IN-SITU OXIDATION MEASUREMENTS OF COPPER USING THE QUARTZ CRYSTAL MICROBALANCE COUPLED WITH RESISTANCE MEASUREMENTS USING AN ATMOSPHERIC CORROSION MONITOR

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ABSTRACT

A method for the detection of in situ corrosion monitoring due to atmospheric gasses has been incorporated to measure not only the amount of corrosion on a copper surface but also the rate of corrosion and a study on the bonding of the adsorbent at the gas solid interface. The Quartz Crystal Microbalance (QCM) has recently been used for this corrosion monitoring. Results indicate a difference in the rate at which the adsorbent reacts with the solid in different atmospheric conditions verses the rate of corrosion as measured when there is no inhibitor present. Tests also indicate an asymptotic threshold may exist in the adsorption process which is reached after (x) amount of time. The adsorption measured was in dry nitrogen with a minimal to negligible effect from the influence of oxygen. This adsorption pre treatment of the surface in a dry inert atmosphere containing an inhibitor has shown to provide the copper surface with protection from atmospheric gasses on what looks to be a very impressive time scale. Furthermore,the frequency change due to the chemical adsorption of the inhibitor is suspected to be identified and indicates excellent protection of the copper surface after the inhibitor has been taken away which may support the BOC theory. The atmospheric corrosion sensor was used to monitor the in situ resistance measurements due to the formation of corrosion.

Keywords: Quartz Crystal Microbalance, adsorption, benzotriazole (BTA), Bond-Order-Conservation Theory (BOC), corrosion, frequency, Vapor Phase Inhibitors (VPI), Volatile Corrosion Inhibitors (VCI), in situ corrosion, copper, adsorption sites, atmospheric corrosion sensor.

INTRODUCTION

For many years Vapor Phase Inhibitors (VPI) have been increasingly used by electronics industry for the protection against corrosion. As the world of electrical circuitry continues to shrink the importance of corrosion control increases. This is because at the microscopic level corrosion can be devastating for the microelectronics market. The use of an inhibitor in liquid and vapor applications has provided for this reduction in corrosion. It is the scope of this paper to show that the use of the Quartz Crystal Microbalance (QCM) has in situ measurements which show a significant change in the mass reduction due to the chemical adsorption effects of a VPI.

The rate at which this adsorption occurs is especially interesting because previous studies show that the corrosion rate of copper in atmospheric conditions is proportional to the square of the exposure time.[2] In situ measurements using the QCM support these studies, but what is interesting is the rate of mass change due to the presence of an inhibitor in the same environment. It displays a linear rate of mass change within the first 1.2 days, which seems a bit paradoxical. What the recent QCM data indicates is happening is the rate of frequency change when an inhibitor is present grows linearly during the early stages of corrosion, time is up to 1.5 days. The model that is proposed, based on observations, is one where the rate of change is linear early in the beginning stages until it reaches a saturation threshold where the limit has an asymptotic value. Then at a later time the uninhibited sample surpasses the mass change of the inhibited sample. This is based on data of other studies and current findings using the QCM. One study which aids in this theory looks at the morphology, adsorption sites, heterogeneity and the bonding characteristics at the metal inhibitor interface it is the Bond-Order-Conservation Theory (BOC).[3] When applied, the correct BOC and coordination bonding angle between the copper and cuprous oxide surfaces could be used to determine accurate monolayer coverage.

It is known that the bonding of BTA is through the triazole-nitrogens during the adsorption process. This observation is useful in forming a model that explains the composition of the oxide and BTA polymer complex that forms the impermeable thin film on copper. Frequency changes as monitored by the QCM could then support models incorporating supportive evidence for adsorption sites, number of monolayers, and other phenomena in the adsorption process.

The QCM method is based on the inverse piezoelectric effect, discovered by Jaques and Pierre Curie, [1] where an applied voltage to an ionic crystalline solid produces distortions, such as quartz. Piezoelecric materials have long been recognized as excellent indicators of mass changes because of the direct relationship between mass change and resonant frequency response.

An equation was developed by Sauerbrey, in 1959, that showed a linear relationship between deposited mass and frequency changes.[1] For an AT cut quartz vibrating in the thickness shear mode the equation is

$$\Delta f= -2.3 \times 10^{6} f^{2} \Delta m/A$$

where Δf (Hz) is the change in resonant frequency, f is the resonant frequency (Mhz) and $\Delta m/A$ is the mass deposited per unit area (g cm^{-2}).

In terms related to this study this change in frequency relates to measuring adsorption of the inhibitor. Adsorption is the presence of a higher concentration of a compound at the surface than is present at the main bulk of the phase. A chemical adsorption is characterized as a non reversible process that leave the surface chemically changed. The effects covered here are of the chemically adsorbed nature. It is this adsorption that makes VPI's so effective against corrosion.

Previous studies have looked into the morphology, surface migration, coverage effects and the heterogeneity of solids from adsorption data that benzotriazole (BTA) has at the surface interface of copper and its alloys.[5,6,7] In these studies it has been confirmed that the BTA molecule bonds with copper at an angle, which has yet to be determined, relative to the normal, but also the bond is formed through the triazole-nitrogens. [5,6] It is debatable at this time to whether the bond is with the nitrogens N1,N2 or N1,N3 or a combination of the three nitrogens of the BTA molecule and if and how the bonding between the C-H and :N should be explained. Fang et al. proposed hydrogen to bond via the benzene C-H but J.O. Nisson et al. believe this to be doubtful based on the bond is a very weak bond, although it may play stabilizing role somewhere in the adsorption process. This theory plays an important role in determining the actual thickness of a BTA monolayer.

For purposes particular to corrosion, studying the rate, thickness, density coverage of the inhibitor, and other essential characteristics directly correlates to the mass changes observed. Part of this study is to help aid in any way in explaining these previously defined kinetics that involve the corrosion of copper. A future publication on this topic is planed that will be elaborated on it but at this time theoretical speculation is all that can be added to aid in these existing models based on existing data.

EXPERIMENTAL

The quartz crystals used are AT cut supplied by Valpey-Fisher they are cut to have a zero temperature coefficient at 25 C. The crystals are then fitted with two key hole type electrodes by means of an Varian Electron Beam Evaporator. First a layer of titanium 500 Å is laid onto the crystal followed by 1500 Å of gold.

Preparation of the crystal for electrodepositon of copper is a ultrasonic cleaning in a mild detergent. This was followed with a 18 MΩ de ionized (DI) water rinse, a 2 propanol rinse, a DI water rinse and then dried with argon.

Equipment: The crystal is then fitted in probe of Kel F which is inserted into a customized 115 ml., 3 neck 2 gas vent flask of my own design. The solution used for copper electrodeposition is 0.5M $CuSO_4$, 1.0 M H_2SO_4. Deposition was accomplished using a EG&G Model 173 Potentiastat at -200 mA over potential to a desired thickness of 2000 Å.

The atmospheric corrosion monitor sensor was purchased from the Rohrback Cosasco Systems. The sensor has a deposited copper film thickness of 2500 Å. The resistance values are recorded by the monitoring instrument and stored in the recording computer.

After deposition the flask is then rinsed with DI water and dried with argon. The probe containing the crystal is then inserted back into the flask for exposure to the various atmospheres. The flask is fitted so that various gasses may be used to contain controlled atmospheres. The frequency of the crystal is then monitored by the power source and frequency counter via IEEE connections to a computer for data collection.

Materials: The benzotriazole Regent Grade (Rg) used was supplied by Aldrich Chemicals without further refinement and the VCI was supplied by the Cortec Corporation of St. Paul, Minnesota.

The ocean water used in the lab experiment conforms to ASTM D 1141 “Standard Specification for Substitute Ocean Water”.

Set up: Figure 1 details the glass chamber used. The glass chamber was placed inside the Plexiglas box which was purged with dry nitrogen. The glass chamber is fitted with a gas inlet and outlet and two probes which can accommodate the inhibitor and a desiccant or other solids.

RESULTS

The numerous testing of five different atmospheres has identified the rates, linear vs. logarithmic, at which the mass change occurs. The five atmospheres are the following: air at 80% RH, air at 80% RH in the presence of BTA, air at 100% RH, air at 100% RH in the presence of BTA, air at 100% RH in the presence of VCI. The experiments performed here represent the early stages of frequency change due to corrosion, i.e. the first 100,000 sec. =1.16 days. The second set of tests span time from zero seconds to 13-15 days. The information presented first represents a paradox to corrosion protection via adsorption and its not until the second set of testing is the paradox accounted for.

AIR AT 80 AND 100% RH

Examining the curves (Fig. 2 and 3) of the mass changes due to the air at 80 and 100% RH one can see the rate is logarithmic in nature. A curve fit to the data gives the following equations for the frequency changes.

$$80\% \text{ RH } \partial f/\partial t=18.3+17.8561og(x) \quad R=.91885$$

$$100\% \text{ RH } \partial f/\partial t= 34.674+19.613\log(x) \quad R=.94998$$

Where, $\partial f/\partial t$ is the slope of the curve at a given point and x=time. The difference in magnitude of frequency change is on the order of 20-30% less for 80% than it is at 100% RH from 0-1.15 days. Which supports findings made by Sungkyu.[8]. The mass change does show a rate that changes with the square root of time which is supported by Lee et al. but also fits the logarithmic equation.

AIR AT 80 AND 100% RH
IN THE PRESENCE OF BTA

The curves for the frequency changes due to air at 80 and 100% RH with BTA present (Fig. 4 and 5) show a dramatic difference in the rate of change. The rate of change here appears to be linear in nature verses the logarithmic changes when there is no inhibitor. The equations for $\Delta f/\Delta t$, when $\Delta f \approx \partial f$ and $\Delta t \approx \partial t$, are

$$80\% \text{ RH } \partial f/\partial t=2.3613+17.17x \quad R=.97256$$

$$100\% \text{ RH } \partial f/\partial t= 7.38+24.475x \quad R=.99578$$

The difference in magnitude for frequency change between the two is still between 20-30% as is seen in with out BTA. This linearity could be the slope from a small section of an exponential equation if this is the case, as suspected, then this would explain the difference in the rates of frequency change. Since BTA is known for its corrosion protection this observation contradicts what actually happens. Actually, more time is needed to see the more pronounced effects of an inhibitor.

AIR AT 100% RH IN THE
PRESENCE OF VCI

Comparing the rate of frequency change of VCI (Fig. 6) to BTA it is clear that the linearity rate of change remains. At first the frequency jumps 20 Hz, due to the crystals adjustment of the change in condition, but then the rate grows at a linear rate of change very similar to the rate of change seen with BTA. The equation that best fits this rate of change is expressed by

$\partial f/\partial t = 18.868+15.094x$ R=.86116

BTA vs. NO BTA 13+ days

The data from the curves (Fig. 7) can be divided into four main parts. The first halves (A&C) of each curve represents the frequency change in dry nitrogen, the nitrogen in the chamber had a flow rate of 15-20 ccu/min in the early stages, days 1-3, followed by a static nitrogen atmosphere, days 3-8. Curve AB is the frequency change when BTA is present in the atmosphere in the vapor phase. Curve CD is the change in frequency without the presence of BTA in the atmosphere. The oscillations of the AB graph is believed to be due to the hypersensitivity of the crystal to the periodic temperature changes of the lab. The first part of CD curve is the same test conducted without the presence of BTA. The noted change in frequency is due to the diffusion of oxygen in the lab air through the glass chamber. This effect was corrected for and the result is seen in the AB curve where the frequency indicates no change due to oxygen diffusion because it was inside the nitrogen purged Plexiglas.

Parts C&D of the two curves represents the frequency change due to the exposure of the copper surface to the lab air, days 7/9-13/14. The frequency change on the sample not exposed to the inhibitor shows a Δf of approximately 150 Hz verses the negligible frequency change and virtually non existent mass loading due to atmospheric corrosion.

ATMOSPHERIC CORROSION SENSOR

In Figure 8 the QCM graph shows an initial decease in frequency and the corrosion monitor graph indicates a slight increase in its reading. These changes are strongly suspected to be from the oxidation and vapor adsorption of the copper from the cylinder of compressed air. When the introduction of ocean humidified air is introduced into the chamber the graphs change significantly. The change in the graph of the QCM is due to the mass change from the adsorption of the vapor molecules with copper. The contact with this thin film then causes the oxidation and the corrosion of the copper surface. The corrosion effects of the copper are seen at the end of the graph after the desorption process is completed. The amount of corrosion as measured by the QCM can be seen as the difference between the initial frequency and the final frequency which indicates a increased mass. The corrosion as measured by the corrosion monitor is seen in the change of the readings. Using Eq. 1 gives the corrosion rate at 24-30 Å/mo. For corrosion rate calculation and metal loss the following equations are given:

$$\frac{.0304 \times \text{Span (Å)} \times \partial\text{Reading}}{\partial T \text{ (days)}} = \text{(Å/mo.)} \qquad \text{Eq.1}$$

$$\underline{\text{Reading} \times \text{Span (Å)}} = \text{mass loss relative to 2500Å} \qquad \text{Eq. 2}$$

1000

Where .034=365 days/12 mos., Span=1/2 of the deposited film thickness

DISCUSSION

From the graphs it is clearly visible that there is significant change going on during the adsorption and corrosion process as measured by the QCM. In interpreting the changes of frequency change to a mass change one must consider the proportions of deposited mass to that in Hertz. This is undetermined based on the proportions of oxide formation, Cu(I)O and Cu(II)O, the bond angle, and other parameters mentioned earlier. But to estimate the frequency to mass relationship for adsorption for example. From figure 7 part A of the curve AB, a frequency change of 8-12 Hz/day can be averaged from the data, this change appears to be due to the adsorption of BTA in a dry static nitrogen atmosphere. Calculating an assumed BTA molecular thickness of 4.57 Å, and a density of 1.33 g/cm,[3] one gets 3.49 Hz per weight of monolayer of BTA from which the interpretation of curve A gives a 20-25 monolayers of CuBTA (based on Fang et al. perpendicular orientation of BTA to copper) and assuming monolayer coverage occurs.

From this date it is also clear that treatment of the copper surface with BTA reduces the corrosion process by a factor of 6+, more reproducibility of this test should yield a more accurate value but at this time this is what the data indicates. Evaluation of the graphs showing the different frequency changes due to the presence of the inhibitor give underlying clues to be investigated further that could be valuable for the BOC theory and adsorption sights and monolayer coverage.

Based on the test results and publications a variety of models are finding their way into explaining the surface chemistry and adsorption process. The consensus of the bonding of BTA to copper is that it occurs from the nitrogens of the BTA molecule, i.e. Fang et al. proposed perpendicular bonding to copper, but it is not concluded as to what the bond angle is at this time. But based on this bonding theory, further testing with the QCM could identify the asymptotic value reached by the adsorption of BTA on copper, then with this information more could be understood in the adsorption process.

What is speculated, at this time, from the observations as a model for the adsorption of BTA and VCI on copper, assuming VCI parallels BTA in its results, in humid air conditions is this:

The rate of corrosion has been shown to grow as the square of time Lee et al.[2] and with QCM tests results. The adsorption rate of BTA in dry nitrogen is presumably an exponential function that reaches an asymptotic limit at approximately 5-6 days, the first day showing a linear rate of change, using a saturated BTA nitrogen gas. BTA coupled with humid air displays this linear rate of change and from the data intersects and surpasses the curve of frequency change (1.5 d) with out the inhibitor present, this is the paradox. What has to happen after this is where the paradox gets solved.

As the adsorption is occurring simultaneously with the oxide formation the additional mass due to the inhibitor changes the rate of frequency change from a logarithmic rate where the limit is infinity to a rate where the limit has an asymptotic value much less than infinity. The part of the graph that is seen in humid air with BTA is only a small segment $\partial f/\partial t$ of the overall log curve. Because the curve has different exponent it crosses the log curve without inhibitor at a later time. This means that there are two cross over points during the inhibited case vs. no inhibited case. The second point of intersection is where the non inhibited sample surpasses the inhibited case, the asymptote, in corrosion and the inhibited sample stabilizes as it moves closer to it's limit, thus the paradox is accounted for.

The results from the atmospheric corrosion sensor and the QCM show a substantial indication of corrosion within the first 24 hours when exposed to humidified marine type air. This data establishes a correlation between the QCM measurements and the atmospheric corrosion sensor that can be used together for further development in corrosion detection.

CONCLUSION

Testing up to now, supported by other test methods, is showing positive prospects for future development in this area. QCM results have shown that the pre treatment with BTA does indeed inhibit the mass change due to corrosion by approximately 70%. VCI was shown to parallel the results, constant rate of frequency change, to that of BTA in humid air conditions. Based on this, VCI could expect to have similar results for inhibiting copper. The first test indicates that adsorption of BTA can be measured with the QCM only when the presence of oxygen has been kept to a minimum or eliminated. Under these conditions it was shown that an adsorption limit is reached in approximately 4-6 days.

It is difficult at this time to formulate any conclusive models based on these QCM results supporting the bonding structure and stochiometry of BTA or VCI adsorption with copper. The results so far are enlightening in the fact that they do establish the QCM as a viable method for detecting the corrosion of copper and the adsorption effects of a VPI in atmospheric gasses and gives conclusive results showing the difference between a VPI inhibited surface and one that was not.

BACKGROUND INFORMATION USED IN DIRECTING THE FOCUS OF THIS STUDY

Initial testing of VPI's in this study began with short term testing based on adsorption data from liquid studies. Data from these studies used in situ measurements incorporating time frames on the order of seconds to hours. This study, however, found that time frame to be inefficient, the time frame used here is on the order of 5-20 days. Early tests indicated (100,000 s) that the frequency change due to corrosion was linear in the presence of an inhibitor verses a logarithmic frequency change for two defined relative humidifies (RH), 80% and 100% RH. Further testing tried to identify the amount of adsorbent in a dry nitrogen atmosphere, this effort was masked by background noise characteristic of the QCM and oxygen diffusion through the glass chamber used in the experiments. It was also found that flowing a gas, nitrogen, saturated with an inhibitor was not an effective way to measure the frequency change due to the adsorption. A static gas approach where the inhibitor was allowed to vaporize proved to be the most effective in actually detecting a frequency change due to adsorption. The latest testing gives substantial proof of corrosion protection and adsorption detection by frequency change without being influenced by oxygen diffusion on the system.

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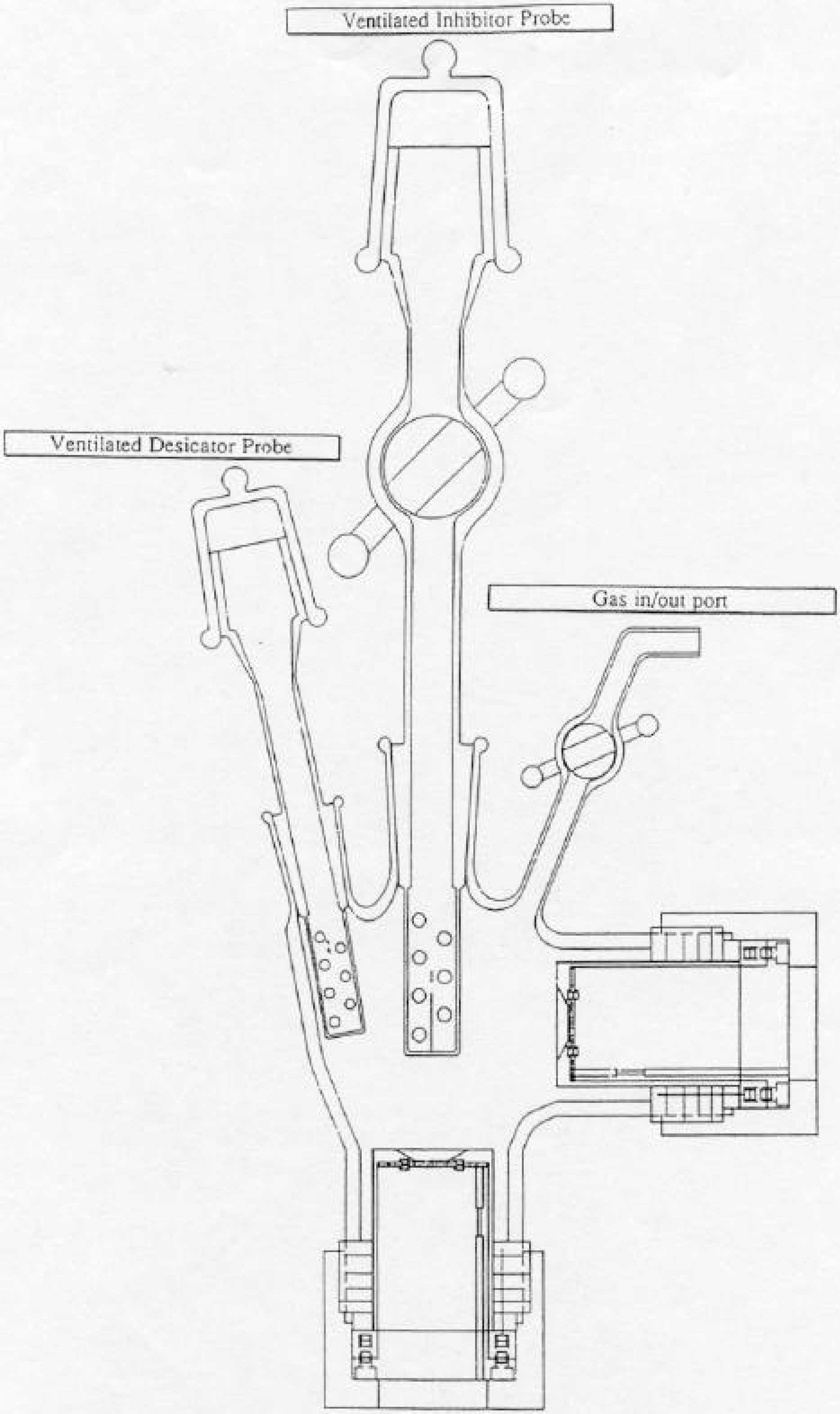
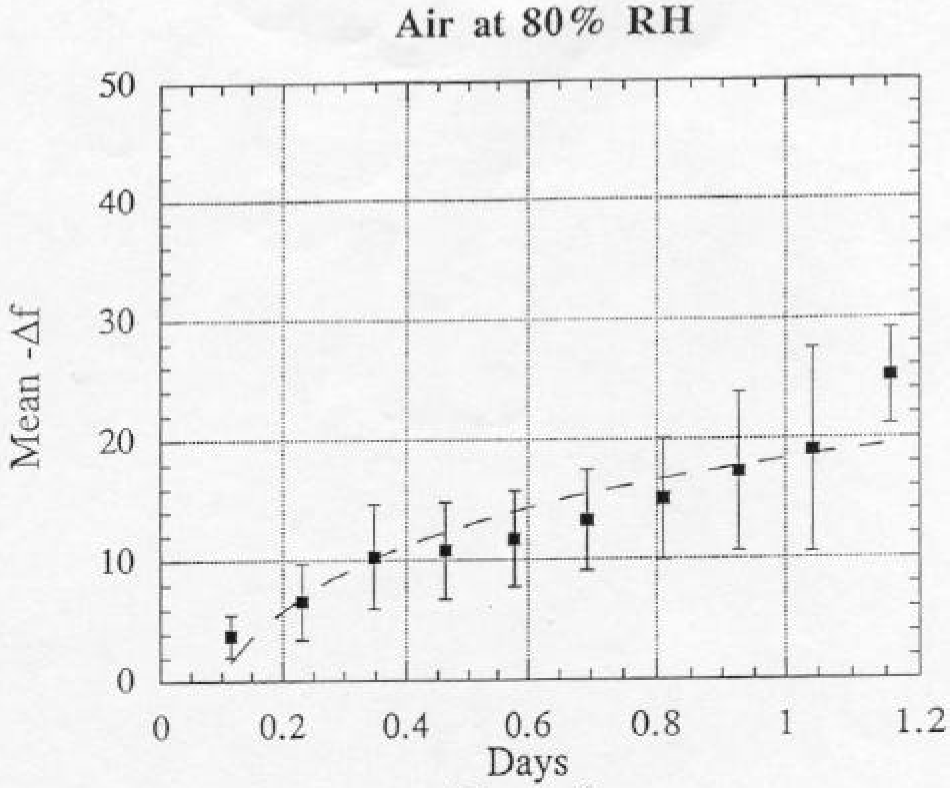
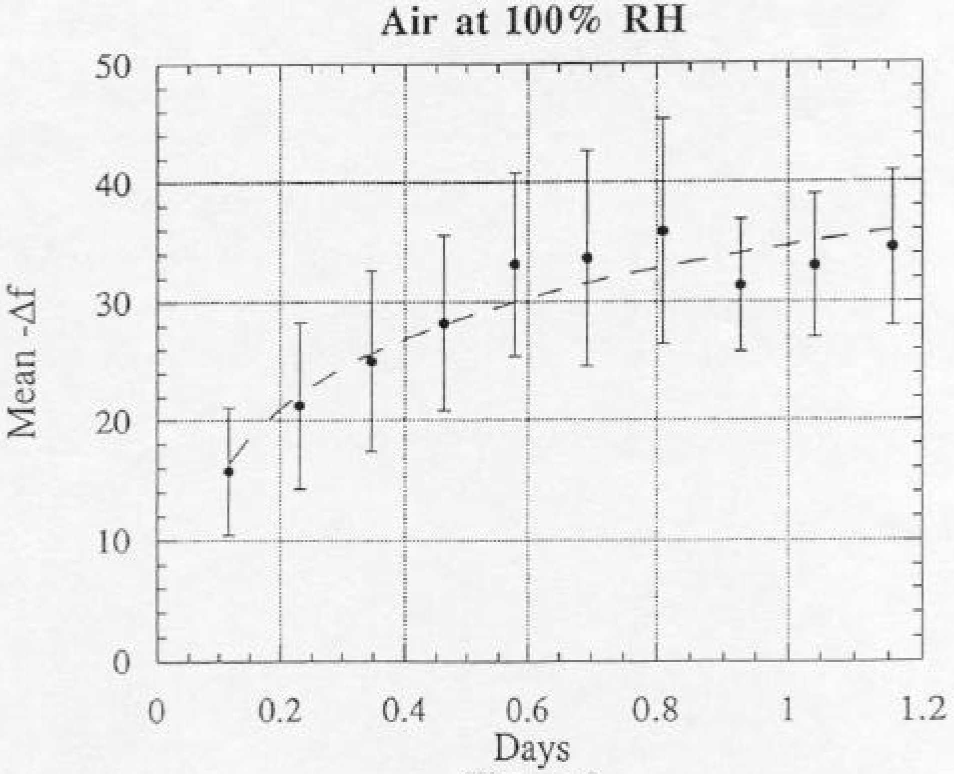


Figure 1 Glass Housing Apparatus for Corrosion Sensors. Used to Monitor the Corrosion of Synthesized Atmospheres



Air at 80% RH

Figure 2



Air at 100% RH

Figure 3

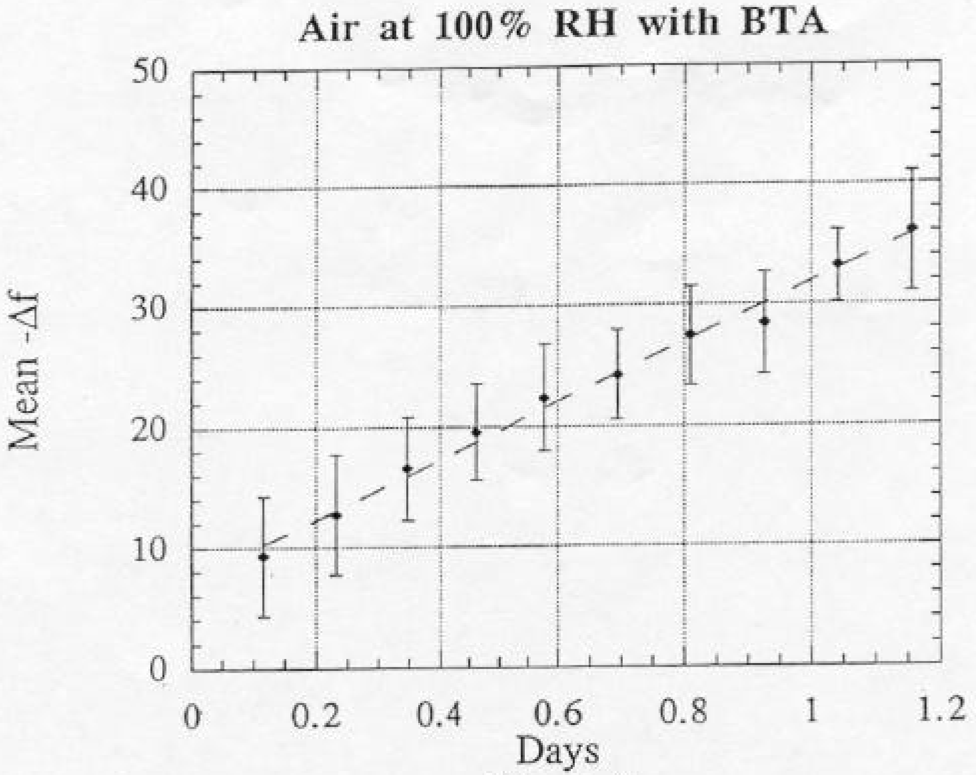


Figure 4

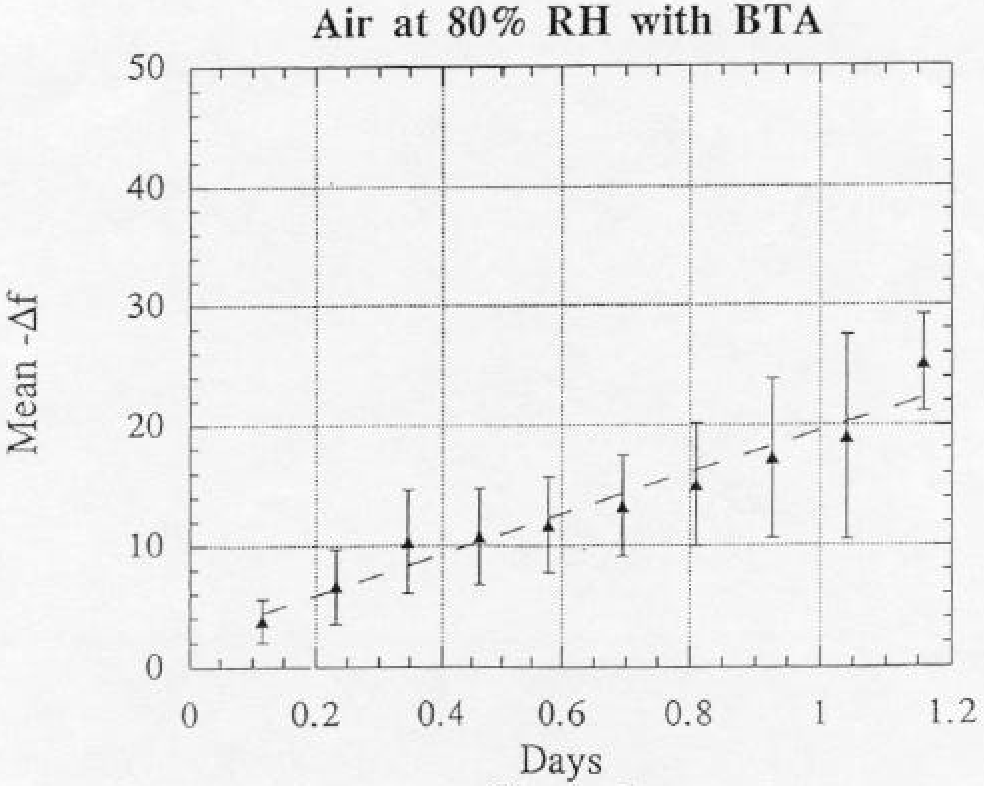


Figure 5

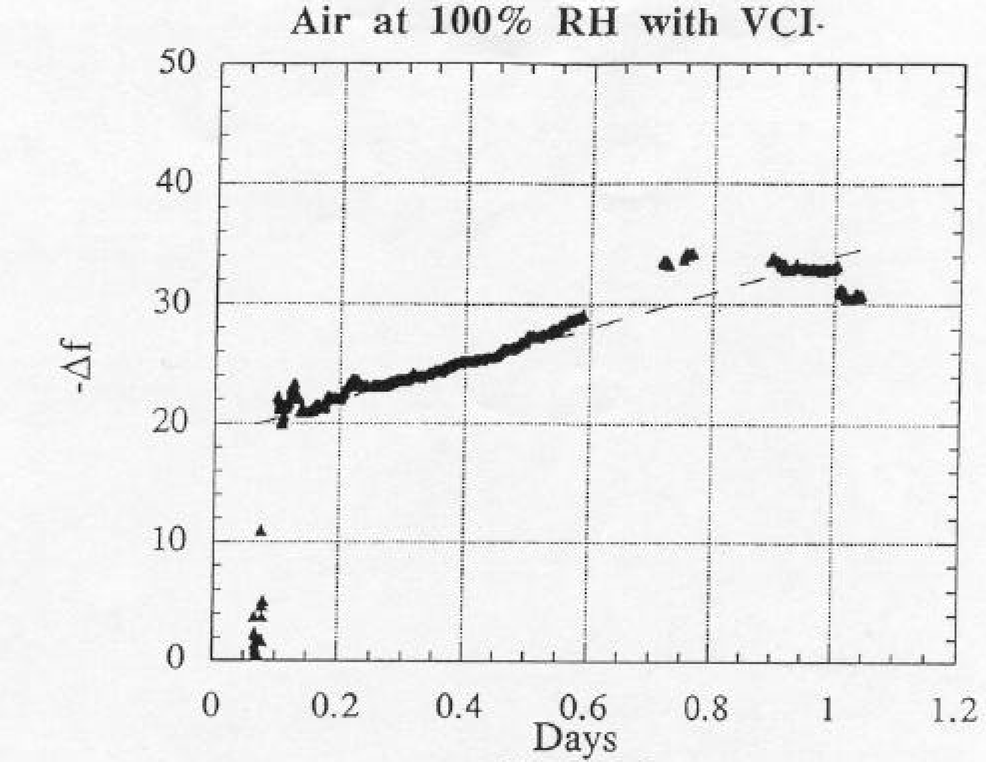


Figure 6

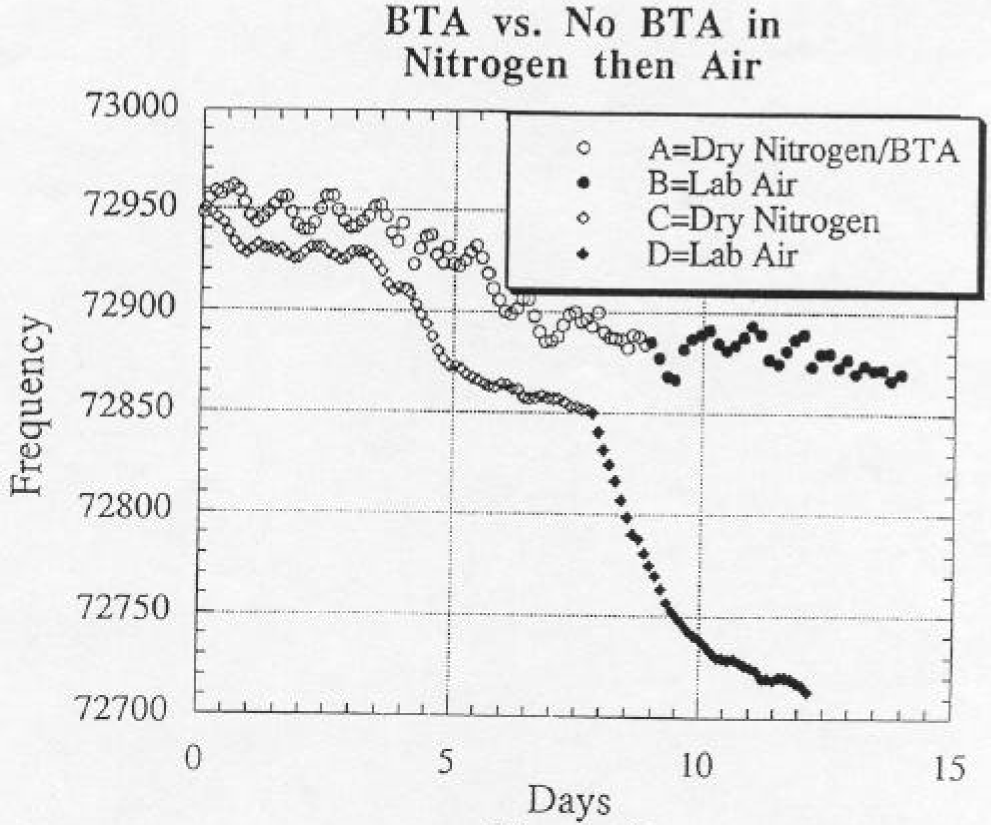


Figure 7

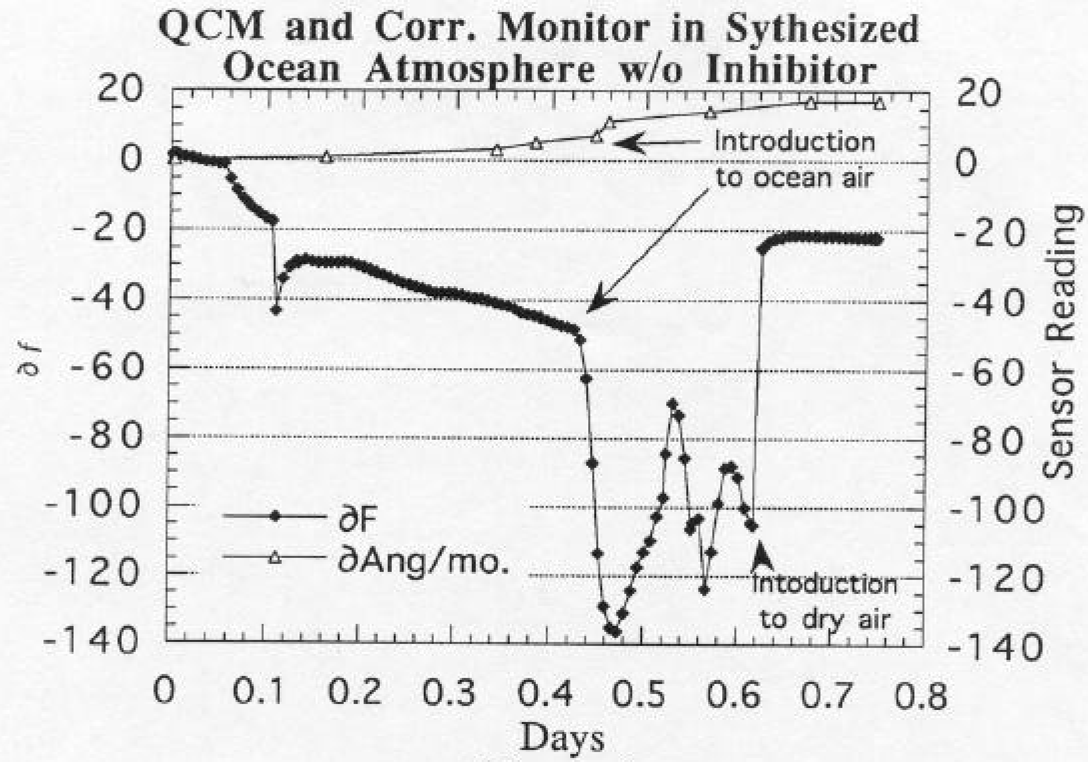

QCM and Corr. Monitor in Sythesized Ocean Atmosphere w/o Inhibitor
∂f
20
0
-20
-40
-60
-80
-100
-120
-140
Sensor Reading
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
Days
∂F
∂Ang/mo.
Introduction to ocean air
Intoduction to dry air

Figure 8