

Micro-environment Corrosion Strength Based on Quartz Crystal Microbalance

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Abstract. Equipment service environment often has a certain corrosive, accelerate equipment corrosion, affect the integrity of equipment. In order to accurately monitor the micro-environment corrosion strength of the equipment, the multi-channel quartz crystal microbalance calibration test and the crystal vibration sensor temperature supplement test were carried out to realize the frequency-quality signal conversion of the quartz crystal vibration sensor and improve the accuracy of data acquisition of the device. Using a multi-channel quartz crystal microbalance, For an equipment micro-environment under the hot and humid ocean environment, Packaging box under warm and wet acid rain environment, For 30h, respectively, 65h Continuous in situ monitoring, The test data showed that the mass gain of a 30h copper crystal vibration sensor is 0.5 μg , The rate of mass change was 0.017 $\mu\text{g/h}$, High corrosion strength, Metal materials in this area are prone to corrosion, Key protection is required; The 65h mass temperature increase: 0.022 μg , The rate of mass change was 0.000034 $\mu\text{g/h}$, Low corrosion strength, The internal metal material is corroded slowly.

Keywords. Multi-channel quartz crystal microbalance, micro-environment corrosion strength, in-situ monitoring.

1. Introduction

Equipment service environment often has a certain corrosive, accelerate equipment corrosion, affect the integrity of equipment. The researchers often use GB/T 19292.1-2018[1] for typical atmospheric environment corrosion grade evaluation, specific method for steel, aluminum, zinc, copper four metal standard metal pieces to different natural environment, calculate the different metal corrosion rate within a year, according to the value of the natural environment rating, this method is widely used, can implement, but not in accurate quantitative evaluation of micro-environment corrosion strength in a short time. However, compared with the natural environment, the equipment micro-environment is more suitable for the equipment, and plays a vital role in the integrity of the equipment[2], and should be regarded as the monitoring object.

Quartz crystal microbalance is a high-precision test device, with simple structure, online, real-time dynamic monitoring characteristics, is widely used in biology, chemistry, physics and many other fields[3]. In the biological field for nucleic acid aptamer screening and detection[4], and protein adsorption detection research[5][6]. In the field of environmental monitoring, organic toxic gases and liquid pollutants such as organic aldehydes, organic acids and dioxins can be detected[7][8], as well as corrosive gases such as SO₂ and

NO₂[9][10]. In the field of electrochemistry, it is used to study the interaction between common-rail/non-co-rail polyelectrolyte pairs, final membrane components and viscoelastic behavior of self-assembled films[11], and the dissolution behavior of pure magnesium sensors in dilute sodium chloride electrolytes[12].

This project takes advantage of the rapid response of quartz crystal vibration sensor to the environment to carry out real-time monitoring of the comprehensive corrosion concentration for 65h and 30h for the packaging cylinder and a wheeled equipment micro-environment respectively. By analyzing the data obtained, the corrosion rate of the crystal vibration sensor in the sampling period is obtained, and the quantitative evaluation of the corrosion ability of the micro-environment is obtained.

2. Experiment

2.1 Materials and instruments

Experimental materials: AgNO₃, KCl, Na₂SO₄, Chengdu Cologne Chemical Co., Ltd.; 49U, copper coated crystal, Nanjing Meixuan Radio and Television Materials Co., Ltd.

Experimental instrument: 5 μL microprototype, Shanghai High Pigeon Industry and Trade Co., Ltd.; Qutro-S field, Thermo, TT711-5 High and low

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temperature test box, Chongqing Harding Environmental Test Technology Co., Ltd.; 53220A frequency meter, USA; calibration module, multi-channel quartz crystal microbalance, laboratory self-research; ME204E electronic balance, METTLER.

2.2 Crystal frequency-corrosion quality calibration test

The crystal mass-frequency relation is shown in Sauerbrey equation[13] as shown in equation (1).

$$\Delta m_f = -\frac{\rho_q h_q}{f_0} \frac{\Delta f}{n} = -C \Delta f \quad (1)$$

In this equation $C = \rho_q h_q / (n f_0)$, ρ_q is quartz crystal density, h_q is quartz crystal vibration thickness, f_0 is the quartz crystal vibration base frequency, n is the general frequency number, for the AT cut quartz crystal, $n=1,3,5,\dots$

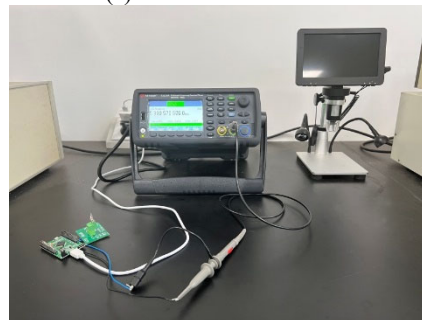
The purpose of the calibration test is to find the C value of the Sauerbrey equation. The specific method is: the first step is to prepare 5~7 concentration gradient $AgNO_3$ with distilled water in a sufficient amount of 50mL beaker, KCl, Na_2SO_4 Salt solution was 5mL each and diluted 1000-fold, See Table 1 for details; the second step, At room temperature, Open the self-developed calibration module (equivalent to the device single-circuit test assembly), Preheat for 10 min after power, Connect the vibration signal end to the frequency meter, Record the crystal vibration base frequency; the third step, The diluted salt A solution prepared in step 1 to the crystal vibration surface with a micro-sampler, Drying at room temperature for 2 to 3 h, Record the frequency after the constant vibration frequency within 15 min, After that, when cleaned with distilled water, drying to constant weight, The same step was used to measure the frequency of the remaining B, C, D, E, F and G, on the basis of $\Delta f = f_1 - f_0$. The fourth step, according to the Sauerbrey equation, when the crystal vibration plating film is uniform, the Δf is only m related, fitting the Δf to the actual salt mass Δm , to obtain the relationship between the crystal vibration frequency change Δf and the crystal vibration mass change m. The materials and equipment required for calibration are shown in Figure 1.

Table 1. Type and concentration of calibration solutions

	Concentration of calibration solutions (mg/mL)						
	A	B	C	D	E	F	G
KCl	20.	31.	57.4	79.9	104.	139.	207.
	84	36		8	44	86	82
Na_2S	22.	67.	102.	141.	181.	230.	276.
	O ₄	92	32	88	38	1	98
AgN	24.	79.	126.	203.	283.	317.	—
O ₃	06	26	88	32	98	56	—



(a) Calibration Materials



(b) calibration data acquisition

Figure 1. Calibration experiment

2.3 Temperature fill test

Temperature and humidity of environmental factors will have a certain impact on the oscillation frequency of QCM sensor, especially the frequency change of 1°C and about 1Hz[14]. In order to obtain the accurate frequency change value of each coating crystal vibration, the relevant study of the device temperature compensation is done, as shown in Figure 2. Specific method: place the device in the temperature control box to slowly cool down to -15°C for 20 min; then to 1°C/ min to -10°C/ min for 20 min; to -5°C at 1°C/ min for 20 min; to 0°C for 1°C/ min for 20 min; and then to 45°C, and finally slow down to room temperature.

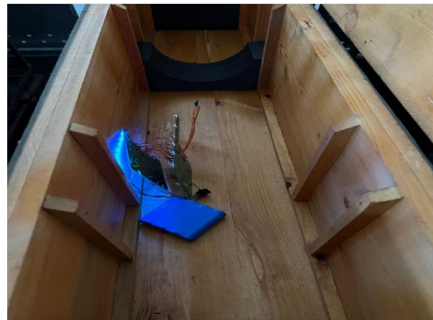


Figure 2. Temperature supplement test

2.4 Micro-environment corrosion and corrosion data collection

The acquisition micro environment mainly includes two micro environments: packaging box and wheel equipment base, as shown in Figure 3. The packaging box used for micro-environment data collection is mainly the

packaging box of an equipment under warm and wet acid rain environment and the upper end micro-environment of a wheeled car base under hot and humid ocean environment. When collecting data, the device is first connected with the upper computer program, and the sampling frequency is set to 10 times/s, the sampling time is set to 65h, and the wheeled equipment is set to 30h. After the device is set in the corresponding micro-environment, the packaging box should close the upper cover for collection.



(a) Box micro-environment



(b) Wheel equipment micro-environment

Figure 3. micro-environment data acquisition

3. Results and Discussion

3.1 Crystal frequency-corrosion quality calibration result

A total of 40 copper coated crystal vibration calibration data were measured. According to the data integration and analysis, the copper crystal vibration test results are shown in Figure 3. Δf and Δm showed an obvious linear relationship: $\Delta f = 644.2 \cdot \Delta m$, and the goodness of fit is 0.982, which conforms to the Sauerbrey equation. The crystal vibration sensor frequency signal can be converted into the corrosion quality signal to directly reflect the crystal vibration corrosion situation, and the corrosion strength of the micro-environment can be monitored through real-time signal processing and transformation.

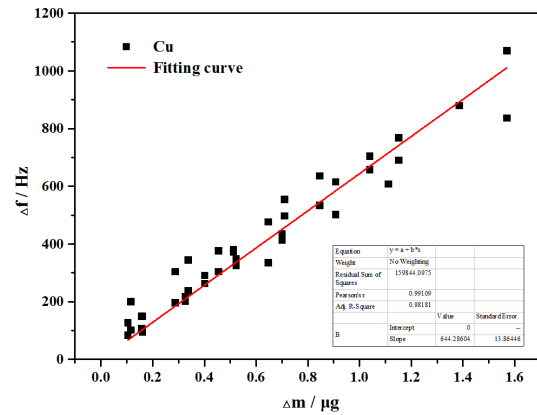


Figure 4. Mass-Frequency data calibration

3.2 Temperature compensation results

The quartz crystal vibration temperature frequency curve of copper coated crystal vibration as measured by the high and low temperature test box is shown in Figure 4. Copper coating crystal vibration frequency is negatively correlated with temperature, and temperature decrease frequency increases and temperature increase frequency decreases. Temperature change-15 °C ~45 °C , the frequency change of 78.4Hz, the temperature of every change of 1 degrees Celsius, the frequency change of about 1.3Hz, the temperature measurement and supplement results will be written to the self-developed quartz crystal micro-balance program, the subsequent data acquisition will be automatically compensated, to improve the accuracy of the data acquisition of the device.

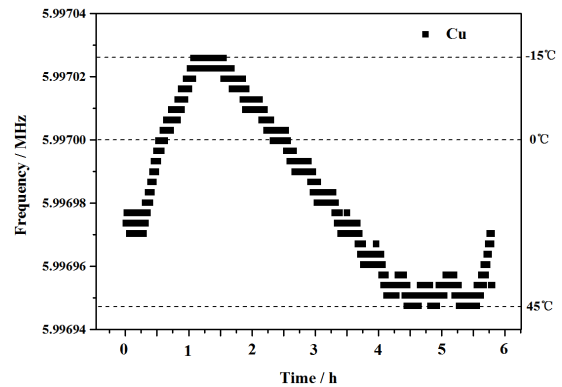
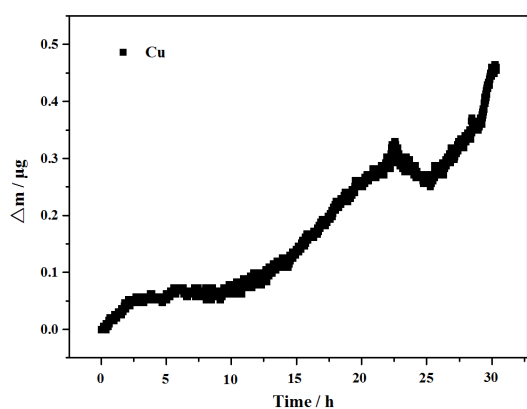


Figure 5. Installation temperature supplement

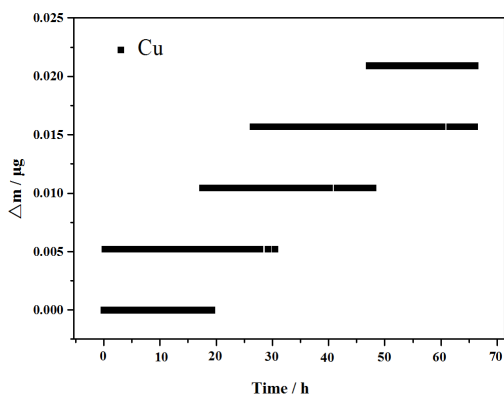
3.3 Analysis of micro-environmental corrosion data

The two micro-environment corrosion data are shown in Figure 5. According to Figure (a), the change of copper crystal vibration quality in the wheeled equipment micro-environment for 30h is about 0.5 μ g, and the mass change rate is 0.017g/h. From Figure (b), the packaging box micro-environment is 65h, the change of copper crystal vibration quality is about 0.022 μ g, and the mass change rate is 0.00034 μ g/h. Through the data comparison, it can be seen that the crystal vibration quality of the wheeled vehicle change is 50 times that of the packing box, and the concentration of corrosion medium is much higher than

that of the packing box. Except for the corrosion concentration difference of two micro-environmental corrosion, It can also be seen that the packaging box sensor is in a relatively stable environmental quality in a constant speed increase state, The micro-environment of HAINAN station wheeled armored vehicle is semi-open, The environment changes greatly, Causes the sensor mass change to fluctuate, See Figure 10 (a) for the data, When the trial lasted for 22h, The mass change reached a peak within 24h, About $0.3\mu\text{g}$, The following 2h showed a significantly decreasing trend, This is due to the high micro-ambient air humidity, When the air temperature is below the crystalline vibration surface temperature, Poor condensation on crystal vibration sensor[15], As the air temperature rises, Evaporation of the surface condensate droplets, The crystal recovered to the initial weight.



(a) Wheel, equipped micro-environment

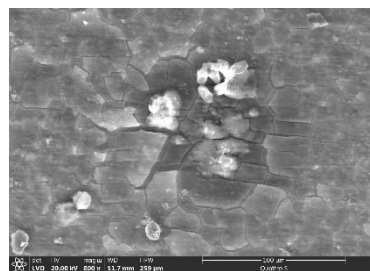


(b) packaging micro-environment

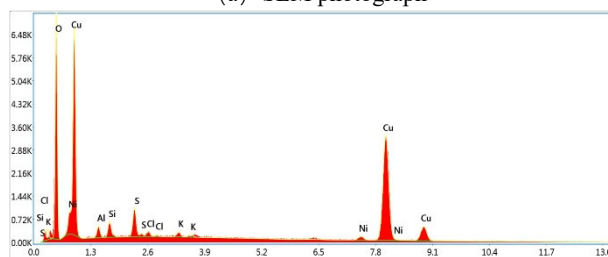
Figure 6. Results of two micro-environment data acquisition

3.4 Analysis of crystal vibration and corrosion mechanism

The microscopic analysis of quartz crystal vibration sensor as shown in figure 6, after the test copper crystal vibration coating metal layer cracks and corrosion serious parts peeling, through the EDS spectrum analysis, weak parts, the main elements of oxygen, copper elements, the total content of 25.54%, 64.77%, can be speculated as copper metal corrosion oxidation product CuO , consistent with copper element corrosion oxidation products.



(a) SEM photograph



(b)EDS analysis results

Figure 7. Microscopic analysis of the quartz crystal vibration sensor after corrosion

4. Summary

This paper uses the laboratory self-developed multi-channel quartz crystal micro-balance to monitor the equipment micro-environment corrosion monitoring. Test data show that a wheeled micro-environment 30h copper vibration sensor mass weight of $0.5\mu\text{g}$, the mass change rate of $0.017\mu\text{g/h}$, high corrosion strength, metal materials prone to corrosion; 65h copper vibration sensor mass weight of $0.022\mu\text{g}$, mass change rate of $0.000034\mu\text{g/h}$, low corrosion strength, slow internal metal corrosion. micro-environment corrosion monitoring data can provide a reliable basis for the service, storage and daily maintenance of equipment.

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