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Analysis of transient characteristics for zinc-nickel single flow battery considering side reactions

S. G. Yao^{1,*}, R. Zhou¹, J. F. Li¹, M. Xiao¹, J. Cheng²

¹ Jiangsu University of Science and Technology, 212003, Zhenjiang, Jiangsu, China

² Zhejiang Yuyuan Energy Storage Technology Co., Ltd., 313100, Huzhou, Zhejiang, China *E-mail: zjyaosg@126.com

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A two-dimensional transient model of zinc-nickel single flow battery considering side reaction is developed and is used to study the effects of concentration, flow rate and applied current density on the side reaction. The results indicate that the generation of oxygen in the positive electrode is mainly at the end of charging, the generation of hydrogen in the negative electrode starts at the beginning of charging. As time goes on, the hydrogen evolution side reaction gradually weakens. The amount of hydrogen produced during charging is much less than that of oxygen. Decreasing the initial hydroxide ions concentration within a certain range can effectively inhibit the oxygen evolution side reaction, but it will aggravate the hydrogen evolution side reaction. Reducing the initial concentration of zincate ions has little effect on the oxygen evolution side reaction, but it will aggravate the hydrogen evolution side reaction, but it will aggravate the hydrogen evolution side reaction. The effect of zincate ions on hydrogen evolution reaction is much smaller than that of hydroxide ions. The increase of the electrolyte flow rate reduces concentration polarization and has inhibitory effect on the side reaction of the battery electrode. Increasing the applied current density within a certain range will aggravate the side reaction of the battery electrode.

Keywords: zinc-nickel single flow battery, side reaction, concentration, flow rate, applied current density.

1. INTRODUCTION

Large-scale development of renewable energy is one of the main ways to alleviate global energy shortages and achieve energy conservation and emission reduction. However, the inherent discontinuity and instability of renewable energy sources urgently require large-scale energy storage technologies that are compatible with them. With its characteristics of high capacity, flexible layout and long life, the liquid flow battery has became one of the most promising large-scale energy storage systems in renewable energy system [1-2]. Among them, the zinc-nickel single flow battery proposed by Cheng Jie et al. uses a single-liquid flow structure, which does not store ions cross-contamination, and to some

extent simplifies the structure of the battery and reduces the cost, so that it gradually develops into a new type of electrochemical energy storage battery that has received much attention [3-4].

At present, the research on zinc-nickel single flow battery is mainly focused on experiments [5-7], and there is little research on the side reaction of zinc-nickel single flow battery. In literature [8], the deposition of electrolytic zinc in alkaline zincate solution of zinc-nickel single flow battery was studied. The effects of process parameters on current efficiency, morphology and specific surface area of zinc powder were analyzed based on excess potential and hydrogen release. In 2013, Cheng Y et al [9] designed a novel serpentine flow field cell structure to effectively reduce the polarization of the positive electrode nickel hydroxide electrode at high operating current density by enhancing mass transport. It has a certain inhibitory effect on the oxygen evolution side reaction of the positive electrode. In 2014, Cheng Y et al [10] designed a new type of electrode with large reaction area and good mass transport structure, and effectively suppresses the side reaction of the negative electrode. However, the limitations of experimental studies on the mechanism revealing of side reactions of zinc-nickel single-flow batteries are obvious. Recently, the internal multi-physics field coupling mechanism model and the numerical simulation analysis for the zinc-nickel single-flow battery show that the work is necessary to further understand the mechanism of battery charge and discharge and the rules of affecting parameters [11-12]. but so far there has not been a report on the mechanism analysis model of zinc-nickel single flow battery considering the side reaction of the battery electrode. Trace back to the history of zinc-nickel singleflow battery electrode research, you can see: 1991 Deyuan Fan et al. [13] have established a complete mathematical model of a sealed nickel-cadmium battery considering the oxygen evolution side reaction of nickel oxide electrode, but this model does not contain the transmission of oxygen as a side reaction product in the electrode and in the flow channel and the transfer of solid phase protons process. 1995 De Vidts Et al. [14] increased the mass transfer process of dissolved oxygen generated during the electrode side reaction process in the quasi-two-dimensional model of the nickel oxide electrode established in the previous stage, and then introduced the gas phase oxygen transfer in the model [15-16]. However, the above research report only describes oxygen evolution of side reaction for the traditional solid secondary battery, and the research on the side reaction of hydrogen evolution of the negative electrode of the battery was rare. The energy conversion of the liquid flow battery no longer depends solely on the solid electrode, at this time, electrolyte circulation has a great influence on the side reaction of hydrogen and oxygen evolution [17-18]. Therefore, it is necessary to construct a mechanism model of zinc-nickel single flow battery considering the side reaction of the battery electrode, and through numerical simulation analysis is used to reveal the influence of side reactions on the performance of zinc-nickel single flow battery.

For this purpose, based on the working principle of zinc-nickel single flow battery, based on the analysis of the hydrogen evolution and oxygen evolution side reaction models of zinc-nickel electrode and all-vanadium flow battery, a two-dimensional transient isothermal model considering the side reactions of zinc-ni single flow battery electrode is presented. On the basis, the effect of the reactant concentration, electrolyte flow rate and external current density on electrode side reactions during battery transients process under multi-physics field coupling.

2. MODEL CONSTRUCTION

2.1. Geometric model

The positive electrode of zinc-nickel single flow battery adopts porous nickel oxide electrode, the negative electrode material is zinc, and the electrolyte is a zincate alkaline solution with higher concentration. The electrolyte circulates in the flow channel of the battery unit through an external circulating pump, and realize charge of the battery. Figure 1 is a schematic diagram of the working principle of a zinc-nickel single flow battery. The formula (1-4) is the main reaction and the side reaction formula of the positive electrode and the negative electrode, respectively.



Figure 1. Schematic diagram of zinc-nickel single flow battery.

Positive electrode main reaction: $2NiOOH + 2H_2O + 2e^- \rightleftharpoons 2Ni(OH)_2 + 2OH^- E^0 = 0.49V \text{ vs. NHE}$ (1) Negative electrode main reaction: $Zn + 4OH^- \leftrightarrows Zn(OH)_4^{2-} + 2e^- E^0 = -1.215V \text{ vs. NHE}$ (2) Positive electrode side reaction: Positive: $4OH^- \rightleftharpoons O_2 \uparrow +H_2O + 4e E^0 = 0.401V \text{ vs. NHE}$ (3) Negative electrode side reaction: Negative: $2e + 2H_2O \leftrightarrows 2OH^- + H_2 \uparrow E^0 = -0.828V \text{ vs. NHE}$ (4)

For the convenience of research, we selected a battery unit in the battery stack as the research object, and simplified it into a two-dimensional model (middle section along the Z axis) for analysis, as shown in Figure 1, this model includes positive electrode (porous nickel oxide) $(0-x_1)$, flow channel $(x_1 - x_2)$ and negative electrode(zinc) boundary (x_2) , the specific parameters are shown in Table 1.

Table 1. battery unit size parameters.

Parameter	Sign	Value	Unit
Channel length	L	24	mm
Positive electrode thickness	d_a	0.32	mm
Channel width	d_l	3.8	mm

2.2. Mathematical model

2.2.1. The equations in the flow channel

This model does not consider the influence of temperature, The flow in the flow channel follows the equations as shown in equations (5) and (6), where \vec{u} is the flow rate, μ is the viscosity of the electrolyte, ρ is the electrolyte density, p is the pressure, and the electrolyte parameters are shown in Table 4.

Mass conservation equation: $\nabla \cdot \vec{u} = 0$ (5)

Momentum conservation equation: $\nabla [\mu (\nabla \vec{u} + (\nabla \vec{u})^T)] - \nabla p = \rho (\vec{u} \cdot \nabla) \vec{u}$ (6)

The ion transport process in the flow channel includes three types of convection, diffusion and migration. The material conservation equation is given by equation (7):

 $\frac{\partial c_i}{\partial t} + \nabla \cdot \vec{N}_i = 0 \tag{7}$

where \vec{N}_i is concentration flux, ϕ_i is liquid phase potential, z_i and D_i is the charge number and diffusion coefficient of substance $i, i \in \{OH^-, Zn(OH)_4^{2^-}\}$, *R* is the molar gas constant and *T* is the temperature.

Concentration flux \vec{N}_i use the Nernst-Planck equation to describe: $\vec{N}_i = -D_i \nabla c_i - z_i c_i \frac{D_i}{RT} F \nabla \phi_l + \vec{u} c_i$ (8)

Electrolytes are considered to be electrically neutral, therefore, it is controlled by the following conditions:

$$\sum_{i} z_i c_i = 0 \tag{9}$$

The total current density in the electrolyte satisfies equation (10), in the formula, k^{eff} is the effective conductivity, \vec{i}_i is the current density generated by the flow of the charged substance i, as shown in equations (11) and (12), respectively.

$$\vec{i}_{l} = \sum_{i} \vec{i}_{i} = -k^{eff} \nabla \phi - F \sum_{i} z_{i} D_{i}^{eff} \nabla c_{i}$$
(10)
$$\vec{i}_{i} = z_{i} F \vec{N}_{i}$$
(11)
$$k^{eff} = \frac{F^{2}}{RT} \sum_{i} z_{i}^{2} D_{i}^{eff} \nabla c_{i}$$
(12)

2.2.2. Equations in porous electrodes

The mass conservation of the porous electrode region is shown in equation (13). In the formula, ε is the porosity of the porous electrode, c_i is the concentration of substance i, S_i represents the

source term of substance *i*, as shown in Table 2. Among them, D_i^{eff} is the effective diffusion coefficient applied to the porous structure and corrected by Bruggemann [18], as shown in equation (14).

$$\frac{\partial}{\partial t} \left(\varepsilon \left(1 - \alpha_g \right) c_i \right) + \nabla \cdot \left(D_i^{eff} \nabla c_i - \frac{z_i c_i}{RT} D_i^{eff} \nabla \phi_l \right) = -S_i$$
(13)
$$D_i^{eff} = D_i \varepsilon^{\frac{3}{2}} (1 - \alpha_g)^{3/2}$$
(14)

According to the law of conservation of matter, the governing equation of solid phase protons in the active substance is as shown in equation (15). In the formula, ε_s is the volume fraction of the solid phase active substance, S_H is the source term of the proton, as shown in Table 2. The transfer of macroscopic protons along the thickness of the electrode is described by Fick's law, as in equation (16), where D_H is the proton diffusion coefficient.

$$\frac{\partial(\varepsilon_s c_H)}{\partial t} + \nabla \cdot \vec{N}_H = S_H$$
(15)
$$\vec{N}_H = -D_H \nabla c_H$$
(16)

According to the principle of conservation of charge, the charge $\nabla \cdot \vec{i}_l$ that enters the electrode is equal to the charge $\nabla \cdot \vec{i}_s$ that leaves the electrode. In combination with Ohm's law, the equation can be written as:

$$\nabla \cdot \vec{i}_l + \nabla \cdot \vec{i}_s = 0$$
(17)

$$\nabla \cdot \vec{i}_s = -\sigma_s \nabla^2 \phi_s$$
(18)

$$\nabla \cdot \vec{i}_l = -\sigma_l \nabla^2 \phi_l$$
(19)

Where, $\nabla \cdot \vec{i}_l$ and $\nabla \cdot \vec{i}_s$ is liquid phase ion current density and solid phase current density, respectively; ϕ_l and ϕ_s are the liquid phase potential and the solid phase potential, respectively.

Source terms	Species	Positive electrode	Negative electrode
Si	OH-	$-a_e j_1/F$	$2 \times j_1/F$
	$Zn(OH)_{4}^{2-}$	-	$0.5 \times j_1/F$
S_H	H^+	$-a_e j_1/F$	-
S_g	<i>O</i> ₂	$M_{O_2} \nabla \cdot j_{O_2} / F$	-
-	H_2	-	$-M_{H_2} \nabla \cdot j_{H_2}/F$

 Table 2.
 Electrode source items.

Solid phase conductivity is corrected according to Bruggemann [18]: $\sigma_{s,eff} = \varepsilon_s^{3/2} \sigma_s$ (20)

2.2.3. Negative surface equation

From the law of conservation of matter, the transfer of ions within the boundary of the zinc negative electrode satisfies:

 $\frac{\partial c_i}{\partial t} + \nabla \cdot \vec{N}_i = S_i \tag{21}$

Where, S_i is the ion source term, as shown in Table 2, the concentration flux \vec{N}_i is the same as formula (8).

The equation for the current density of each ion in the electrolyte due to the transfer is the same as equation (11).

The conservation of charge equations are the same as equations (17), (18), and (19).

The positive and negative electrode parameters are shown in Table 3.

Parameter name	Symbols	Value	Unit
Porosity	8	0.44	m s ⁻¹
Conductivity of porous nickel oxide electrode	σ_s	2.5×103	S m ⁻¹
Zinc electrode conductivity	σ_s	1.83×107	$S m^{-1}$
Specific surface area of the positive electrode	a_e	3.864×105	m ⁻¹

Table 3. Electrode parameters [11].

Table 4. electrolyte parameters.

Parameter name	Symbols	Value	Unit
Density	ρ	0.03139	Pa s
Electrolyte conductivity	σ_l	65	$S m^{-1}$
Electrolyte dynamic viscosity	μ	0.003139	Pa s ⁻¹

2.5. Reaction kinetic equation

The transfer current density of the positive and negative electrodes is expressed by the Butler-Volmer expression.

Positive electrode:

Main reaction:
$$j_{Ni} = i_{01,ref} \left[\frac{c^{OH}}{c^{OH}_{ref}} \frac{c^{H}}{c^{H}_{ref}} \exp\left(\frac{\alpha_{1,a}F}{RT}\eta_{1}\right) - \frac{c^{H}_{max} - c^{H}}{c^{H}_{max} - c^{H}_{ref}} \exp\left(-\frac{\alpha_{1,c}F}{RT}\eta_{1}\right) \right]$$
 (22)
Side reaction: $j_{O_{2}} = i_{O_{2},ref} \left[\left(\frac{c_{OH}}{c_{OH,ref}}\right)^{2} \exp\left(\frac{\alpha_{1,b}F}{RT}\eta_{2}\right) - \left(\frac{c_{O_{2}}}{c_{O_{2},ref}}\right)^{\frac{1}{2}} \exp\left(-\frac{(1 - \alpha_{1,b})F}{RT}\eta_{2}\right) \right]$ (23)
Negative electrode:

Main reaction:
$$j_{Zn} = i_{Zn,ref} \left[\left(\frac{C^{OH}}{C_{ref}^{OH}} \right)^4 \exp \left(\frac{2\alpha_{2,a}F}{RT} \eta_2 \right) - \frac{C_{Zn}}{C_{Zn,ref}} \exp \left(- \frac{2\alpha_{2,c}F}{RT} \eta_2 \right) \right]$$
 (24)
Side reaction: $j_{H_2} = i_{H_2,ref} \left[\exp \left(\frac{\alpha_{2,b}F}{RT} \eta_4 \right) - \exp \left(- \frac{(1-\alpha_{2,b})F}{RT} \eta_4 \right) \right]$ (25)

Where, j_{Ni} and j_{Zn} represent the the transfer current density of the main reaction of the positive and negative electrodes, respectively. $i_{01,ref}$ and $i_{Zn,ref}$ espectively represent the exchange current density of the main reaction of the positive and negative electrodes in the reference state; j_{02} and j_{H_2} represent the transfer current density of the positive and negative electrodes side reactions, respectively. $i_{O_2,ref}$ and $i_{H_2,ref}$ respectively represent the exchange current density of the positive and negative electrodes side reactions in the reference state, and other parameters are shown in Table 5.

The overpotential of the main reaction and the side reaction for the positive electrode and the negative electrode is shown in the formula (26-29). In the formula, $E_{eq,pos}$, $E_{eq,neg}$, $E_{eq,pos,side}$ and $E_{eq,neg,side}$ are the equilibrium potentials of the main and side reactions of the positive and negative electrodes, respectively, as shown in equation (30-33).

$$\begin{aligned} \eta_{1} &= (\phi_{s} - \phi_{l}) - E_{eq,pos} & (26) \\ \eta_{2} &= (\phi_{s} - \phi_{l}) - E_{eq,neg} & (27) \\ \eta_{1,side} &= (\phi_{s} - \phi_{l}) - E_{eq,pos,side} & (28) \\ \eta_{2,side} &= (\phi_{s} - \phi_{l}) - E_{eq,neg,side} & (29) \\ E_{eq,pos} &= E_{eq,pos}^{0} + \frac{RT}{F} \lg(\frac{(c_{max} - c_{H})/c_{H}^{0}}{(c_{H}/c_{H}^{0})(c_{OH}/c_{OH}^{0})}) & (30) \\ E_{eq,neg} &= E_{eq,neg}^{0} + \frac{RT}{2F} \lg(\frac{c_{ZNOH4}/c_{ZNOH4}^{0}}{(c_{OH}/c_{OH}^{0})^{4}}) & (31) \\ E_{eq,pos,side} &= E_{eq,pos,side}^{0} + \frac{RT}{nF} \lg(\frac{P_{O_{2}}/P_{0}}{(c_{OH}/c_{OH}^{0})^{4}}) & (32) \\ E_{eq,neg,side} &= E_{eq,neg,side}^{0} + \frac{RT}{nF} \lg(\frac{1}{(P_{H_{2}}/P_{0})(c_{OH}/c_{OH}^{0})^{2}}) & (33) \end{aligned}$$

Table 5. Equation parameters for simulation [11].

Parameter name	Symbols	Value	Unit
Positive electrode main reaction transfer coefficient	$\alpha_{1,a}$	0.5	-
Negative electrode main reaction transfer coefficient	$\alpha_{2,a}$	0.5	-
Positive electrode main reaction transfer coefficient	$\alpha_{1,c}$	0.5	-
Negative electrode main reaction transfer coefficient	$\alpha_{2,c}$	0.5	-
Positive electrode side reaction transfer coefficient	$\alpha_{1,b}$	1.5	
Negative electrode side reaction transfer coefficient	$\alpha_{2,b}$	0.05	
Positive electrode main reaction exchange current density	i _{01,ref}	1.04	A m ⁻²
Negative electrode main reaction exchange current density	i _{Zn,ref}	300	A m ⁻²
Positive electrode side reaction exchange current density	$i_{O_2,ref}$	1e-7	A m ⁻²
Negative electrode side reaction exchange current density	i _{H2} ,ref	3e-8	A m ⁻²
Positive electrode main reaction equilibrium potential	\overline{U}_1^0	0.49	V
Negative electrode main reaction equilibrium potential	U_{2}^{0}	-1.26	V
Positive electrode side reaction equilibrium potential	$E_{eq,pos}^0$	0.401	V
Negative electrode side reaction equilibrium potential	$E_{eq,neg}^0$	0.828	V
Hydroxyl ion reference concentration	C _{OH,ref}	7.1×10^{5}	mol L ⁻¹
Zinc ion reference concentration	C _{Zn,ref}	4×10^{5}	mol L ⁻¹
Proton reference concentration	C _{H,ref}	1.765×10^{7}	mol L ⁻¹
Proton maximum concentration	$C_{H,\max}$	3.53×10^{7}	mol L ⁻¹
Oxygen reference concentration	C _{O2} ,ref	100	mol L ⁻¹
Oxygen diffusion coefficient	D_{O_2}	5e-10	$m^2 s^{-1}$
Hydrogen diffusion coefficient	D_{H_2}	1e-9	$m^2 s^{-1}$
Hydroxide ion diffusion coefficient	D _{OH}	3.26×10 ⁻⁹	$m^2 s^{-1}$
Zincate ion diffusion coefficient	D_{Zn}	2×10^{-10}	$m^2 s^{-1}$
Proton diffusion coefficient	D_H	4.6×10 ⁻¹¹	$m^2 s^{-1}$

2.6. Boundary and initial conditions

Assume that the reactant or charge does not leak from the outer surface of the unit, and regardless of heat loss. Set the inlet velocity by assuming that the electrolyte is laminar steady flow, see equation (34). In addition to the inlet and outlet, the liquid pressure at the boundary of the other regions adopts Neumann condition, as in equation (35). The outlet pressure satisfies the pressure outlet condition, as in equation (36). All solid wall boundary conditions are set to no slip.

$$v = v_{in}(y = 0)$$
 (34)
 $\nabla p \cdot \vec{n} = 0(x = x_1, x_2)$ (35)
 $p = p_{out}(y = L)$ (36)

The concentration of the electrolyte at the inlet boundary varies with time, and depending on the reaction of the electrolyte in the battery and the drive of the pump. Assume that the electrolyte flows back into the storage tank after the reaction in the battery, after mixing fully, pump again into the battery to participate in the reaction. The concentration boundary conditions are of the formula (37-38)

$$cOH_{in} = cOH_{int} - \frac{L}{V} \left(\int_0^{x_1} (\vec{N}_{outlet} \cdot \vec{n}) dS - \int_0^{x_1} (\vec{N}_{inlet} \cdot \vec{n}) dS \right)$$
(37)
$$cZn_{in} = cZn_{int} - \frac{L}{V} \left(\int_0^{x_1} (\vec{N}_{outlet} \cdot \vec{n}) dS - \int_0^{x_1} (\vec{N}_{inlet} \cdot \vec{n}) dS \right)$$
(38)

Where, *L* is the electrode height, *V* is the tank volume, and \vec{N}_{inlet} , $\vec{N}_{ioutlet}$ are the molar fluxes of ions on the inlet and outlet boundaries, respectively.

In the charging process, assume that the current uniformly enters through the plates, the flux conditions of the voltage distribution for the porous nickel oxide electrode and the surface of the negative electrode are as shown in the formula (39). In the equation, I_{app} is the applied current density.

$$-\sigma_{s,eff} \nabla \phi_s \cdot \vec{n} = \begin{cases} I_{app} & (x = 0) \\ -I_{app} & (x = x_2) \\ 0(x = x1, y = 0, y = L) \end{cases}$$
(39)

According to the charge conservation law, the amount of charge leaving the solid phase and entering the liquid phase should be equal. It can be obtained that the boundary condition of the potential distribution in the electrolyte is as shown in the formula (40).

$$-k_{\rm eff} \nabla \phi_l \cdot \vec{n} = \begin{cases} l & (x = x1) \\ 0(x = 0, y = 0, y = L) \end{cases}$$
(40)

The negative electrode is grounded, and the boundary condition between the negative electrode and the electrolyte is as shown in equation (41).

$$\phi_{s,\text{ext}} = 0 \tag{41}$$

The basic operational parameters of the model are shown in Table 6.

Tal	ble	6.	Basic	operating	parameters	[1	1]	ŀ
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Parameter name	Symbols	Value	Unit
Rate of flow	u	2.85-8.55	mL/s
Temperature	Т	295.15	Κ
Electrolyte outlet pressure	p_{out}	0	Pa
Applied current density	I	100/300	A m ⁻²
Initial concentration of hydroxide ions	C_0^H	9×10^{6}	mol L ⁻¹
Initial concentration of zincate ion	$c_0^{\check{Z}n}$	8×10^{5}	mol L ⁻¹

3. RESULTS AND DISCUSSION

3.1. Model verification

Constant current charging at 100 A/m^2 , the initial hydroxide ion concentration of the electrolyte is $9 \times 10^6 \text{ mol/L}$, and the zincate ion concentration is $8 \times 10^5 \text{ mol/L}$. The comparison of voltage simulation value and experimental value under different SOC is shown in Figure 2. Due to ignoring of the resistance of the current collector, the contact resistance between the collector and the electrode, the resistance caused by connection of load/power to battery, so add 0.2V to the simulated battery voltage [19-20]. The simulation results fit well with the experimental values, the maximum error does not exceed 3%, and the average error does not exceed 2%.



Figure 2. comparison between simulated charging curve and experimental value.

3.2. Positive and negative electrode side reaction analysis

Figure 3 (a) and (b) respectively show the distribution cloud diagram of oxygen concentration generated by the positive electrode side reaction in battery unit during charging process and the curve diagram of the average oxygen concentration generated by the reaction changing with time. It can be seen from the Figure 4 (a) that the oxygen bubbles generated by the positive electrode side reaction are mainly concentrated inside the positive electrode porous medium away from the flow channel. The maximum concentration appears at the positive electrode plate near the exit of the flow channel. The reason for this phenomenon is that oxygen bubbles are generated in the porous medium and flow along the flow direction of the electrolyte inside the porous medium, and finally a small portion of them accumulate on the positive electrode plate, most of them exit the battery flow path as the electrolyte flows. As can be seen from the Figure(b), the generation of oxygen is mainly at the end of charging. The reason for this phenomenon is that as the charging progresses, the hydroxide ions on the surface of the positive electrode are consumed. When the concentration of hydroxide ions is low, a large concentration overpotential is generated. After the oxygen evolution side reaction overpotential reaches a certain level, the oxygen evolution side reaction rate will increase sharply.



Figure 3. (a) Cloud concentration distribution in the flow channel,(b) Curve of average oxygen concentration over time in the case of u =5.70mL/s, I = 100A/m², c_0^{Zn} =8×10⁵ mol/L, c_0^H = 9×10⁶ mol/L.

Figure 4(a) and (b) respectively shows the distribution cloud diagram of hydrogen concentration generated by side reactions on the negative electrode surface in battery unit during charging process and the curve diagram of the average hydrogen concentration generated by the reaction with time.



Figure 4. (a) Cloud concentration distribution on the surface of the negative electrode,(b) Curve of average hydrogen concentration over time in the case of u=5.7mL/s, I=100A/m², c_0^{Zn} =8×10⁵ mol/L, c_0^H =9×10⁶ mol/L.

As can be seen from the Figure5(a) and (b), the hydrogen evolution side reaction begins in the early stage of charging. Hydrogen bubbles are generated on the surface of the negative electrode. As the charging progresses, the hydrogen evolution reaction decreases and the average hydrogen concentration decreases, the maximum concentration of hydrogen appears at the negative electrode plate near the exit of the flow channel. The reason for this phenomenon is that the negative electrode reaction is the process of zinc deposition, zinc has a high hydrogen evolution overpotential. As the zinc content of the negative electrode increases, the precipitation of hydrogen is suppressed, and the rate of hydrogen evolution is

slowed down. The bubbles flow along the flow direction of the electrolyte in the flow channel, and a small number of the hydrogen bubbles adhere to the surface of the negative electrode plate, and most of hydrogen bubbles flow out of the unit passage as the electrolyte flows. In addition, comparing Figure 3(b) with Figure 4(b), it can be found that the hydrogen gas generated by the negative electrode is much less than the oxygen bubbles generated by the positive electrode side reaction. Ito [21] used experimental methods to quantitatively measure the hydrogen and oxygen precipitated by the side reactions in the zinc-nickeloxide battery under the same conditions. The results showed that the negative hydrogen evolution side reaction occurred throughout the charge. In the process, this is consistent with the law we have drawn.



3.3. Effect of initial concentration

Figure 5. Concentration distribution of (a) proton inside the porous positive electrode, (b) hydroxide ion in the electrolyte (c) zincate ion in the electrolyte.

Figure 5 shows the concentration distribution of solid phase protons inside the porous positive electrode and liquid phase ions in the electrolyte at the middle period of battery charging (SOC=0.5) when the initial concentration of hydroxide ion is 9×10^6 mol/L and the initial concentration of zincate ion is 8×10^5 mol/L. Figure 6 shows the concentration change curve of liquid phase ions in the electrolyte along the x direction at the mid-stage of battery charging (SOC=0.5) and y=12mm when initial concentration of hydroxide ions at 9×10^6 mol/L and the initial concentration of zincate ions at 8×10^5 mol/L. As can be seen from the figure, during the charging process, protons are transferred in the solid phase of the porous electrode and consumed on the surface of the solid phase. Therefore, the proton concentration in the positive electrode increases along the direction away from the flow channel as a whole. The concentration of hydroxide ion and zincate ion in the flow channel is relatively uniform in the main channel due to convective diffusion, while there is a gradient change on the porous surface of the positive electrode and the surface of the negative electrode, and the concentration of hydroxide ions in the positive porous electrode decreases gradually along the direction away from the flow channel, however, it is much smaller than the concentration gradient of hydroxide and zincate ions in the negative electrode surface boundary layer. In the flow direction of the electrolyte, the generation of hydroxide ions near the surface of the negative electrode and the consumption of zincate ions near the surface of the negative electrode increases with the increase of the distance from the inlet, and the maximum concentration of hydroxide ion and the minimum concentration of zincate ion appear at the intersection of the negative electrode surface (x=4.12 mm) and the outlet surface (y=24 mm). The simulation found that changing the initial concentration of each ion in the battery only changed the overall concentration of ions in a certain SOC state inside the battery, and did not affect the distribution of the concentration.



Figure 6. Changing curve along the X axis direction (SOC= 0.5, y=12mm) (a) hydroxide ion concentration; (b) zincate ion concentration.

Hereby, when the electrolyte flow rate (5.70 mL/s) and the applied current density (100 A/m²) are constant, for the following two case: 1) remain the initial concentration of zincate ion is constant (8×10^5 mol/L) and the initial concentration of hydroxide ion is selected: 9×10^6 mol/L, 5×10^6 mol/L, 2×10^6 mol/L; 2) remain the initial concentration of hydroxide ion is constant (2×10^6 mol/L), and the initial concentration of hydroxide ion is constant (2×10^6 mol/L), and the initial concentration of hydroxide ion is constant (2×10^6 mol/L), and the initial concentration of positive electrode and negative electrode side reactions gases is investigated.



Figure 7. Changing curve of (a) oxygen concentration at different initial concentration of hydroxide ion,(b) Curve of hydrogen concentration at different initial concentration of hydroxide ion, (c) oxygen concentration curve at different initial concentration of zincate ion, (d) hydrogen concentration curve at different initial concentration of zincate ion.

Figure 7 shows the changing curves of positive electrode and negative electrode side reaction gases under different initial concentration of hydroxide ion and zincate ion. It can be seen from Figure 7 (a) and (b), during the charging process, as the initial hydroxide ion concentration decreases, the time for the oxygen evolution rate of the positive electrode to be accelerated will be delayed, and the duration of the severe side reaction will be reduced. And the hydroxide ion concentration is lowered within a certain range, the maximum concentration of oxygen is also lowered. At the same time, the severity of the hydrogen evolution reaction of the negative electrode increases with the decrease of the initial hydroxide ion concentration of hydroxide ion decreased from 9×10^6 mol/L to 5×10^6 mol/L, the time for accelerating oxygen evolution of positive electrode is shortened by about 61min, the maximum concentration of hydroxide ion is reduced from 5×10^6 mol/L to 2×10^6 mol/L, the time for accelerating oxygen evolution of positive electrode is shortened by about 18 minutes,

the maximum concentration is decreased by about 1.05%, and the average concentration of negative electrode hydrogen is increased by about 24.9%.

It can be seen from Figure 7(c) and (d) that as the initial concentration of zincate ions decreases, the severity of the oxygen evolution reaction of the positive electrode is substantially unchanged, the severity of the hydrogen evolution reaction of the negative electrode increases, and the hydrogen concentration increases significantly. However, as the reaction time progresses, the severity of the reaction decreases. The initial concentration of zincate ion is reduced from 8×10^5 mol/L to 5×10^5 mol/L, the average hydrogen concentration is increased by about 8.7%; the initial concentration of zincate ion is reduced from 5×10^5 mol/L to 3×10^5 mol/L, the average hydrogen concentration is increased by about 4.4%. The simulated quantitative data indicates that the effect of zincate ions on the hydrogen evolution reaction of the negative electrode is much smaller than that of the hydroxide ion.



Figure 8. Overpotential changing curves of positive electrode side reactions at different initial concentrations of (a) hydroxide ion and (b) zincate ion.



Figure 9. Local current density changing curve of positive electrode side reaction at different initial concentrations of (a) hydroxide ion and (b) zincate ion.

Figure 8 and 9 show the overpotential and local current density changing curves of positive electrode side reaction at different initial concentrations of hydroxide and zincate ion, respectively. It

can be seen from Figure 8(a) and Figure 9(a), with the decrease of initial hydroxide ion concentration, the overpotential of oxygen evolution side reaction at the positive electrode decreases in the early and middle stages of charging, this is because lowering the hydroxide ion concentration causes the side reaction equilibrium potential to increase, as shows in equation (32).



Figure 10. Overpotential changing curve of negative electrode side reaction at different initial concentration of (a) hydroxide ion and (b) zincate ion.



Figure 11. Local current density changing curve of negative electrode side reaction at different initial concentrations of (a) hydroxide ion and (b) zincate ion.

However, side reaction overpotential is small in the early and middle stages of charging, so the effect of the change in the concentration of hydroxide ions on the reaction current density is negligible. In the late stage of charging, after the oxygen evolution side reaction overpotential first to reach a larger value (about 0.2V), the rate of oxygen evolution side reactions increases sharply, accelerating the consumption of hydroxide ions on the surface of the positive electrode. Therefore, when the initial hydroxide ion concentration is low, a large concentration overpotential is generated, which confirms that in the later stage of charging, when the initial hydroxide ion concentration is lowered, large overpotential

phenomenon in Figure 8(a). Figure 8(b) and Figure 9(b) show the effect of the initial zincate ion concentration on the oxygen evolution side reaction overpotential and reaction current density, respectively. Since the zincate ion does not directly participate in the main reaction and the side reaction of the positive electrode, reducing the initial concentration of the zincate ion has little effect on the positive electrode overpotential and the local current density.

Figure 10 and 11 show the overpotential and local current density changing curves of negative electrode side reaction at different initial concentrations of hydroxide and zincate ions, respectively. It can be seen from the figure that the reduction of the initial hydroxide ion and zincate ion concentration makes the negative electrode value of the overpotential and local current density for hydrogen evolution reaction of the negative electrode larger, the hydrogen evolution reaction of the negative electrode is intensified. This is consistent with the law that Lao [22] studied the influence of the concentration of potassium hydroxide and the initial concentration of zincate ions on the hydrogen evolution reaction of zinc-air flow battery. It can be found from the formula (33) that the decrease in the concentration of the zincate ion has little effect on the equilibrium potential of the side reaction. However, the ion acts as a reaction substance for the main reaction of the negative electrode, the decrease in concentration causes an increase in the overpotential of the main reaction, which causes an increase in the solid-liquid potential difference, and then leads to an increase in the absolute value of the side reaction overpotential and current density. During the charging process, both the main reaction and the side reaction of the negative electrode are constantly generating hydroxide ions. This causes a large increase in the hydroxide ion concentration on the surface of the negative electrode. If the initial hydroxide ion concentration is lowered, a large gradient of hydroxide ions on the surface of the negative electrode is caused, which leads to an increase in concentration overpotential and aggravation of the occurrence of side reactions.



3.4. Effect of electrolyte flow rate

Figure 12. (a) Oxygen concentration (b) Oxygen mass fraction during positive electrode side reaction during charging at different electrolyte flows.

Figure 12 and Figure 13 shows the applied current density is $100A/m^2$, zincate ion concentration is 8×10^5 mol/L, hydroxide ion concentration is 9×10^6 mol/L, under three different electrolyte flow rate

(2.85 mL/s, 5.70mL/s and 8.55mL/s), the oxygen and hydrogen concentrations and mass fraction α_g produced by the electrode side reaction vary with SOC during the charging process.



Figure 13. (a) Hydrogen concentration (b) Hydrogen mass fraction during negative electrode side reaction during charging at different electrolyte flows.

The simulation results show that the flow rate increases from 2.85 mL/s to 5.70 mL/s, the average mass fraction of oxygen decreases by about 41.55%, the average concentration decreases by 35.27%, the average mass fraction of hydrogen decreases by about 0.59%, and the average concentration decreases. 34.31%; Flow rate increased from 5.70 mL/s to 8.55 mL/s, the average oxygen mass fraction decreased by about 49.76%, the average concentration decreased by 47.45%. The average mass fraction of hydrogen was reduced by about 3.57%, and the average concentration was decreased by 23.54%. Increase in electrolyte flow rate, the mass transfer process inside the battery is improved, and the concentration polarization is reduced. Therefore, the increase in the flow rate of the electrolyte has a certain inhibitory effect on the gas evolution of the positive electrode and the negative electrode. H. Al-Fetlawi [16,17] also proposed a similar rule when studying all-vanadium flow batteries, that is, increasing the electrolyte flow rate can effectively inhibit the occurrence of hydrogen and oxygen evolution reactions, and further improve the coulombic efficiency.

In the operation of the battery, the electrolyte flow rate is an important control mechanism, and the flow rate should not be too high or too low. Too low a flow rate results in low cycle efficiency, and the internal concentration of the battery is heavily polarized; too high a flow rate increases power consumption and risk of leakage, or may not provide sufficient performance gains for the extra power required. By simulation, the proper flow rate of the zinc-nickel single flow battery unit ranges from 2.85 mL/s to 8.55 mL/s.

3.5. Effect of applied current density

Figure14 and Figure15 show that the electrolyte flow rate is 5.70 mL/s and the initial concentration of zincate ion is 8×10^5 mol/L and the initial concentration of hydroxide ion is 9×10^6 mol/L, the overpotential, local current density and side reaction gas concentration of positive electrode

oxygen evolution reaction and negative electrode hydrogen evolution reaction change with SOC under charging at different application current density, respectively. As seen in the figure, in the same SOC, applied current density increased from 100 A/m^2 to 300 A/m^2 , the average concentration of oxygen increased by about 3 times, and the average concentration of hydrogen rose by 13.68%. The A.A.Shah team [16,17] obtained the same qualitative law when studying the influence of the applied current density of the all-vanadium redox flow battery on the hydrogen evolution and oxygen evolution reactions, that is, increasing the applied current density will promote the occurrence of side reactions. This is because the higher the applied current density, the more intense the ion reaction on the surface of the electrode, the faster the substance is produced or consumed, and the higher the degree of polarization. The overpotential of the positive electrode oxygen evolution reactions. The positive electrode side reaction occurs and the oxygen concentration increases. The hydrogen evolution reaction of the negative electrode has a more negative overpotential, and the local current density decreases, which exacerbates the occurrence of negative electrode side reactions.



Figure 14. Changing curve of the positive electrode oxygen evolution reaction at different applied current density (a) overpotential, (b) local current density, (c) oxygen concentration.





Figure 15. Changing curve of the negative electrode hydrogen evolution reaction at different applied current density of during charging (a) overpotential, (b) local current density, (c) hydrogen concentration.

4. CONCLUSION

Based on the two-dimensional transient isothermal model of zinc-nickel single flow battery established by electrode side reaction, the multi-physics coupling analysis of flow process, mass transfer process and electrochemical reaction process in zinc-nickel single flow battery was carried out. The influence of initial concentration of reactant ions in the electrolyte, electrolyte flow rate and charging current density on the side reactions of the battery electrodes ware studied. The specific conclusions are as follows:

(1) During the charging process of the battery, when the positive electrode overpotential reaches a large value (0.2V) in the late charging phase, the oxygen evolution rate of the positive electrode increases sharply; the generation of the negative electrode side reaction hydrogen gas starts at the initial stage of charging, and it gradually weakens along with the charging process. In addition, the amount of oxygen generated by the side reaction of the positive electrode is much more than the amount of hydrogen generated by the negative electrode during charging.

(2) Decreasing the initial hydroxide ion concentration within a certain range can effectively suppress the occurrence of the oxygen evolution side reaction of the positive electrode, but it will aggravate the occurrence of the negative electrode hydrogen evolution side reaction and increase the hydrogen evolution of the negative electrode. Zincate ion do not directly participate in the main reaction and the side reaction of the positive electrode, so the influence on the oxygen evolution side reaction of the positive electrode is not large, but the decrease of the zincate ion concentration will aggravate the occurrence of the negative electrode side reaction and increase the concentration of hydrogen evolution. At the same time, the simulated quantitative data indicates that the effect of zincate ions on the hydrogen evolution reaction of the negative electrode is much smaller than that of the hydroxide ion.

(3) The increase of the electrolyte flow rate improves the mass transfer process inside the battery and reduces the concentration polarization. Therefore, the increase in the flow rate of the electrolyte has a certain inhibitory effect on the gas evolution of the positive electrode and the negative electrode.

(4) Increasing the applied current density within a certain range, the overpotential of the positive electrode oxygen evolution reaction has a more positive, and the overpotential of the negative electrode

hydrogen evolution reaction has a more negative, which aggravates the occurrence of positive and negative electrode side reactions.

CONFLICTS OF INTEREST

There are no conflicts to declare.

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