac{c_{R,a}^{0}}{c_{R,a}^{0*}}
\]  
(13)

the cathode Nernst voltage loss is:

\[
v_{Nernst,c} = \frac{RT}{nF} \ln \frac{c_{R,c}^{0}}{c_{R,c}^{0*}c_{R,c}^{\frac{1}{2}}}
\]  
(14)

From (13), (14) it can be seen that Nernst voltage loss is actually also a concentration loss.

2.2 Activation overvoltage loss
When the external circuit of the fuel cell is closed, the accumulated electrons are conducted from the anode to the cathode, and the hydrogen ions are transmitted from the anode side of the electrolyte to the cathode side. The electrode potential of the anode must be reduced, that is activation overvoltage. Activation overvoltage is a part of the voltage that must be sacrificed to start the operation of the fuel cell. As the activation overvoltage is generated, the activation barrier for the forward reaction decreases $\alpha_a nFv_{act_a}$, and the activation barrier for the reverse reaction increases $(1 - \alpha_a) nFv_{act_a}$, the rate of forward reaction exceeds the rate of reverse reaction, and the fuel cell produces a net current density. Taking into account the influence of the net current generation on the concentrations of reactant and product, net current density is [2, 9-11]:

$$j_a = j_0 a \frac{c^{\ast}_a}{c^{\ast}_R} \exp(\frac{\alpha_a nFv_{act_a}}{RT}) - j_0 a \frac{c^{\ast}_a}{c^{\ast}_P} \exp[-\frac{(1-\alpha_a) nFv_{act_a}}{RT}]$$  \hspace{1cm} (15)

Where

$c^{\ast}_R$ and $c^{\ast}_P$ – Concentrations of Anode electrode reactants and product at any time when the circuit is closed, mol · cm$^{-2}$;

$v_{act_a}$ – Anode activation overvoltage.

Similarly, the net current density of cathode is:

$$j_c = j_0 c \frac{c^{\ast}_c}{c^{\ast}_R} \exp(\frac{nFv_{act_c}}{RT}) - j_0 c \frac{c^{\ast}_c}{c^{\ast}_P} \exp[-\frac{(1-\alpha_c) nFv_{act_c}}{RT}]$$  \hspace{1cm} (16)

Where

$c^{\ast}_R$ and $c^{\ast}_P$ – Concentrations of cathode electrode reactants and product at any time when the circuit is closed, mol · cm$^{-2}$;

$v_{act_c}$ – Cathode activation overvoltage.

When the net current density is small, the concentration of the reactant and product on the catalyst layer does not change much compared with the concentration of the reactant and product at equilibrium potential, and the activation overvoltage is small, so for the anode, there are:

$$\frac{c^{\ast}_a}{c^{\ast}_R} \approx 1, \frac{c^{\ast}_a}{c^{\ast}_P} \approx 1$$

When $\alpha_a = 0.5$, the anode net current density can be written as follows:

$$j_a \approx j_0 a \exp(\frac{\alpha_a nFv_{act_a}}{RT}) - j_0 a \exp[-\frac{(1-\alpha_a) nFv_{act_a}}{RT}]$$
From equation (16) can get the relationship between overvoltage and net current density (Figure 4).

\[
\Delta \varphi = 2j_0^0a\sinh\left(\frac{nFv_{act,a}}{2RT}\right)
\]  

(16)

Fig.4. Effect of activation overvoltage on fuel cell performance without considering the concentration loss. Reaction kinetics typically inflicts an exponential loss on a fuel cell’s \(j–V\) curve as determined by the Butler–Volmer equation. The magnitude of this loss is influenced by the size of \(j_0^0\). (curves calculated for various \(j_0^0\) values with \(\alpha = 0.5, \ n = 2\) and \(T = 298.15\) K.)

It can be seen from this figure that the activation overvoltage increases rapidly at very small net current densities and at very large net current densities increases slowly and is almost constant. Obviously the higher the exchange current density, the smaller the activation overvoltage required to reach the same net current density. Should pay attention to the fact that the voltage at which the net current density is zero is not the ideal electromotive force but is the thermodynamically reversible voltage determined by the concentration of the reactants on catalytic layers of the anode and cathode at equilibrium potentials (not necessarily equal to 1.1 V but must be less than ideal reversible voltage). The difference between voltage at which the net current density is zero and the ideal electromotive force is the Nernst voltage loss, which is caused by the concentration difference between the reactants on the catalyst layer at the equilibrium potential and the reactants in the flow channel.
2.3 Concentration loss

The effect of change of the concentration of the reactants is neglected when the overvoltage is determined by equation (16). In fact, the net reaction rate will affect the surface concentration of reactants and products. For example, when the forward reaction rate increases drastically and the reverse reaction rate decreases sharply, the surface concentration of the reactants tends to be depleted. Obviously for a certain net current density, the lower the concentration of the reactants, the greater the activation overvoltage required to reach the same net current density, which leads to a sharp increase in the demand for additional activation overvoltages. This additional activation overvoltage is the concentration loss. At high current densities, the reactants in the catalytic layer are rapidly consumed, which leads to a sharp increase in the need for an activation overvoltage. The excess activation overvoltage is called concentration loss (concentration overvoltage) [12-14].

At high current densities, the second term in the Butler-Volmer equation can be discarded. The net anode current density simplifies to:

\[
j_a = j^0_a \frac{c_{R_a}^0}{c_{R_a}^*} \exp\left(\frac{\alpha_a nF \nu_{act_a}}{RT}\right) \quad (17)
\]

(17) can be expressed in the form of activation overvoltage:

\[
\nu_{act_a}(c_{R_a}^*) = \frac{RT}{\alpha_a nF} \ln \frac{j_a c_{R_a}^0}{j^0_a c_{R_a}^*} \quad (18)
\]

In this way concentration loss can be expressed as

\[
\nu_{conc_a} = \nu_{act_a}(c_{R_a}^*) - \nu_{act_a}(c_{R_a}^0) = \frac{RT}{\alpha_a nF} \ln \frac{j_a c_{R_a}^0}{j^0_a c_{R_a}^*} - \frac{RT}{\alpha_a nF} \ln \frac{j_a c_{R_a}^*}{j^0_a c_{R_a}^*}
\]

\[
= \frac{RT}{\alpha_a nF} \ln \frac{c_{R_a}^0}{c_{R_a}^*} \quad (19)
\]

The sum of the Nernst voltage loss and the concentration overvoltage in anode can be obtained from (13), (19):

\[
\nu_{conc_a} + \nu_{Nernst_a} = \frac{RT}{\alpha_a nF} \ln \frac{c_{R_a}^0}{c_{R_a}^*} + \frac{RT}{nF} \ln \frac{c_{R_a}^0}{c_{R_a}^*} \quad (20)
\]

Obviously, (20) is different from the concentration loss in the literature \(\nu_{conc_a} + \nu_{Nernst_a}\)_{literature} = \(1 + \frac{1}{\alpha_a} \frac{RT}{nF} \ln \frac{c_{R_a}^0}{c_{R_a}^*}\)
Concentration loss in literature \((v_{conc,a} + v_{Nernst,a})_{\text{literature}}\) has been increased compared to (20):

\[
\Delta = (1 + \frac{1}{\alpha_a} - \frac{RT}{nF} \ln \frac{c_R^0_a}{c_R^a}) - (\frac{RT}{\alpha_a nF} \ln \frac{c_R^0}{c_R^a} + \frac{RT}{nF} \ln \frac{c_R^0}{c_R^a})
\]

\[
= \frac{RT}{nF} \ln \left(\frac{c_R^0}{c_R^a}\right)^\frac{1}{\alpha_a} \times \left(1 - \frac{1}{(\beta_a - 1)}\right)
\]

(21)

Since \(0 < \alpha_a < 1\) and concentration of the reaction gas in the flow channel is constant, the smaller concentration of the reaction gas \(c_R^0_a\) at equilibrium potential, the greater the deviation of the concentration loss calculated in literature and from equation (20), the greater the error.

As mentioned above, the typical voltage loss of a fuel cell is shown in Fig. 5. When the fuel cell supplies electronic power, the actual voltage will drop due to several non-reversible factors.

**Fig. 5.** Ideal voltage and actual voltage diagram of oxyhydrogen fuel cell.

(1) Open circuit voltage which is lower than reversible voltage due to Nernst voltage loss caused by difference in concentration of reaction gas in flow channel and reaction gas at the time of generation of equilibrium potential; (2) Activation overvoltage assuming that the concentration of the reaction gas at the time of generation of net current is equal to concentration of the reaction gas at the generation of equilibrium potential. It slowly increases in the high current density region because the decrease in the reactant concentration is not taken into consideration. At this time, the concentration term is large, and only a few increase of activation
overvoltage can intensively increase the current density. When the concentration of reactant is greatly reduced, in order to achieve the same current density, the contribution of the activation overvoltage increases; (3) Linear ohmic voltage loss; (4) Additional activation overvoltage due to low concentration of reaction gas at net current compared to concentration of reaction gas at equilibrium potential

3. Summary

From the above discussion, it can be concluded that the voltage loss that causes the open circuit voltage to fall can be divided into four categories: (1) Nernst voltage loss caused by difference in concentration of reactants at equilibrium potential and concentration of reactants in flow channel; (2) Voltage loss due to activation overvoltage at low current density; (3) The linear ohmic voltage loss inside the fuel cell; (4) The concentration overvoltage due to the intensive decrease of concentration of reactants on the catalytic layer in the high current density. The concentration difference at high current density is the concentration difference of the reactants on the catalytic layer and reactant at equilibrium potential, not the concentration difference of the reactants on the catalytic layer and reactants in the flow channel mentioned in the literature. Therefore, the voltage loss (Nernst voltage loss and concentration overvoltage) caused by the concentration difference are (in the case of anode) \( \frac{RT}{nF} \ln \frac{c_{R_a}}{c_{R_a}} \) and \( \frac{RT}{\alpha_a nF} \ln \frac{c_{R_a}^\circ}{c_{R_a}} \) respectively, not \( \frac{RT}{nF} \ln \frac{c_{R_a}}{c_{R_a}} \) and \( \frac{RT}{\alpha_a nF} \ln \frac{c_{R_a}^\circ}{c_{R_a}} \) respectively mentioned in the literature.

References