The Mathematical Construction of the Battery Mechanism Function

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Abstract: The corrected mechanism model of battery voltammetric function is helpful to guide the development and application of battery. There are two scientific issues that need to be answered: First, how many mechanisms do batteries have; Second, how to establish the mechanism model separately under the overlapping of these mechanisms. Volt-ampere characteristics of both linear state and nonlinear state exist; the monotonic decreasing of volt-ampere characteristics indicates that the battery have only three kinds of mechanisms. Without changing the basic form of the function and under the principle of the mechanism function's working region considered, we propose a mechanism function which satisfies the monotonic decreasing characteristic of the voltammetric curve of battery, via the derivative law of each mechanism function in the voltammetric function of battery. By using the voltammetric data, the obtained cell mechanism function can accurately predict the potential (current or voltage) when the independent variable of the cell is zero, and provide the theoretical basis for the internal working mechanism of the cell, which can guide the practice.

Keywords—*volt-ampere characteristics, battery mathematical model, mechanism function, fuel cell*

1. Introduction

With the increasing consumption of fossil fuels, the energy crisis has become increasingly apparent. Battery, as a kind of chemical energy, can realize the conversion between electric energy and chemical energy, and also is one of the effective ways to solve the energy crisis. Therefore, battery is of great significance in the field of power energy and energy storage.

Fuel cell was invented by Britain's William Grove in 1839, and in the same year, Alexander-Edmond Becquerel, a French physicist, discovered the photovoltaic effect, which opened the curtain of battery research [1,2,3].Battery, as high efficiency of energy conversion device, has attracted more and more attention. The mode of electrical energy transmission has changed from the earliest development of direct current to alternating current, from the non-mobile power supply device to the mobile one.

In recent years, the mobile device power battery research is in full swing[4]. It is one of the hot topics in battery research to determine the specific form of nonlinear volt-ampere battery function, at the same time. Also, a great deal of research work has been done on the issues of nonlinear volt-ampere battery function. Battery is a device that produces potential difference between two poles by chemical reaction or physical change of substances. It can be divided into physical battery and chemical battery. The working process of chemical battery is the chemical reaction between two electrodes, in which the electrodes gain or lose electrons[6-9]. Physical battery, like solar battery, are made the ones according to different physical effects or physical phenomena; solar cells are the ones to convert light energy into electricity, or convert heat energy directly into electricity[12,15].

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In the research of chemical battery, qualitative experimental research is the most, while quantitative mathematical expression is less. In the research of physical battery, more attention is paid to its physical essence. In the study of the working principle of battery, the working mechanism of linear battery is mostly studied. In practical application, battery volt ampere characteristic plays an extremely important role.

Many scholars use modeling and simulation methods to get the battery volt ampere function[13]. Few scholars have studied the volt-ampere function theory of nonlinear batteries[16,17], and yet, their conclusions have not reached the effect of guiding practice. Thus, It is the key to the theoretical research of battery to establish the explicit expression of volt ampere characteristic of battery, which is of great scientific significance and technical value for the development of battery.

2. Basic phenomena of battery volt-ampere characteristics

For any physical experiment, its mathematical function can be expressed as follow:

$$y = f\left(x\right) \tag{1}$$

The rectangular coordinate system constructed by current and voltage is called the volt-ampere coordinate system [10, 11]. The value of output current and output voltage by the battery can draw the volt-ampere characteristic curve of that battery in the volt ampere coordinate system, and the curve is located in the first quadrant of the coordinate system, namely $x \geq 0, f\left(x\right) \geq 0$.

Experiments show that [5], the volt-ampere function of the battery has the characteristic of monotone decreasing, which can be expressed mathematically as follows $f_k'\left(x\right) < 0$.

When the independent variable x is 0, value of the function must be constant, and there is $f\left(x\right) = A$; At the same time, the numbers and the forms of the specific battery mechanism are unknown, caused by the volt-ampere function of the battery. And from the perspective of dimension, the explicit function of the volt-ampere characteristic of the battery can be represented by the form of sum, namely

$$f(x) = A - \sum_{k=1}^{N} f_k(x) \geq 0\left(0 \leq f_k(x) \leq A\right) \tag{2}$$

Thus:

$$\sum_{k=1}^{N} f_k(0) = 0 \tag{3}$$

$f_1(0)+f_2(0)+\cdots+f_N(0) = 0$, whose solution of is not closed, but the experimental data of each mechanism function cannot be separated separately. The specific number of function N and the specific form of each term $f_k(x)$ in Eq. (3), both cannot be determined by this formula. That is a defect in the expression form of explicit function summation of the current volt ampere characteristic of the battery.

The volt-ampere characteristic curve of the battery contains the influencing factors that determine the number of mechanisms, namely $f(x)$ □ N;

$$\sum_{k=1}^{N} f_k(x) \Rightarrow f_k(x), k = 1, 2, ...N \tag{4}$$

By separating the functions in $f_k(x)$ from each other, the specific form of the battery volt-ampere function can be accurately expressed:

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$$f_1(x)+f_2(x)+\cdots+f_N(x), k=1,2,....N \to f_1(x),\ f_2(x),\cdots,\ f_N(x), k=1,2,....N \quad (5)$$

Therefore, it is the main content of this paper to express the battery volt-ampere function accurately, find the method of separating the battery volt-ampere function, and determine the mechanism function form respectively.

3. Construction of the correct battery volt ampere function

3.1 Establishment of the specific number of battery mechanisms

Since all types of batteries have monotonically reduced volt-ampere characteristics [1,2,5,14],namely $f_k(x)<0$,the volt-ampere curve of the battery can be expressed by $f(x)$ in the plane coordinate system.

From the point of view of mathematical physics, the independent variables and dependent variables of the battery voltammetric function need to meet the conditions $0 \le x \le x_{\max}, 0 \le f(x) \le A$.

The mathematical property of the battery volt-ampere characteristic shows $f'(x)<0$,and the following volt-ampere function can be obtained by definite integral:

$$f'(x) = -B \xrightarrow{\text{definite integral}} f(x) = A - Bx \quad (6)$$

After nonlinear treatment of (6), the nonlinear function can be expressed as:

$$f(x,n) = A - Bx^n \ge 0(A,B,n>0) \to \begin{cases} n=1, linear \\ n \ne 1, nonlinear \end{cases} \quad (7)$$

Such a volt-ampere function is suitable for all types of batteries. The key is to give the three parameters $(A,B,n>0)$ in the equation explicit physical connotation.

In this paper, the mathematical expression of Eq. (7) is called the "universal volt ampere function" of the battery because the battery has the mathematical characteristic of monotonically decreasing $f'(x)<0$.

The analysis of the experimental curve of the battery voltammetric function should be carried out from both the local and global perspectives, that is, the analysis is from the slope at any point in the voltammetric curve and the overall trend. The first derivative corresponds to any point on the volt-ampere curve, and the second derivative reflects the overall trend of the volt-ampere curve.

Take the first derivative of the universal voltammetric function of the battery:

$$f'(x) = -nBx^{n-1} < 0 \quad (8)$$

The first derivative of the universal voltammetric function obviously satisfies the condition of $f'(x)<0$.

The Second derivative of the battery voltammetric function can be obtained as follows:

$$f''(x) = -n(n-1)Bx^{n-2} \Rightarrow \begin{cases} \xrightarrow{n=1} f''(x)=0 \\ \xrightarrow{n\ne1} \begin{cases} \xrightarrow{n>1} f''(x)<0 \\ \xrightarrow{n<1} f''(x)>0 \end{cases} \end{cases} \quad (9)$$

In Eq. (9), the independent variable exponential n is related to the internal working mechanism of the battery and determines the opening direction of the curve of universal voltammetric function. The battery mechanism should also be reflected on the curve of the voltammetric

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function, that is, the symbol state of exponential n represents the corresponding form of the battery mechanism function.

When $n=1$, $f(x)=A-Bx$ is the linear voltammetric function of the battery. When $n<1$, the second derivative is greater than 0, $f''(x)>0$, and the voltammetric curve of the function opens upwards; when $n>1$, the second derivative is less than0, $f''(x)<0$, and the voltammetric curve opens downwards.

Table 1 Relationship between weighted parameters n and cell mechanism

Explicit expression of volt ampere function	Numerical state of independent variable index	Second derivative case	Mechanism model of battery
$f(x,n)=A-Bx^n$	$n=1$	$f''(x)=0$	First mechanism model
	$n>1$	$f''(x)<0$	Second mechanism model
	$n<1$	$f''(x)>0$	Third mechanism model

The volt-ampere curve of the battery can usually reveal the working mechanism of the battery. The numerical state of the independent variable exponent n in the battery volt-ampere function can be used as the judgment criterion of the battery mechanism. The parameter n can be shared .Thus, it can be determined that there are only three kinds of mathematical properties in the working mechanism of a battery: when the second derivative equals zero (the first mechanism of battery), less than zero (the second mechanism of the battery) and greater than zero (the third mechanism of battery).

The conclusions are shown in Table 1. Compared with the analysis results in Table 1, the numerical state of independent variable index n corresponds to the working mechanism of the battery.

After obtaining the universal voltammetric function expression containing the mechanism of the battery, the expression can be decomposed to determine whether the universal voltammetric function can be used as the battery mechanism function, or not, then:

$$f(x)=A-Bx-Bx\left(x^{n-1}-1\right)=A-f_1(x)-f_2(x)\geq 0,\quad x\geq 0$$

$$\Rightarrow\begin{cases} n=1\rightarrow f_1(x)=Bx\geq 0, x\geq 0 \\ n\neq 1\rightarrow\begin{cases} n>1\rightarrow f_2(x)=Bx\left(x^{n-1}-1\right)\geq 0, x\geq 1\leftarrow f_2''(x)<0 \\ n<1\rightarrow f_3(x)=Bx\left(x^{n-1}-1\right)\geq 0, x\leq 1\leftarrow f_3''(x)>0\end{cases}\end{cases} \tag{10}$$

The above has shown three kinds of mechanism functions in generalized voltammetric function containing the mechanism of battery. Those three mechanisms are of the characteristics of piecework and exist independently, so they need to be described separately.

By integration, in Eq. (10) shows the universal voltammetric function obtained can only be decomposed into the mechanism functions with two different expressions; that does not meet the conditions of three mechanism functions.

In addition, when $n<1$, $f_3(x)=Bx\left(x^{n-1}-1\right)\geq 0, x\leq 1$, the value of n makes the mechanism function not meet the requirements of $0\leq x<x_{\max}, 0\leq f_k(x)\leq f(x_{\max})$.

Therefore, the universal voltammetric function, obtained by mathematical integration , cannot be applied to the construction of the concrete form of mechanism function $f_k(x)$.

3.2 Construction of the specific mechanism function form of battery $f_k(x)$

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The volt-ampere characteristics of battery mechanism function are different from each other. Given the $f_k(x), k=1,2,3$ of the battery mechanism function, it is usually studied separately by separating the $f_k(x)$,and the linear mechanism function $f_1(x)=Bx\geq 0, x\geq 0$ has been separated from the universal volt-ampere function, and only two more nonlinear mechanism functions need to be constructed.

In this paper, a mathematical deduction is attempted from the derivative direction of the battery volt-ampere function, and an appropriate function form is found according to the derivative law of each mechanism function. The original function $f_k(x)$ of the battery volt-ampere function, the first derivative $f_k'(x)$ and the second derivative $f_k''(x)$ are respectively expressed to separate the $f_k(x)$:

$$f'(x)=-\sum_{k=1}^{n} f_k'(x)<0 \rightarrow f_k'(x)>0$$
$$f''(x)=-\sum_{k=1}^{n} f_k''(x)\begin{cases}>0, 0\leq x<x_1 \leftarrow n<1\\ =0, x_1\leq x\leq x_2 \leftarrow n=1\\ <0, x_2<x\leq x_{\max} \leftarrow n>1\end{cases} \quad (11)$$

By comparing (11) with the conditional $f_k(x)\geq 0, x\geq 0$ of mechanism function, it can be obtained that only $f_1(x)=Bx\geq 0, x\geq 0$ under $n=1$ can satisfy the condition of mechanism function.

$$f_1(x)=Bx\geq 0, B>0, x\geq 0 \quad (12)$$

Meet the conditions $f_1'(x)>0, f_1''(x)=0, n=1$.

When $n\neq 1$, there are two mechanisms are $f_2(x)$ and $f_3(x)$, since $(n<1)$ corresponds to $f''(x)>0$, and $(n>1)$ corresponds to $f''(x)<0$;In nonlinear functions, there are inversely proportional functions, trigonometric functions, logarithmic functions, exponential functions.

Among those functions, the trigonometric function is periodic, which does not accord with the monotonicity and convexity of the battery volt-ampere function. For the inversely proportional function $f(x)=\frac{k}{x}$, there is no intersection point between the function curve and the coordinate axis, which does not conform to the characteristics of the battery.

The cell mechanism function presented by previous studies does contain logarithmic and exponential function forms [19-24]. In view of the above functions, they are the objective reflection of nature law phenomenon in mathematics. When the mathematical functions are constructed, from the perspective of mathematics, it should not change the symbols and exponential form of the function to meet the data obtained from such experiments. Only in this way, it can be ensured that the physical phenomenon of the functions will not be distorted by the change of symbol or the adjustment of index. In addition, the selected mathematical functions should be proportioned according to the dimensional and physical requirements.

The mechanism function of $f_2(x)$ should satisfy $f_2'(x)>0, f_2''(x)>0, n>1$, that is, the first derivative and the second derivative have the same sign. Take the form of the exponential function with natural constant as the base, $f_2(x)=\exp(x)$:

$$f_2'(x)=\exp(x)>0, f_2''(x)=\exp(x)>0 \tag{13}$$

In order to satisfy $f_k(0)=0$, the function is expressed as $f_2(x)=\exp(x)-1$, and after dimensioning, the mechanism function becomes:

$$f_2(x)=C_0\left[\exp(C_1x)-1\right]\geq 0, x\geq 0 \tag{14}$$

The mechanism function of $f_3(x)$ should satisfy $f_3'(x)>0, f_3''(x)<0, n<1$, that is, the first derivative and the second derivative appear variable signs. The form of natural logarithm function $f_3(x)=\ln(x)$ can be selected:

$$f_3'(x)=\frac{1}{x}>0, f_3''(x)=-\frac{1}{x^2}<0 \tag{15}$$

In order to satisfy $f_k(0)=0$, the function is expressed as $f_3(x)=\ln(1+x)$, and the mechanism function becomes:

$$f_3(x)=D_0\ln(1+D_1x)\geq 0, x\geq 0 \tag{16}$$

Table2 Derivative characteristics of the battery mechanism function

Battery mechanism	First mechanism model	Second mechanism model	Third mechanism model
First derivative	$f_1'(x)>0$	$f_2'(x)>0$	$f_3'(x)>0$
Second derivative	$f_1''(x)=0$	$f_2''(x)<0$	$f_3''(x)>0$
Mechanism function form	$f_1(x)=Bx$	$f_2(x)=\exp(x)$	$f_3(x)=\ln x$
Mechanism function requirement	$f_1(x)=Bx$	$f_2(x)=\exp(x)-1$	$f_3(x)=\ln(1+x)$

The volt-ampere characteristics of the battery mechanism function need to satisfy the two basic conditions of monotone $f'(x)<0$ and $\sum_{k=1}^{n} f_k(0)=0$, but the volt-ampere characteristics are different from each other: $f_1''(x)=0, f_2''(x)>0, f_3''(x)<0$.The voltage-ampere characteristics of the battery mechanism function can be sorted out, as shown in Table 2.

The battery mechanism function which satisfies the conditions can be obtained:

$$f(x)=A-\sum_{k=1}^{3} f_k(x)=A-Bx-C_0\left[\exp(C_1x)-1\right]-D_0\ln(1+D_1x) \tag{17}$$

4. Application and value of the universal voltammetry function

There exists a theoretical potential value: $A_{theoritical}$ in the cell (for example, chemical electromotive force of chemical cell, photoelectric conversion efficiency of photovoltaic cell), which usually cannot reach the theoretical potential value; so the applied potential value $A_{experimental}$ of battery can be adopted in the experiment. The difference between the two potential values $A=A_{theoritical}-A_{experimental}$ can be used to effectively evaluate the state of the battery electrode.

However, the battery data $\left(A_{experimental}, x_{\max}\right)$ on the coordinate axis in the voltammetric coordinate system is always difficult to measure, so it is impossible to measure $A_{experimental}$

effectively.

4.1 Determination and value of the parameters of the universal voltammetry function

There are six parameters in the universal volt ampere function of the battery, as shown in (17), in which parameter A is the "power parameter" of the battery and is the very key value in the battery.

The closed solution parameter $(A, B, C_0, C_1, D_0, D_1)$ is used to determine the power supply parameters when $x = 0$ and $x = x_{\max}$ are

$$\begin{cases} f(0) = A_{experimental} - \sum_{k=1}^{3} f_k(0) = A \\ f(x_{\max}) = A_{experimental} - \sum_{k=1}^{3} f_k(x_{\max}) = 0 \end{cases} \tag{18}$$

In the measurement of the battery volt-ampere characteristics, it is extremely difficult to conduct the zero value phenomenon in the experimental measurement and achieve the result of $V = E$, when the current of the voltage source battery is 0.

As for the current source battery, it is also extremely difficult to achieve the result of $I = I_s$ in the experimental measurement, when the voltage is 0.Therefore, in battery experimental research; it is always difficult to measure the exact value of open circuit voltage or short circuit current.

From the theoretical level of battery, there is $f(0) = A_{\text{theoritical value}}$, and from the aspect of experiment, there exist experimental measurements namely, $f(0) = A_{\text{experimental value}}$.

But when the current is zero, the experimental value and the theoretical value of the battery are not exactly the same, then the theoretical study of the battery mechanism function can judge the gap between the actual value and the theoretical value of the battery open circuit voltage, namely $\Delta A = A_{\text{theoritical value}} - A_{\text{experimental value}}$. The error between the theoretical value and the experimental value is determined, consequently.

4.2 Application of nonlinear batteries

Fuel cell is the most typical non-linear cell, and its volt-ampere characteristic curve is the most complex curve at present, which can reveal three working mechanisms inside the cell: activation polarization loss, ohm polarization loss and concentration polarization loss [18], As shown in Figure.1.

Therefore, taking fuel cells as an example, this paper analyzes and studies various V-I function models that have been widely used in the analysis and research of proton exchange membrane fuel cells from the perspectives of the first and second derivatives and the voltage value when the current is 0.

In[22], an improved mass transport item model is proposed for theoretical analysis of fuel cells:

$$U = E - A\ln\left(\frac{I + I_0}{I_0}\right) - m\exp(nI) - IR \tag{19}$$

In[23], The mold is constructed after the current density of electron leakage being considered:

$$U = E - X\ln\left(\frac{I + I_{in}}{I_0}\right) + Y\ln\left(1 - \frac{I + I_{in}}{I_0}\right) - (I + I_{in})R \tag{20}$$

In [24], exponential expressions of activation and mass are introduced:

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$$U = E - b\lg\frac{I}{I_L} - m\exp(nI) - RI \tag{21}$$

In [25], a model considering anode and cathode is proposed:

$$U = E - \left[b_a \ln(\frac{I}{I_{o.a}}) + b_c \ln(\frac{I}{I_{o.c}}) \right] - B\ln(\frac{I_L}{I_L - I}) - IR \tag{22}$$

In [26], the model is proposed:

$$U = E - \frac{RT}{F}\ln\left[\frac{I}{2I_0} + \sqrt{1 + (\frac{I}{2I_0})^2} \right] - \frac{RT}{nF}\ln(1 - \frac{I}{I_L}) - IR \tag{23}$$

From the above analysis of the first and second derivatives of the volt-ampere function and the voltage value when the current is zero for the five common fuel cells (see Eqs. (19) to (23)). The first derivatives of the Eqs. (22) And (23) in the five functions (see Eqs. (19) to (23)) are greater than, equal to and less than zero, which do not conform to the monotonously decreasing characteristics of the battery volt-ampere function. When the current is zero, the voltage values in the formulas from Eqs. (19) to (22) are not the open circuit voltage E, or even infinite voltage value is produced. That does not conform to the actual experimental measurement. Second derivative reflects the opening direction of battery volt-ampere characteristic curve, and the opening direction of fuel cell volt-ampere characteristic curve is not a single opening direction mechanism. Moreover, the second derivative of volt-ampere function of fuel cell in Eqs. (19) and (23) is only less than zero. Therefore, the theory cannot fully reflect the battery's internal mechanism.

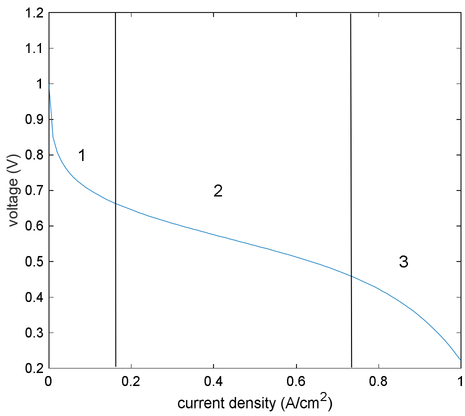

Figure1. Volt-ampere characteristic curve of fuel cell

Via the analysis of the common functions from the first and second derivative and the voltage value when the current is zero, it can be concluded the existing theoretical function form of fuel cell is the result of fitting the experimental data based on experiment.

Therefore, there is no sufficient basis to add or reduce the constant term, so that the voltage value of the fuel cell volt-ampere function does not appear infinite when the current is zero, which is not in line with the actual situation, and makes the first derivative of the volt-ampere function meet the characteristics of monotonic decline.

When there is a big difference in the fitting of fuel cell volt-ampere function to experimental data, it will try to change the symbol in front of the independent variable for a new data fitting. In order to meet the experimental data, the symbol in front of the independent variable changed, which changes the unequal sign direction of the second derivative of the fuel cell mechanism function.

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5. Conclusion

This paper presents a new type of battery volt-ampere function model, $f(x)=A-Bx^n$. From the mathematical level, it demonstrates the battery volt-ampere characteristic curve of monotone decreasing $f'(x)<0$ and opening direction and so on characteristics, determines the numbers of the internal mechanism of the battery.

Under the overlapping effect of different mechanisms, the battery mechanism function in physical level is established, and the correct battery mechanism function is obtained as $f\left(x\right)=A-Bx-C_0\left[\exp\left(C_1x\right)-1\right]-D_0\ln\left(1+D_1x\right)$ .The open circuit voltage and short-circuit current of the battery can be calculated accurately with the help of the voltammetric data of the battery, which lays a foundation for the theoretical research of the battery.

By establishing the mechanism function of the battery in physical layer, it is possible to apply the explicit function of the universal volt-ampere characteristic of the battery to the practical theoretical research. Three different working mechanisms matched with specific mathematical descriptions respectively, and the value range of weighted factor n determines the matching of specific mechanism functions.

When $n=1$, corresponds to the cell mechanism model function $f_1(x)=Bx$, is the first mechanism model function.

When $n>1$, corresponds to the battery mechanism model function $f_2(x)=C_0\left[\exp(C_1x)-1\right]$, and is the second mechanism model function.

When $n<1$, corresponds to the cell mechanism model function $f_2(x)=D_0\ln(1+D_1x)$, and is the third mechanism model function.

The common feature of all types of batteries is the monotone reduction of the volt-ampere curve and the downward opening of the power curve. Therefore, there is a universal volt-ampere characteristic function, which can be obtained by combining mathematical deduction with physical properties. The numerical range of the exponent n in the function corresponds to the three working mechanisms of the fuel cell, and the specific value of the battery open-circuit voltage can be obtained through that function. Consequently, not only does the construction of battery mechanism function provide the theoretical guidance for the research of battery, but it provides great convenience for the theoretical research of battery as well.

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