Materials

An improvement to the data processing course of electrochemical impedance technique

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Abstract: For some electrochemical systems the traditional data processing methods can not be met, so it is necessary to develop a new method to deal with these problems. When processing the electrochemical AC impedance data of titanium alloy TA12 in 3% NaCl solution (at free corrosion potential, room temperature) a new method is developed which can detach the information of the interface resistance demonstrably from the interface capacitance. The results show that the interface resistance and capacitance are all functions of frequency. And the AC impedance of the resistance and capacitance obey the following relations: $C(f) = 10^{4.01982} f^{-0.9292}$, $R(f) = 10^{4.80011} (f + 0.008)^{-0.90897}$, which is completely different from the traditional conception that the interface resistance and capacitance are constants. And this phenomenon is ubiquitous in titanium alloys according to the study. So perhaps it is an innate characteristic of interface.

Key words: titanium alloy; electrochemical impedance; corrosion

The electrochemical impedance technique has been widely used to test the surface characteristics of materials [1-6]. But for some electrochemical systems the traditional data processing methods can not be met. For example, when a Bode diagram is made, there is a line section with a slope of −0.85 on the curve instead of the expected section with a slope of −1. When the above problem appears, new components are generally added on the classical equivalent circuit. But maybe no new components need to be added once the assumption that the resistance and capacitance are constants is changed. This paper focuses on this situation and an improvement on the data processing course in accordance with this situation is made.

1 Experimental

The tested material was the commercial titanium alloy TA12. Its chemical composition is listed in **table 1**. The area of the work specimen was 0.785 cm². After being polished, the specimen was immersed in 5% HCl solution for 10 min, then placed in the desiccator for 24 h before test. The testing solution was 3% NaCl solution. The test and measurement were carried out at free corrosion potential and at ambient temperature. The AC signal frequencies were over a range of 10^{-3}-10^5 Hz and the amplitude of AC signal was 5 mV. The test system was P/G Model 273 A of EG&G PAR Company, and the sampling program was M398.

Table 1   The components of titanium alloy TA12 (mass fraction)   %

Al	Sn	Fe	Si	C	N	H	O	Mo	Zr	Ti
5.76	4.20	0.07	0.26	0.01	0.01	0.004	0.09	0.86	2.03	86.7

2 Results and discussion [7, 8]

2.1 The problem in electrochemical impedance technique

For the systems controlled by charge transfer, their equivalent circuit can be shown in **figure 1**, where R_L is the solution resistance, C the interface capacitance and R_S the Faraday resistance.

The traditional Bode diagram was used to analyze the electrochemical impedance data, but this method has its own limitations. The Bode diagram of titanium alloy TA12 in 3% NaCl solution is shown in **figure 2**.
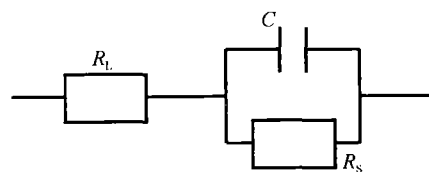

Figure 1   Equivalent circuit of an electrolytic cell.

The Bode diagram is a dual-logarithm graph of impedance module *vs.* frequency. When a Bode diagram

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was analyzed, a straight segment with a slope of −1 must be found. Then the capacitance can be gotten by extrapolating the straight segment. Its principle is as follows.
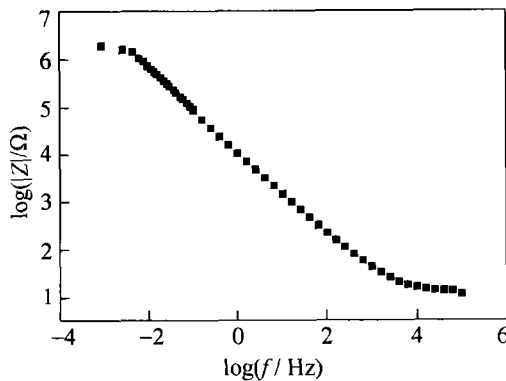

Figure 2 Bode diagram of TA12 alloy in 3% NaCl solution.

Assuming the interface impedance is Z, then

$$Z=R_L+R(f) \ C(f)^2/[C(f)^2+R(f)^2]+jR(f)^2C(f)/[C(f)^2+R(f)^2] \tag{1}$$

where R_L is the solution resistance; $jC(f)$ the impedance of the interface capacitance; $R(f)$ the interface resistance.

If R_L is much smaller than the whole real part, then

$$|Z|^2=R(f)^2C(f)^2/[C(f)^2+R(f)^2] \tag{2}$$

If $R(f)$ is a constant, $C(f)$ is $(2\pi fC)^{-1}$ and $R(f)$ is much bigger than $C(f)$, then

$$\log(|Z|)= -\log(2\pi C)-\log(f) \tag{3}$$

So there is a straight segment with a slope of −1, and the interface capacitance can be calculated when it is extrapolated at the point where f is equal to 1.

But in figure 2 the slope of the straight is −0.85, and this phenomena is ubiquitous in all the tested specimens. And that the slope equals −1 is a certain

result when the resistance and the capacitance are assumed as a constant, which is doubtable here.

Assume that the resistance and the capacitance are not constants but functions of the frequency, the above principle will not be apposite again. Now a new method is introduced as follows.

2.2 An improvement in data processing method

The equivalent circuit of electrolytic cell could be thought as figure 1. R_L is assumed as a constant; $jC(f)$ and $R(f)$ are the capacitance impedance and the resistance at interface, respectively. Then the real component of the impedance is

$$Z_R=R_L+R(f)C(f)^2 \ / \ [C(f)^2+R(f)^2] \tag{4}$$

and the imaginary component of the impedance is

$$Z_I=R(f)^2C(f) \ / \ [C(f)^2+R(f)^2] \tag{5}$$

obviously

$$(Z_R-R_L)/Z_I=C(f) \ / \ R(f) \tag{6}$$

Assume $K= -R(f) \ / \ C(f)$, then

$$Z_I=C(f)/(1+K^{-2}) \tag{7}$$

and $R(f) = -KC(f)$.

If the frequency is lower than 1, the value of R_L would be much smaller than that of Z_R, then we can omit R_L when dealing with the data within this frequency range. Besides, R_L perhaps also has an effect of frequency at high frequency area, and then R_L is too big to be omitted compared with the whole real component, in this paper only the condition of frequencies lower than 1 is considered. Another paper will focus on the high frequency condition specially.

The data processing course of the testing data of titanium alloy TA12 in 3% NaCl solution is listed in **table 2**.

Table 2 Data processing course of the testing data of titanium alloy TA12

f	Z_R	Z_I	$K=-Z_I/Z_R$	log (f / Hz)	$C(f)=Z_I*(1+K^{-2})$	$\log(-C(f))$
0.00266	1244800	−981280	0.7883	−2.5759	−2560370	6.4083
0.00443	636480	−1298000	2.0393	−2.3540	−1610100	6.2068
0.00620	376880	−973620	2.5833	−2.2079	−1119510	6.0490
...	...	...	...	...	...	...
0.25119	6065	−35332	5.8251	−0.6000	−36373	4.5607
0.39811	4037	−23370	5.7885	−0.4000	−24067	4.3814
0.63096	2778	−15544	5.5953	−0.2000	−16040	4.2052
1.00000	1950	−10330	5.2958	0.0000	−10698	4.0293

Figure 3 shows the dual-logarithm graph of $-C(f)$ vs. the frequency. It is a straight line with a slope of −0.9292. The mathematic analysis of this straight line is listed in **table 3**.

For $R(f) = -KC(f)$, so we can get a dul-logarithm

graph of the interface resistance as shown in **figure 4**.

From figure 4, it seems $R=af^{-k}$, but in low frequency range the curve deviates from this relation. Furthermore from the curve's trend, there seems to be an asymptote. Assume the relation is $R=a(f+b)^{-k}$, where b

is a constant. From physics view this formula is more suitable because it gives us a resistance at zero Hz. The slope 'k' and the intercept 'a' can be estimated from the straight segment of the curve in figure 4. So $b=(R(f)/a)^{-1/k}-f$ can be achieved. Constant b is achieved from the average of several estimation values in the lowest frequency range. The processing course of value b is listed in **table 4**.
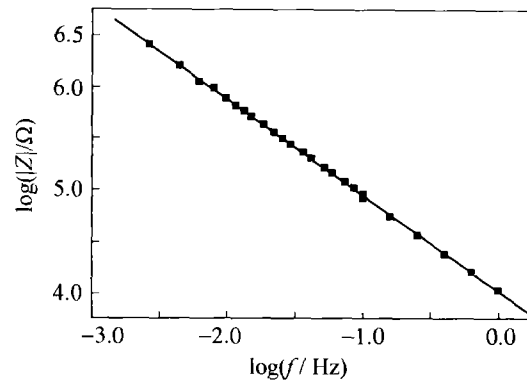
The mathematic analysis of **figure 5** is listed in **table 5**.

Figure 3   The dual-logarithm graph of $-C(f)$ vs. frequency.

Table 3   The calculated parameters in line of figure 3

Item	A	B	Re	SD	N
Calculated value	4.01982	−0.9292	−0.99983	0.01177	25
Error	0.00556	0.0036	—	—	—

Note: $Y = A + BX$, where Y is $\log(-C(f))$, X is $\log(f)$, A is the intercept, B the slope, Re the reliability, SD the standard deviation, N the sampling number.

Table 4   Estimating process of b

$\log(f)$	$R(f) = -KC(f)$	$\log(R(f))$	$b=(R(f)/a)^{-1/k} -f$
−2.3540	3283550	6.5163	0.00790
−2.2079	2892100	6.4612	0.00797
−2.0987	2687610	6.4293	0.00738
...	...	...	...
−0.6000	211880	5.3260	−0.00369
−0.4000	139315	5.1440	−0.00647
−0.2000	89752	4.9530	0.00275
0.0000	56656	4.7532	0.04856

Note: The formula of a straight segment in figure 4 is $\log(R(f)) = 4.77206-0.91359\log(f)$, i.e. $a =10^{4.77206}$, $k=0.91359$.
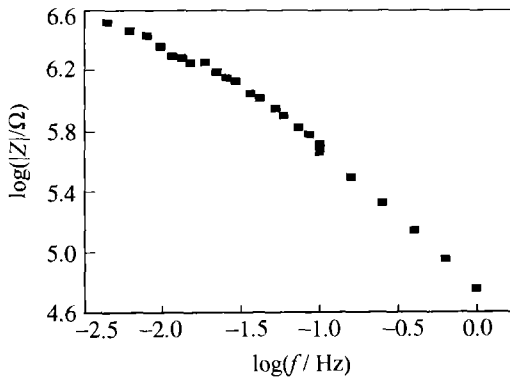

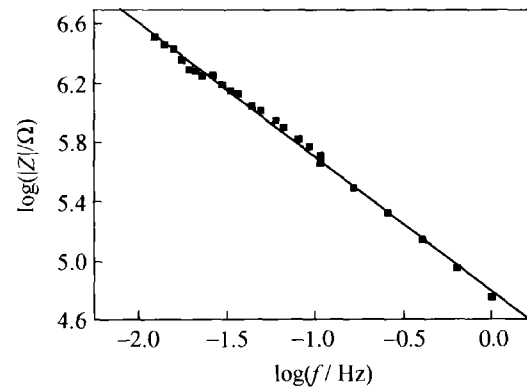**Figure 4   The dual-logarithm graph of interface resistance vs. frequency for $R(f)=-KC(f)$.**

Figure 5   The dual-logarithm graph of interface resistance vs. $f+0.008$.

Table 5   The calculated parameters in line of figure 5

Parameter	A	B	Re	SD	N
Value	4.80011	−0.90897	−0.998	0.03121	24
Error	0.01632	0.01228	—	—	—

Note: $Y = A + BX$, where Y is $\log(R(f))$, X is $\log(f+0.008)$, A is the intercept, B the slope, Re the reliability, SD is the standard deviation, N is the sampling number.

According to the above analysis the following two formulae can be gotten.

$$C(f) = 10^{4.01982} f^{-0.9292}, R(f) =10^{4.80011}(f+0.008)^{-0.90897}$$

(8)

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This processing method is an improvement to Bode method. It detaches the capacitance information from the resistance information. From the formulae it can be concluded that the interface capacitance has a linear relation with $f^{0.9292-1}$, which means higher frequency causes more ion exchange. Also the interface resistance will decrease with the frequency, which means the interface reaction rate will be accelerated with the frequency increasing.

3 Conclusions

(1) The new method to process the AC impedance data is acceptable. It can detach the capacitance information from the resistance information demonstrably.

(2) Both the interface capacitance and the resistance of titanium alloy TA12 in 3% NaCl solution are the functions of frequency. Their formulae can be expressed as

$$C(f)=10^{4.01982}f^{-0.9292}, \quad R(f)=10^{4.80011}(f+0.008)^{-0.90897}.$$

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