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ELECTROCHEMICAL INSTRUMENTATION

APPLICATION OF ION SELECTIVE ELECTRODES FOR CORROSION MONITORING-I CORROSION OF COPPER

V YEGNARAMAN, G SUBRAMANIAN and G PRABHAKARA RAO
Central Electrochemical Research Institute Karaikudi-623 006

ABSTRACT

Ion Selective Electrodes (ISE) developed recently have established themselves as powerful analytical probes for estimation of ionic species present in trace and ultra trace levels in solution. The ease of operation coupled with high sensitivity has enabled their successful applications in multifarious fields. Studies on the use of ISE for estimation of metallic corrosion by resorting to solution analysis are scarce. The results of evaluation of corrosion of copper in chloride and acetate media have been described. Use of ISE's for estimation of inhibition efficiency has also been attempted. The results have been compared with data obtained from weight loss and atomic absorption spectroscopy.

Key Words : Ion selective electrode, corrosion, monitoring, corrosion of copper

INTRODUCTION

Methods employed for determination of corrosion rates can generally be classified as electrochemical and nonelectrochemical methods. Electrochemical methods envisage a model for the behaviour of the corroding system. A wide spectrum of electrochemical techniques [1, 2] are available. All these methods consist in disturbing the corroding system from its open circuit potential with suitable excitation signals and measuring the response of the system.

Non-electrochemical methods, on the contrary enable the measurement of corrosion rate without disturbing the system. Weight loss and solution analysis are examples of this category. The former requires the exposure of the specimen to the corrosive medium and monitoring the loss in weight of the specimen which then can be converted to corrosion rate. The solution analysis procedure assumes that the mass of material disintegrating from the specimen as a result of corrosion dissolves in the corrosion medium which can then be suitably analysed and correlated to corrosion rate. The solution analysis procedure has not been much followed, probably due to the fact that ordinary solution analysis procedures are not sensitive enough to estimate the concentration of species at very low levels.

In this communication the authors report their attempts to evaluate corrosion rate by monitoring the concentration of the dissolved ionic species in corrosive medium by using ion selective electrodes.

Ion selective electrodes [3](ISE's) have established themselves as powerful analytical tools especially for trace analysis in the recent years. The electrode when dipped in a solution of ionic species to which the ISE is selective, develops characteristic potential depending upon its concentrati This potential can be measured with a mV/pH meter. ISE's enable speedy and simpler methods of analysis involving less expensive and less sophisticated equipments. Further, a wide range of concentrations down to ppm and ppb levels can be determined with the same precision and accuracy with ISE's. Moreover ISE's are amenable to on-line monitoring. Hence they are finding a variety of applications [4-7] in diverse fields as agriculture, nuclear technology, petroleum refining, environmental pollution etc. Utility of these electrodes for the analysis of the various constituents of electroplating and metal finishing baths [8-11] has been reported from these laboratories.

The use of ISE's for determining corrosion rates by solution analysis procedure has earlier been reported [12]. The author has evaluated the corrosion of rate of copper in neutral sodium chloride solutions.

EXPERIMENTAL

The present authors have studied the corrosion of copper in acidified sodium acetate solutions with and without the addition of organic substances. The acidic system is chosen so that corrosion products will easily dissolve into the corrosion medium. The organic substances were added to the corrosion medium to see whether these additions influence the performance of the ISE. Diethylamine, 2-butyne 1,4-diol and benzotriazole were used. Sodium acetate solutions of 0.2 M concentration were prepared and their pH was adjusted to 4.0 by addition of acetic acid. Copper specimens in the form of thin panels were mechanically polished, degreased and then introduced to the corroding medium. Just prior to introduction, the weight of the panels were measured with an accuracy of ± 0.1 mg. The solutions were protected so as to minimise the loss of solution due to evaporation.

After known intervals of time the panels were taken out, washed thoroughly with a forced flow of water, dried and weighed. Known amount of corrosion medium was taken out and analysed after appropriate dilution. Standard addition procedure with cupric ISE (developed in CECRI)was used. ORION double junction reference electrode was employed and ORION Ionalyser Model 901 was used for potential measurements. For comparison the solutions were subjected to analysis by atomic absorption spectroscopy (AAS) with Perkin Elmer Model-380 AAS Unit.

RESULTS

Data obtained from three different methods viz. weight loss, solution analysis by ISE and solution analysis by AAS are converted into corrosion rates and expressed in mpy (mils per year) units. (cf. Table). Corrosion rates calculated from ISE and AAS data are in good agreement. This shows the utility of ISE for evaluating corrosion rate. Weight loss data in all cases tend to yield a slightly higher corrosion rate which may be attributed to the difference in procedure. Further the results clearly indicate that the addition of organic substances do not influence the performance of the ISE. The addition of diethylamine and 2-butyne-1, 2-diol accelerates

Table I: Corrosion rates of copper

Corrosion medium	pH	Hours of exposure	Corrosion rate (× 10) in mpy		
			ISE	AAS	Wt. loss
1) Sodium acetate 0.2 M	pH 4.0	93	3.12 ± 0.1	3.097 ± 0.014	3.47 ± 0.05
2) Sodium acetate 0.2 M	pH 4.0	595	3.19 ± 0.1	3.58 ± 0.02	4.07 ± 0.05
3) Sodium acetate 0.2 M, Diethylamine 0.1%	pH 4.0	240	3.52 ± 0.2	3.45 ± 0.25	3.7 ± 0.3
4) Sodium acetate 0.2 M, Diethylamine 0.1%	pH 4.0	720	4.06 ± 0.2	4.35 ± 0.25	4.95 ± 0.3
5) Sodium acetate 0.2 M, Diethylamine 0.3%	pH 4.0	240	3.34 ± 0.2	3.35 ± 0.2	3.75 ± 0.2
6) Sodium acetate 0.2 M, Diethylamine 0.3%	pH 4.0	720	3.98 ± 0.2	4.08 ± 0.2	4.77 ± 0.2
7) Sodium acetate 0.2 M, 2-Butyne 1,4-diol 0.1%	pH 4.0	93	5.4 ± 0.2	5.5 ± 0.2	6.6 ± 0.2

the corrosion rate, especially the latter accelerates appreciably. The accelerating effect noted with diethylamine remained practically same over the concentration range of 0.1 to 0.3% by weight.

The addition of benzotriazole results in localised corrosion leading to formation of pale blue crystals on some sites of the panel surface while the other portions of the surface remain unaffected. Hence the data could not be processed further.

CONCLUSIONS

1) Reliable estimates of corrosion rates of copper in acidified sodium acetate solutions can be obtained using ISE.

2) Addition of organic substances does not influence the performance of ISE. Hence they can be used for evaluating corrosion inhibition efficiencies of different inhibitors.

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