CORROSION SCIENCE AND TECHNOLOGY, Vol.7, No.3(2008), pp.179~181

Study of the Application of Gel Electrolyte in the Reference Electrode of $Cu/CuSO_4$

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With nano-SiO_2 and sulphate acid, a kind of colloid electrolyte is synthesized by sol-gel method. It is placed outside the reference electrode as a layer of gel electrolyte so as to decrease the leaching of Cu^{2+} and increase the life of the reference electrode. The performance of the gel electrode in simulating soil solution is measured as follows: the potential of the electrodes ranging from 60 mV to 80 mV (vs. SCE) with potential variation no more than ±10 mV, enough resistance to polarization. The Cu^{2+} effusion rate of the reference electrode without gel electrolyte is 3 times that with colloid electrolyte, which means that gel electrolyte can extend the life of the reference electrode significantly.

Keywords *: gel electrolyte, reference electrode, $Cu/CuSO_4$, service life.*

1. Introduction

Usually, the reference electrode used in cathodic protection has two uses, the first one is to measure the potential of the protected metals, and this potential can help to make clear whether the metal is in the protection range of designed, it also can monitor the distribution of potentials on metals to provide basis for further regulate or improve the system design; another use is to applied as controlling electrode, and this means to provide a comparing signal to potential rectifier, i.e. feedback the measured potential to comparizer, then compare with the potential set earlier, the result will be the base for further regulating the potential of protected metals. Therefore, reference electrode is a necessary monitoring tool for cathodic protection.

$Cu/CuSO_4$ electrode has many advantages like stable potential, sensitive, low polarization and easy manufacture. However, there are still many factors influencing the electrode's performance of $Cu/CuSO_4$,[1)] such as the chloride pollution, light as well as solution leaking of $CuSO_4$. When the chloride effuses into the electrode body, its potential will move towards the negative side obviously. Additionally, copper salt is very sensitive to light, when there is strong light shining onto the electrode body, the potential will also appear a dramatic fluctuation. If there is $CuSO_4$ solution leaking, it will probably lead the inside $CuSO_4$ solution becomes unsaturated, the electrode potential will show a large variation. All of the above factors will influence the electrode's performance and service life significantly.

Since the present reference electrode of saturated $Cu/CuSO_4$ used in cathodic protection just have a service life of 5~10 years, and usually show poor stability, therefore it is necessary to develop a new reference electrode with longer life and better performance.

In this paper, a gel electrolyte with nano-SiO_2 is developed and used as the medium between the electrode body and outside environment, the influence of the gel electrolyte to the performance of $Cu/CuSO_4$ electrode is studied.

2. Experimental

Preparation of gel electrolyte: the gel electrolyte is prepared by sol-gel method with nano-SiO_2 and polyacrylamide, this gel electrolyte has many characteristics like stable, hard to be hydrated, and has an ideal conductivity of about 80S cm^{-1}.

An inner electrode body of $Cu/CuSO_4$ is made through the traditional method, the specification of the ceramic body is Φ25 mm×100 mm, the insert is pure copper stick. The saturated solution of $Cu/CuSO_4$ is prepared with analytical grade $Cu/CuSO_4$ and distilled water. When the electrode assembly is completed, then put into the $CuSO_4$ sol-

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ution for 24 hours, when the electrode potential become stable, then set into the fired ceramic shell, and then gel electrolyte is dumped into the space between the body and shell, then connect the cable line and packed the electrode for the following test use.

Performance test of the prepared reference electrode: firstly, number the reference electrode without gel electrolyte N1~N3, A1~A3 for those ones with a gel electrolyte of 5 mm thick, B1~B3 for those ones with gel electrolyte of 10 mm thick, C1~C3 for those ones with gel electrolyte of 15 mm thick.

A302-5 model high internal resistance digital voltmeter and 202 model saturated calomel electrode (SCE) were used to measure the potential variation with time, the salt bridge is saturated KCl solution 25℃, and the test period is 30 days.

Galvanostat polarization test were carried out on Cu/ $CuSO_4$ reference electrode of N1, A1, B1and C1 with Pt as the auxillary anode as well as SCE as the reference electrode, the electrolyte is simulated soil solution,[2] its composition includes Mg^{2+} of 0.6×10^{-3} moll-1, Ca^{2+} of 0.6×10^{-3} moll-1, SO_4^{2-} of 0.7×10^{-3} moll-1 and HCO_3^- of 0.5×10^{-3} moll-1, the pH is 4.9. The instrument is EG&G2273 model potetiostat/galvanostat with a polarization current of ±10 μA, the samples were polarized stepwise in the cathodic and anodic directions, and the polarization time lasts 8h, the potential-time curve of the electrode were recorded, the control software is Powersuite.

The effusion rate of Cu^{2+} from the electrode to simulated soil solution was measured by using PE 3300 atomic absorption spectrophotometer.

3. Results and discussion

3.1 Gel electrode potential

The potential-time curves of electrode N1~N3, A1~A3, B1~B3 and C1~C3 show the potential variation as follows,

electrode N1 ranges from 61 mV to 72 mV, while N2 from 61 mV to 78 mV and N3 from 61 mV to 81 mV.

electrode A1 ranges from 65 mV to 72 mV, while A2 from 65 mV to 73 mV and A3 from 67 mV to 80 mV.

electrode B1 ranges from 60 mV to 76 mV, while B2 from 61 mV to 83 mV and B3 from 64 mV to 79 mV.

electrode C1 ranges from 66 mV to 84 mV, while C2 from 60 mV to 81 mV and C3 from 60 mV to 76 mV.

In practical projects, the potential of Cu/$CuSO_4$ reference electrode usually is required to be stabilized in the range of ±10 mV,[3] i.e. the potential variation shall not be more than 20 mV. All of the four kinds mentioned above can meet this requirement, and the electrode A1~A3 have the best stability, in contrast, the potential stability of N1~N3 and B1~B3 is a little poorer than A1~A3 while C1~C3 shows the most poor stability. The reasons may be the existence of certain thickness gel electrolyte decrease the tendency of foreign impurities diffusing from outside environment into electrode body, therefore the electrode body is not very easy to be polluted and thus its potential is very stable. When the gel electrolyte is too thick, the resistance will increase, the conductivity between the electrode body and the outside environment shall be influenced, so electrode C1~C3 shows poorer potential stability than others.

3.2 Polarization performance

The potential-time curve of N1, A1, B1 and C1 with the anodic and cathodic constant current cyclic polarization shows that the potential movement of N1's cathodic polarization and anodic polarization are -1.5 mV and 2.5 mV, respectively, while A1's are -6.2 mV and 0.1 mV, B1's are -1.0 mV and 3.2 mV, C1's are -13.2 mV and 12.0 mV. When the experiment completed, the potential can resume the initial value very soon. All of them show excellent polarization resistance, and the potential resumes well after cyclic polarization. Usually, the reference electrode technical specification for ship require that the polarization potential variation shall not be more than ±20 mV, all of the four above electrodes can satisfied with this. Among the four electrodes, the potential movement of C1 is larger than the others, the reason may be that with the gel electrolyte become thicker, the resistance of gel electrolyte will increase, and this will leads a remarkable IR decrease, therefore the polarization potential movement will be larger.

3.3 Effusion velocity of Cu^{2+}

The effusion velocity of Cu^{2+} in the reference electrode are measured at different time, the results are shown in Table 1.

The velocity V is defined as follow equation:

$$V = M / ST$$

Where M is the effusion quantity of Cu^{2+} from the inside electrode body to outside environment, S is the outside surface area of the studied reference electrode, T is time for test continued.

From Table 1 can see that the Cu^{2+} effusion velocity in the first 24 hours has the following order from high to low:

$$N > A > B > C$$

Table 1. Effusion velocity of copper ions from the reference electrode at different time

No.	0h~24h/ $\mu mol \cdot h^{-1} \cdot cm^{-2}$	48h~72h/ $\mu mol \cdot h^{-1} \cdot cm^{-2}$	144h~168h/ $\mu mol \cdot h^{-1} \cdot cm^{-2}$	312h~336h/ $\mu mol \cdot h^{-1} \cdot cm^{-2}$
N1	8.3	5.6	11	6.5
N2	10	6.0	7.1	9.6
N3	11	7.7	9.5	10
A1	3.2	3.2	3.4	3.1
A2	3.1	2.7	3.1	3.6
A3	3.2	3.3	3.4	3.0
B1	2.9	2.6	3.0	3.1
B2	3.1	2.9	2.7	3.4
B3	2.9	2.6	3.1	2.5
C1	1.8	2.9	3.1	2.5
C2	1.7	2.4	3.1	2.4
C3	1.7	2.4	2.9	3.1

Since the gel electrolyte become thicker and thicker from N to C, thus the above result shows clearly that the gel electrolyte has a very remarkable blocking effect to the effusion of Cu^{2+}, the time for which effuses from inside solution to outside environment will become longer with the gel electrolyte becomes thicker. With the time continuing longer than 24 hours, the effusion procedure of Cu^{2+} tend to reach a equilibrium, the average velocity is about 3.0 μ $molh^{-1}cm^{-2}$, the effusion velocity follows the order of A>B>C, while the electrode N larger than all of them remarkably.

In this test, the average effusion velocity of Cu^{2+} is about 8.5 μ mol $h^{-1}cm^{-2}$, which is 3 times that of electrode with gel electrolyte. This blocking effect of Cu^{2+} effusion surely will make the service life of reference electrode longer.

4. Conclusions

Gel electrolyte can effectively block the effusion of Cu^{2+} from the reference electrode body to outside environment, this can give the electrode longer time to keep the $CuSO_4$ solution saturated, and also this blocking effect can reduce the pollution opportunity of impurities from the environment to inside electrode body, thus the service life of the reference electrode will be extended. The test results show that the $Cu/CuSO_4$ reference electrode with gel electrolyte has a good potential stability and polarization resistance.

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