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Electrochemical Corrosion Studies in Low Conductivity Media

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FOREWORD

This final report was submitted by the Jet Propulsion Laboratory, Pasadena CA on completion of JON: 573000WC with the Astronautics Laboratory (AFSC), Edwards AFB CA. AL Project Manager was Maj William C. Hurley.

This report has been reviewed and is approved for release and distribution in accordance with the distribution statement on the cover and on the DD Form 1473.


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<p>Because the reliability and compatibility of spacecraft components is of utmost importance in propulsion systems, there is a need for accurate and, preferably, short-term evaluation techniques. In this study, electrochemical impedance spectroscopy has been used to determine the corrosion rates of metals in liquid hydrazine. The electrochemical information was obtained in a relatively short time (hours) and the corrosion rates thus derived compared favorably with those obtained from the classical, real-time method.</p>			
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TABLE OF CONTENTS

INTRODUCTION 1

BACKGROUND 2

OBJECTIVES 3

 Technical Approach 3

 Electrochemical Impedance Spectroscopy 3

 Polarization Curves with Compensation of the Ohmic Drop 4

 Polarization at Constant Potential with Compensation of the Ohmic Drop 6

EXPERIMENTAL RESULTS 6

ADDITIONAL RESULTS 9

 Workshop 9

 Conductivity Measurement 9

 SS304L in Hydrazine 10

SUMMARY AND CONCLUSIONS 11

RECOMMENDATIONS AND FUTURE RESEARCH 12

ACKNOWLEDGMENT 13

REFERENCES 14

TABLES

1. Preliminary Results for 304L/N₂H₄ System
2. Preliminary Results for SS430/MON-1 System
3. Preliminary Results for 304L/MON-1 System
4. Preliminary Results for A16061/MON-1 System
5. Computer Printout for Tafel Measurements on 304L/N₂H₄
6. Computer Printout for Tafel Measurements on 430/MON-1
7. Conductivity of Different Electrolytes

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FIGURES

1. Bode Plot for 304L/N₂H₄
2. Tafel Plot for 304L/N₂H₄
3. Tafel Plot for 430/MON-1
4. Bode Plot for 304L/MON-1.6
5. Bode Plot for A16061/MON-1.6
6. Bode Plot for KCl (0.01M) Solution
7. Bode Plot for Deionized H₂O
8. Nyquist Plot for Deionized H₂O
9. Bode Plots for 304L as Function of Exposure Time to N₂H₄: (1) one day (2) 5 days (3) 12 days
10. Time Dependence of R_p, C_d, R_u for 304L in N₂H₄
11. Bode Plots for 304L in 10⁻⁴N HCl in Ethanol
12. Effect of Electrode Area on the Values of Uncompensated Resistance
13. Polarization Resistance Measurements for 304L/N₂H₄; Area=0.06 cm²
14. Potentiodynamic Polarization Curves for 304L/N₂H₄: (1) 23 days (2) 60 days

INTRODUCTION

The reliability and compatibility of spacecraft components is of utmost importance to all of NASA missions. As a NASA lab, JPL has been involved for several years in the determination and evaluation of propellant/materials compatibility (Refs. 1a, 1b). These propellants include hydrazine (N_2H_4), monomethylhydrazine (CH_3NHNH_2) and nitrogen tetroxide (N_2O_4). Because of the chemical and physical properties of these materials (air sensitive, toxic, very low conductivity, etc.), only real-time evaluation tests have been possible, causing estimates of reliability to be costly and time consuming. Most propellants and oxidizers react slowly with their containers, leading to slow corrosion which is acceptable for most missions. However, certain minor changes in alloy composition or operating conditions can lead to dangerous consequences as evidenced by a shuttle APU fire. This incident appears to have been caused by stress corrosion induced by ammonia or ammonium hydroxide (NH_4OH) produced as a consequence of hydrazine decomposition. This example underlines the need for a reliable, short term evaluation technique.

Recently, advances in electrochemical theory and instrumentation indicate that short-term, accelerated tests are possible. The idea of using electrochemical techniques to study corrosion phenomena follows from the fact that corrosion phenomena can be explained in terms of electrochemical reactions. A unique advantage of electrochemical techniques is that they can yield kinetic and mechanistic information of processes occurring at the interface between material and solution. The electrochemical information is obtained in a relatively short time and can subsequently be used to predict corrosion rates and compatibility.

The Air Force is evaluating several advanced materials and propellants for use in future spacecraft. A major problem in the evaluation of these components is the lack of an accurate and rapid evaluation of the materials' compatibility. Historically, materials compatibility has been determined by placing material samples into the propellant and observing any reactions over a period of time greater than the required service life. Therefore, when a service life in the tens of years is needed, the normal compatibility determination techniques preclude the use of new materials and/or propellants. For these reasons, the Air Force is looking at ways to avoid this critical materials compatibility obstacle. To that end they asked JPL to develop a process which will provide accurate materials compatibility data within a few days rather than several years.

BACKGROUND

The reliability and compatibility of spacecraft components is of utmost importance to all of NASA's and DoD's missions. JPL has been involved for over twenty years (Refs. 1a, 1b) in the evaluation and determination of propellant/materials compatibility over long term periods. Using conventional techniques, it has been determined that most propellants/oxidizers react slowly with their containers at low corrosion rates which are acceptable for most missions. However, relatively minor changes in alloy composition and/or operation conditions can sometimes lead to dangerous consequences as evidenced by the space shuttle APU fire. The presence of nitrates on shuttle hardware also suggests that nitric acid was formed when metal surfaces were exposed to N_2O_4 in the presence of moisture. The mechanism of this corrosion process and the rates at which the corrosion process proceeds are unknown at present. Progress in this direction has been very slow, since due to the special chemical and physical properties of these materials (very low conductivity, air sensitivity, etc.) only real-time evaluation tests have been possible. This problem makes attempts to obtain estimates of reliability costly and time consuming. Recent advances in electrochemical theory and instrumentation indicate that short term accelerated tests are possible. The idea of using electrochemical techniques to study corrosion phenomena is not new and follows from the fact that corrosion phenomena can be explained in terms of electrochemical reactions. A further unique advantage of electrochemical techniques is that they can yield kinetic and mechanistic information on processes occurring at the interface between electrode and solution.

While electrochemical techniques have been used very successfully in most aqueous media in the evaluation of corrosion mechanisms and reaction kinetics which form the basis for lifetime predictions, great experimental difficulties have been experienced in non-aqueous media of low conductivity. The latter property of most propellants is the reason that very few electrochemical studies of the corrosion behavior of container materials in propellants have been reported. Traditional dc techniques measure mainly the ohmic drop in the test solution which usually masks the polarization of the electrode due to an applied potential. Brown (Ref. 1c) has used electrochemical measurements in a limited potential region for various materials in hydrazine and has shown that the polarization resistance measurements were in good agreement with the corrosion rate data obtained by weight loss and solution analysis for long term tests. Since Brown's work, new electrochemical techniques have been developed to a point where they show great promise for application in low-conductivity, non-aqueous media with the goal to evaluate corrosion kinetics and mechanisms and use this information to predict long term compatibility. A first step has been made at JPL where Lawton, Moran and DiStefano (Ref. 2a) have used ac impedance measurements in a study of the corrosion behavior of stainless steel in hydrazine. Electrochemical impedance spectroscopy (EIS) has been shown by Mansfeld and co-workers to be especially useful in low-conductivity aqueous media (Ref. 3) and in systems with surface films of large resistance such as polymer coatings on steel and aluminum (Refs. 4-6) and anodized Al (Ref. 7). Potentiodynamic polarization with real-time compensation of the ohmic drop has also been shown to produce data in low conductivity media which contains valid information concerning corrosion kinetics and mechanisms (Ref. 3).

OBJECTIVES

The goal of the proposed investigation is to develop EIS and potentiodynamic polarization with real-time compensation of the ohmic drop as accelerated compatibility tests which are based on a thorough understanding of the kinetics and mechanism of the interaction of container surfaces with the propellants. Those studies employing surface analyses techniques could provide information concerning the nature of surface films and their changes with exposure time. The results obtained with the electrochemical techniques are being validated with existing data from JPL's real-time propellant/materials compatibility program. If the project is successful in providing the basis for a lifetime prediction methodology, the newly developed technology will be transferred to DOD for further use in the area of materials/propellants compatibility and other applications of relevance.

Technical Approach

At this time instrumentation exists for electrochemical studies of corrosion phenomena in low conductivity media, where traditional methods have failed or provided unsatisfactory or even misleading results. Electrochemical impedance spectroscopy (EIS) (Refs. 3-9) and recording of polarization curves with continuous compensation of the ohmic drop by the interrupter technique (Ref. 3) has been used to study the interaction of container materials such as stainless steels and titanium alloys with propellants such as hydrazine and N_2O_4 . EIS allows an evaluation of the properties of the metals surface and the reaction rate at a given constant potential, while the interrupter technique can be used to obtain potentiodynamic polarization curves from which kinetic and mechanistic information can be obtained. Since the ohmic drop can be eliminated continuously in these measurements, the polarization curves are not distorted and the sweep speed would be constant. These measurements can be performed for fresh metals and fresh propellants as a function of exposure time, and for metal/propellant combinations which have been stored in ampoules for many years at JPL's Edwards Facility. The latter tests could be very important for practical applications since they present the only possibility to determine instantaneous corrosion rates and changes of corrosion mechanisms after long periods of storage. Such data are not available at present; only average corrosion rates over the entire exposure period can be obtained by solution analysis or other non-electrochemical techniques.

Electrochemical Impedance Spectroscopy

The work of Mansfeld and co-workers (Refs. 4-7) has shown that EIS can be applied successfully to "difficult" systems such as anodized Al and polymer coated steel and Al, where traditional DC techniques fail due to the large ohmic resistance of the surface layers. Similar success was achieved in low conductivity media (Ref. 3). Lawton et. al. and DiStefano, et. al. at JPL have reported some preliminary data obtained with EIS for stainless steel (SS) type 304L in hydrazine (Refs. 2a, 2b, 5). The advantage of EIS is that -- within certain limits -- the low conductivity of the test electrolyte does not affect the accuracy of the measurement, in fact this parameter and its changes are determined in the impedance measurement and can be used for interpretation of the corrosion behavior.

In this effort the Solartron model 1250 Frequency Response Analyzer together with the model 1286 potentiostat (and the PAR Lock-in Amplifier together with the model 273 potentiostat) was used to obtain EIS data as a function of applied potential and time. A frequency range between 60 kHz and 10 MHz was used, which should be sufficient for an analysis of the corrosion behavior. The impedance data was stored on magnetic tape and analyzed using previously discussed models (Refs. 8,9). The parameters of particular interest are the electrode capacitance, which is determined by surface properties (passive film thickness and its dielectric constant) and the electrolyte double layer, and the polarization resistance, which is the dc limit of the impedance and is inversely proportional to the corrosion rate. The electrolyte resistance can be determined from the high-frequency limit of the impedance.

EIS data was collected primarily at the corrosion potential as a function of exposure time and also at selected anodic and cathodic potentials in order to determine the effects of polarization as it could occur due to galvanic coupling to a dissimilar metal. The majority of the experiments were performed in monopropellant grade hydrazine. The effect of temperature could also be studied in a similar way. The materials of interest are SS 304L, Al6061, and Ti-6Al-4V. For these systems compatibility data have been compiled earlier at JPL (Refs. 1a, 1b) by determination of the NH_3/N_2 ratio in the decomposition gas products, surface examination and metals analyses by atomic absorption (AA) or inductively coupled plasma (ICP) spectrometry techniques. EIS data was also obtained in N_2O_4 as a function of water. It was hoped that the formation of HNO_3 , which is possible under these conditions, would lead to changes in the surface properties and corrosion rates which could be determined with EIS, however, the inherent limitations of the instrumentation, due to low conductivity allowed only solvent resistance measurements, but not polarization resistance measurements (which are related to the corrosion rates).

Plans were made to obtain a variety of different metal/environment combinations which had been stored by JPL in ampoules for several years. The evaluation of the EIS data for these systems and comparison with the data for "fresh" systems could reveal the changes due to exposure in terms of properties of surface films and corrosion rates. However, the restrictions of time and resources did not allow for this.

Polarization Curves with Compensation of the Ohmic Drop

At the University of Southern California (USC), a Solartron model 1286 potentiostat which employs the interrupter technique (Ref. 3) was used for the recording of anodic and cathodic polarization curves which are compensated for the ohmic drop in the electrolyte. This technique allows an evaluation of the electrode kinetics which determine the corrosion rate and can provide information concerning formation and reduction of passive films. The approach is especially promising for hydrazine which has sufficient conductivity for the proposed test and was also tried for N_2O_4 although over a much narrower potential range. From extrapolation of the Tafel region in the vicinity of the corrosion potential E_{corr} the corrosion current density (c.d.) i_{corr} and the anodic (b_a) and cathodic (b_c) Tafel slopes were obtained which contain mechanistic information. Corrosion rates may be calculated for the various experimental conditions using Faraday's

law. For systems which show passivation the critical potential and c.d. for passivation and the passive c.d. were determined where propellant properties allowed. The anodic polarization curves can also provide information concerning the occurrence of localized corrosion.

A Tafel Plot is obtained by polarizing a metal specimen about 300 mV anodically (positive-going potential) and then cathodically (negative-going potential) from the corrosion potential, E_{corr} . The potential can be either scanned or stepped. The resulting current is then plotted on a logarithmic scale. The corrosion current, i_{corr} , is obtained from a Tafel Plot by extrapolating the linear portion (the Tafel region) of the curve to E_{corr} . The Tafel constants b_a (anodic Tafel constant) and b_c (cathodic Tafel constant) are the slopes of the linear region of a plot of voltage, $E - E_{\text{corr}}$, versus the logarithm of current, $\text{Log } [i]$, for the anodic and cathodic regions respectively. These Tafel constants are used to calculate a value of the proportionality constant, B (see equation 3); a typical value of B is 100mV/decade.

While recording the polarization curves over extended potential regions provides mechanistic information, polarization in the vicinity of E_{corr} provides a measure of the instantaneous corrosion rate. This so-called polarization resistance technique (Ref. 10) provides a valuable tool for routine measurements of corrosion rates of metal/propellant systems. The tests allowed an assessment of the extent to which this technique can be used for routine investigations in non-aqueous media. The corrosion c.d. i_{corr} is calculated as:

$$i_{\text{corr}} = B/R_p \quad (1)$$

from the measured polarization resistance R_p , which is the slope of the polarization curve at E_{corr} :

$$R_p = (\delta \Delta E / \delta i)_{\Delta E=0} \quad (2)$$

and the Tafel slopes:

$$B = b_a b_c / 2.3(b_a + b_c). \quad (3)$$

A computer program has been developed and tested earlier which allows simultaneous determination of R_p and B from measurements within a polarization range $\Delta E = \pm 30$ mV (Ref. 11).

The results obtained with the electrochemical techniques, both at USC and JPL were validated by comparison with existing data from JPL's real-time propellant/materials compatibility program. Wherever the program proves to be successful in providing the basis for a life-time prediction methodology, the newly developed technology can be transferred to interested laboratories where appropriate equipment for impedance studies already exists. It can then be used not only for studies in the areas of materials/propellants compatibility, but also for other applications of relevance to NASA and DoD, such as the evaluation of fuel cell materials compatibility and state of health of spacecraft batteries as well as the determination of interfacial properties of solid state devices.

Polarization at Constant Potential with Compensation of the Ohmic Drop

Polarization at constant potential with compensation for the ohmic drop can also provide an answer to the question whether the corrosion mechanism is of electrochemical or chemical nature (Ref. 12). In the first case, dissolution rates should have a dependence on applied potential which must be in agreement with the observed polarization curve. In the second case dissolution rates should be independent of applied potential. The observed potential dependence of the current would then be solely due to reduction and oxidation of the electrolyte, but not due to metal dissolution. An evaluation of the mechanism of corrosion for these non-aqueous media is of extreme importance, since knowledge of this mechanism will guide the selection of techniques for corrosion protection and materials selection.

Samples of appropriate alloys can be polarized at potentials which are about 100 mV anodic and cathodic to E_{corr} and at E_{corr} for time periods which produce an amount of dissolved metal which is sufficient for analysis by either the atomic absorption or inductively coupled plasma technique. This time can be calculated based on the measurements of i_{corr} . If the electrochemical mechanism is valid, as in the majority of aqueous media, then the corrosion rate should be the highest at the anodic potential and the lowest at the cathodic potential. For the first case the dissolution rate should correspond to the integrated anodic current provided that no additional oxidation reaction occurs. For a chemical mechanism, dissolution rates should be independent of applied potential. Since the time dependence of the current flow at each potential is recorded, it should be possible to obtain qualitative information concerning the changes of the electrode kinetics with time which is important for the prediction of long term compatibility.

EXPERIMENTAL RESULTS

The major activities in the initial part of this effort mainly involved the sub-tasks of Phase I: (1) design and construction of electrochemical cells for use with hydrazine and nitrogen tetroxide propellants; (2) testing of the cells, both integrity and component propellant compatibility, as well as suitability for measurements with available DC and AC (EIS) electronic instrumentation; (3) preliminary experimental measurement of corrosion rates for two of the three chosen alloys (i.e., CRES 304L and Al-6061, but not yet Ti-6Al-4V); (4) preliminary progress in validation of the electrochemical techniques, as evidenced by the encouraging agreement of electrochemical corrosion rates with those calculated from data obtained by standard methods which involve relatively long-term storage, and analysis for the component metals which have undergone dissolution into the propellant.

Some lesser activity has taken place with respect to the sub-tasks of Phase II. A Phase II Implementation Plan was prepared, after consultation and concurrence as to its contents. The intent of this implementation plan was to determine the limitations of the electrochemical method, and establish baseline criteria for very-low conductivity propellant measurements. To this end, JPL planned to employ deprotonated ("dry") nitrogen tetroxide, with which we have done a fair amount of pioneering work, as a simulant for OF_2 and N_2F_4 advanced propellants (and concomitantly make measurements, if possible, to illustrate

the dependance of the corrosion rate on the conductivity and concentration of protonated species in N_2O_4).

For the Phase II activity, a literature survey was initiated, design of computer models and electronic "black-box" equivalent circuits for testing instrumental limitations was begun, and conceptual models of two possible simplified cells for possible corrosion/conductivity measurements in deprotonated N_2O_4 (and, hopefully, OF_2) have been developed.

Although a numerical value has not yet been found, an upper limit of 5×10^{10} ohm-cm for the specific conductance of OF_2 , at $-195^\circ C$, has been determined, and is reported by S.M. Toy (Ref. 14). Interestingly, it would appear that the same electronics that are used for electrochemical corrosion measurements might be employed for conductivity measurements, when used in conjunction with a cell containing two platinum or stainless steel electrodes of appropriate geometry (i.e., low cell constant value) which is simply calibrated with a standard solution of known specific conductivity.

A very important item of progress was the research contract with Professor Florian Mansfeld, Materials Science Department, USC. Prof. Mansfeld is the preeminent expert in the field of Electrochemical Impedance Spectroscopy (AC Impedance) corrosion measurements, and the collaboration with him and his university research group greatly enhanced our effort. The resultant expansion in capability, together with a parallel investigative effort, greatly increased the scientific productivity in this work. After a few trials with a non-hazardous substitute, such as alcohol, Prof. Mansfeld's students tested the hydrazine/alloy systems. At this point we were planning to be ready to break up the nitrogen tetroxide (normal and dry simulant) work in such a way that our two laboratories could optimize the chances for a successful outcome of a difficult set of experimental goals.

The first three models of electrochemical cells (employing platinum as reference and counter electrodes) for corrosion studies with hydrazine and nitrogen tetroxide propellants have been used successfully for experimental measurements; however, these have been of limited duration (of the order of a few days in most cases) due primarily to problems with leaking seals. This problem was addressed by procuring elastomeric Kalrez O-rings for use with nitrogen tetroxide, and ethylene-propylene O-rings for use with hydrazine. Cells should minimize the number of very small seals, which are most prone to failure. One positive development has been that whenever a design change has given moderate improvement for oxidizer measurements, it has normally resulted in a greater degree of improvement for the higher conductivity hydrazine systems.

Some of the early experimental results have been presented at appropriate scientific meetings. Early collaborative hydrazine work with CRES 304L (together with Hastelloy-B alloy), supported in part by NASA, was carried out in one of the first cells used for nitrogen tetroxide trial runs; these hydrazine results were presented (Ref. 1b) at the 1986 Electrochemical Society Meeting. In addition to this, results of early experiments with stainless steels in hydrazine and nitrogen tetroxide were presented at the 1986 JANNAF Propulsion Meeting (Ref. 2c). Some of the more recent results were given at the Liquid Propellants Panel Meeting of the 1986 JANNAF Propellant Characterization Sub-committee Meeting in Monterey, California (Ref. 2d), and also in 1987 in Laurel, MD (Ref. 2e).

A summary (together with old data on CRES 430/MON-1, required for Tafel slope approximation) is contained in Tables 1 through 4. The systems studied were:

1. CRES 304L with pure N_2H_4 (no aniline; approximately 30 ppm CO_2 .)
2. CRES 430 with MON-1 spiked with water (0.19% H_2O), giving a conductivity high enough to permit some DC measurements required for determination of approximate Tafel slope values, as well as the AC measurements. This was our earliest MON/CRES concept trial experiment.
3. CRES 304L with the "MON-1" oxidizer provided from WSTF as a sample for the 1986 JANNAF Round Robin analysis; this should probably be the best characterized oxidizer possible to use for electrochemical measurements.
4. Al-6061 with the same "MON-1" (actually NO=1.6%) JANNAF Round Robin oxidizer.

In all cases, the electrochemical values for corrosion rates agreed to better than an order-of-magnitude with the (not exactly comparable) results from standard metal dissolution analysis, after a much longer exposure time. These results are very encouraging, but must be treated as preliminary results subject to reinterpretation as the result of future experimentation and insight gained into the basic processes involved. New cells, with even closer proximity of the platinum reference and counter electrodes are obviously required for nitrogen tetroxide measurements. On the other hand, it should be noted that, for $N_2H_4/304L$, both DC and AC(EIS) measurements were possible, and very close agreement was found for the corrosion rates obtained from corrosion currents as calculated from Tafel plot (DC) and polarization resistance (R_p from AC/EIS) experimental data.

Even if improved results become possible, it is evident that the corrosion rates must be measured as a function of time (for days to weeks) in order to ascertain how best to compare the nearly instantaneous (real-time) electrochemical values to past long-term storage values; likewise a passivation pre-treatment may need to be utilized, rather than simply pre-polishing plus a DI water cleaning.

The raw experimental data, on which the preliminary results in Tables I-IV are based, are presented in the additional Tables 5 to 6 and Figures 1 to 5.

Note that the Bode Plot ($\log |Z|$ vs $\log f$) presentation of the electrochemical impedance spectroscopy (EIS) data has been used here. Except for some hydrazine data, the data are presently too scattered to use a Nyquist Complex Plane Plot (Z_{imag} vs Z_{real}) presentation and fit parameters to a resultant circular function.

In the Bode plot, the logarithm of the absolute value of the impedance, $\log |Z|$, is plotted versus the logarithm of the frequency, $\log f$. For the simplest (equivalent circuit) case, such a plot will give a high frequency limit or asymptotic value corresponding to the solution resistance, $\log [R_0]$, and a low

frequency limit or asymptotic value corresponding to the sum of the polarization resistance and the solution resistance, $\log [R_p + R_Q]$.

In the Nyquist plot (also known as a Cole-Cole plot or a complex impedance plane diagram) the imaginary component of impedance (Z_{imag}) is plotted versus the real component of impedance (Z_{real}) at each excitation frequency; the frequency dependence is thus implicit for this plot rather than explicit as for the Bode plot. For the simplest (equivalent circuit) case, a Nyquist plot results in a semi-circle which intersects the real axis at values of R_Q (at high frequency) and $R_Q + R_p$ (at low frequency).

ADDITIONAL RESULTS

Workshop

A workshop on Electrochemical Corrosion Measurements in Low Conductivity Propellants was held at JPL in January 1987 during a visit by Drs. Norman Logan and Michael Dove from the Chemistry Department faculty of the University of Nottingham in the United Kingdom. Participants were from the University of Nottingham, AFAL, JPL, and the University of Southern California, with attendees from additional organizations (e.g., Aerospace Corporation). The Nottingham group reported some early Electrochemical Impedance Spectroscopy (EIS) measurements on nitrogen tetroxide containing relatively high water concentrations (>0.2%), thus also having relatively high conductivities. JPL preliminary results were also presented.

Conductivity Measurement

The trial conductivity runs have been carried out using the EIS electronics. A standard conductivity cell with platinized platinum electrodes and a cell constant ($\theta = l/A$) equal to 0.100 cm^{-1} was employed. The two liquids measured were a standard salt solution (0.7453 gKCl/kg solution) of known specific conductance, and a sample of deionized water. The EIS measurements were made over the frequency range of 6 Hz to 100 kHz, while comparison measurements with a standard conductivity bridge were made at 60 Hz and 1 kHz (the only frequencies available).

Excellent agreement was found between the measured specific conductance ($1330 \mu\text{S/cm}$) and the tabulated value ($1336.6 \mu\text{S/cm}$) at 22°C for the standard (0.01 molal) KCl solution. As is expected, relatively high frequency data is required to adequately express the specific conductance of a solution made up of ions of high equivalent conductance, which is the case here. A Bode plot ($\log |Z|$ vs $\log f$) representation of the data for KCl is shown in Figure 6.

Good agreement was also found for the deionized water. The EIS measured value for the specific conductance ($1.19 \mu\text{S/cm}$) was approximately 20% lower than that measured with the conductivity bridge at 60 Hz (at a somewhat later time during which additional CO_2 could have been absorbed from the air). A Bode plot and a Nyquist plot (Z_{imag} vs Z_{real}) for this water data are shown, respectively, in Figures 7 and 8.

It thus appears that the EIS instrumentation may be used to determine the conductivity of low conductivity propellants. For example, a conductivity cell,

such as that used at JSC/WSTF for NTO water analysis, could obviously be used for the MIL-SPEC and "dry" MON-1 simulant. A variant of this type of cell might possibly be used for the measurement of the conductivity of OF_2 . By replacing the stainless steel center rod with one of platinum in a small Hoke cylinder (i.e., the WSTF design) with an optimal geometry, it might be possible to make EIS corrosion rate measurements of the cylinder material (e.g., stainless steel, aluminum).

"Dry" (deprotonated) MON-1 has been obtained from column treatment utilizing activated LZ-Y82 zeolite. This nitrogen tetroxide is extremely pure, with a water level of 0.004 percent (from NMR analysis) and an iron level of less than 0.03 parts per million (from AAS analysis). This propellant, originally intended mainly for use as a simulant, can be used to make measurements bearing on instrumental limitations as well as to provide baseline data for the effect on corrosion rates of contaminants such as water (actually HNO_3 , HNO_2 , and H_2O).

SS304L in Hydrazine

For SS304L in deaerated hydrazine, EIS measurements have been carried out for a fifteen-day exposure period. Typical impedance spectra are plotted in Fig. 9, where curve 1, 2 and 3 are the spectra measured during the first, fifth and twelfth day, respectively. One time constant is observed for all the impedance spectra between 65 KHz and 10^3 Hz. The impedance data were analyzed by the integration method (Fig. 7) and a new fitting method (Fig. 8). The resulting values of R_u , R_p and C_d are plotted in Fig. 10. Both R_p and C_d reached relatively constant values after eight days' immersion in hydrazine. Small gas bubbles accumulated on the working electrode during these measurements which were most likely due to the decomposition of hydrazine on the electrode surface. The increase of R_u -values with time during the first four days was due to gas bubble accumulation on the electrode surface. After removing the bubbles, R_u -values decreased with exposure time. After 10 days' immersion, the cell was rearranged due to leakage to air through the reference electrode junction. This may have influenced the consistency of the EIS-data. The slope of the spectra in the capacitive region was about -0.7 similar to SS430 in 10^{-4} N ethanolic HCl in Figs. 11 and 12. The mechanisms and the interface model which explain such behavior need further investigation.

Polarization resistance measurements and potentiodynamic polarization curves have been measured for two months. The experimental results are shown in Fig. 13 and Fig. 14. In Fig. 13, curve 1 was recorded without compensation after 15 days' immersion and curve 2 was recorded with compensation after two months' immersion. Since the ohmic drop was smaller than 0.5 mV due to the small cell current resulting from very low corrosion rates, the measurement for curve 1 was performed without the compensation of the ohmic drop. After two months' immersion, the cell current increased and the ohmic drop (about 2 mV) became more significant. Therefore, the measurement had to be carried out with compensation of the ohmic drop by the interrupter technique. The experimental results showed that R_p -values were 120 Kohm-cm² and 30 Kohm-cm², respectively. Since the cell current may contain contributions from the decomposition of hydrazine on the electrode, the dissolution of the SS304, or both, the R_p -values obtained from EIS- and R_p -measurements are considered as reaction resistance and the corresponding corrosion currents are considered as reaction currents. It is obvious that the

reaction current increases with immersion time. Similar results were observed for the potentiodynamic polarization curves as shown in Fig. 14. Curve 1 was recorded after 23 days' of immersion without compensation and curve 2 was recorded with the compensation of the ohmic drop by the interrupter technique after two months' immersion. The interrupter parameters were off-time 0.03 msec, On:Off ratio = 9 and bandwidth type J. Curve 2 was plotted as ΔE versus $\log I$. Reaction current densities were determined by Tafel extrapolation as $0.2 \mu\text{A}/\text{cm}^2$ and $8 \mu\text{A}/\text{cm}^2$, respectively. An active-passive transition and a cathodic limiting current were observed in these curves. The cathodic limiting current densities of $0.32 \text{ mA}/\text{cm}^2$ and $0.64 \text{ mA}/\text{cm}^2$, respectively, are fairly large compared to the values for dilute acid solutions or even the limiting current for the reduction of oxygen in neutral media. The increase of I_{lim} and the increase of the anodic reaction rates with time suggest significant changes in the system which need further examination.

SUMMARY AND CONCLUSIONS

1. The results of this study have shown that it is possible to perform electrochemical studies in low conductivity solutions such as pure hydrazine with existing instrumentation provided a number of experimental considerations are followed.
2. A thorough evaluation of the interrupter technique for continuous elimination of the uncompensated resistance R_u with the Solartron potentiostat model 1286 has shown that the experimental parameters such as interrupter frequency and potentiostat bandwidth have to be carefully selected for each corrosion system. Recording of impedance spectra provides information concerning the frequency dependence of the corrosion cell which can be used to select these parameters.
3. An important finding of this study is the need for the correct choice of the reference electrode. Only electrodes such as the Ag/AgCl electrode or a Pt or Au wire can be used with the interrupter technique.
4. Cell design plays a very important role in electrochemical studies of the corrosion behavior in low conductivity media. This aspect could not be studied in sufficient detail in this study. However, it was found that it is advantageous to use large-size working electrodes in order to lower the experimental values of the polarization resistance and R_u and to increase the capacitance. Since the use of larger electrodes lowers the maximum available current density, the choice of the electrode size will have to depend on what kind of experiment the investigator wants to perform.
5. Only very few tests have been performed with the PAR model 276 potentiostat. Since the interrupter time is fixed in this instrument, it would be difficult to take advantage of some of the possibilities to optimize the interrupter measurements which have been found in the studies with the Solartron instrument.
6. The positive feedback technique has also been evaluated for the Solartron model 1286 and the PAR 173 potentiostat. The design of the model 1286 allows almost 100% compensation provided the proper adjustments are made

on the instrument. For the PAR model 173, less than 100% compensation has to be chosen since the instrument will oscillate at 100% compensation. The residual ohmic drop can be eliminated by numerical methods after the test. The main problem with the positive feedback technique is that a constant compensation resistance has to be used which gives erroneous results or causes oscillations of the potentiostat when R_u changes during the experiment. This will occur most likely in the recording of anodic polarization curves.

7. The interrupter technique has been applied to model systems: steel or stainless steel in ethanolic HCl in which the conductivity and corrosivity can be varied by varying the HCl concentration. It was found that a cathodic limiting current and a passive region which was limited by the pitting potential could only be observed when the ohmic drop was completely eliminated. The polarization curves for SS304L in hydrazine showed a cathodic limiting current which increased with exposure time and an active-passive transition in the anodic polarization curve. Tafel extrapolation resulted in a reaction current density which reached several $\mu\text{a}/\text{cm}^2$ after a few days of exposure. However, it is not clear from these data whether this value is due to corrosion of the stainless steel, decomposition of the hydrazine, or both.

RECOMMENDATIONS AND FUTURE RESEARCH

1. A thorough analysis of the details of proper cell design must be conducted before the electrochemical studies can be extended to lower conductivities such as those for N_2O_4 . The geometry and relative size of the working, counter and reference electrodes need to be optimized. Since the currents in N_2O_4 probably will be very small, approaches for the reduction of noise problems have to be investigated.
2. The use of the interrupter technique in the PAR model 273 potentiostat needs to be evaluated. Since the design concept of this instrument, which is widely used in the corrosion community, is different from that of the Solartron model 1286, which has been used in the present study, the evaluation of the optimum experimental parameters for studies in low conductivity media has to be repeated.
3. As the conductivity of the test solution becomes lower and lower, the performance characteristics of the potentiostats available commercially at present might reach their limit. Suggestions for improvements in the design of potentiostats must be made to the manufacturers.
4. The impedance spectra obtained for stainless steel in hydrazine suggest that the very simple model of a polarization resistance in parallel with a double layer capacitance does not apply in this case. A combination of electrochemical impedance spectroscopy and polarization curves needs to be used to establish a model for the electrochemical behavior of stainless steel, aluminum alloys and titanium in hydrazine. The question whether the observed polarization behavior is due to metal dissolution, hydrazine decomposition, or both needs to be resolved.

5. Once the electrochemical behavior of different container materials in N_2H_4 is well understood, it should be possible to tackle the same question for N_2O , provided that the existing instrumentation can be used.

Acknowledgment

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TABLE 1. Preliminary Results for 304L/N₂H₄ System
(T = 25° Celsius; A = 0.06 cm²; pretest exposure time = 7 hours)

Quantity	Approximate Value	Units	Comments
Experimental			
b _a (anodic Tafel slope)	191.83	millivolts	
b _c (cathodic Tafel slope)	181.64	millivolts	
B = b _a b _c / 2.303 (b _a + b _c)	40.512	millivolts	
R _p (polarization resistance)	6.95 x 10 ⁴	ohm - cm ²	
i _{corr} = B/R _p	5.83 x 10 ⁻⁷	amperes/cm ²	
Derived			
dmv/Adt = iM/zF	1.69 x 10 ⁻¹⁰	gram/cm ² -sec	for Fe ⁺²
dmv/Adt = iM/zF	1.46 x 10 ⁻⁵	gram/cm ² -day	
dmv/Adt = iM/zF (T=25°C)	9.40 x 10 ⁻⁵	gram/in ² -day	AC/EIS
dmv/Adt = iM/zF (T=25°C)	8.06 x 10 ⁻⁵	gram/in ² -day	DC; Tafel
dmv/Adt = iM/zF (T=43°C)	=1.0 x 10 ⁻⁵	gram/in ² -day	JPL/EF (15 day)

TABLE 2. Preliminary Results for SS430/MON-1 System
 (T = 0° Celsius; A = 5.51 cm²; pretest exposure time = 4 days)

Quantity	Approximate Value	Units	Comments
Experimental			
b_a (anodic Tafel slope)	347.93	millivolts	
b_c (cathodic Tafel slope)	260.54	millivolts	
$B = b_a b_c / 2.303 (b_a + b_c)$	64.689	millivolts	
R_p (polarization resistance)	3.8×10^7	ohm - cm ²	
$i_{corr} = B/R_p$	3.1×10^{-10}	amperes/cm ²	
Derived			
$dmvAdt = iM/zF$	6.0×10^{-14}	gram/cm ² -sec	for Fe ⁺³
$dmvAdt = iM/zF$	5.2×10^{-9}	gram/cm ² -sec	
$dmvAdt = iM/zF (T=0^\circ C)$	3.3×10^{-8}	gram/cm ² -day	AC/EIS
$dmvAdt = iM/zF (T=25^\circ C)$	1.1×10^{-7}	gram/in ² -day	Rel. CR=3.35
$dmvAdt = iM/zF (T=25^\circ C)$	$=1 \times 10^{-7}$	gram/in ² -day	WSTF

TABLE 3. Preliminary Results for 304L/MON-1 System
 (T = 0° Celsius; A = 3.48 cm²; pretest exposure time ≤7 hours)

Quantity	Approximate Value	Units	Comments
Experimental			
b_a (anodic Tafel slope)	(347.93)	millivolts	
b_c (cathodic Tafel slope)	(260.54)	millivolts	
$B = b_a b_c / 2.303 (b_a + b_c)$	(64.689)	millivolts	
R_p (polarization resistance)	1.6×10^9	ohm - cm ²	
$i_{corr} = B/R_p$	4.0×10^{-11}	amperes/cm ²	
Derived			
$dm/Adt = iM/zF$	7.7×10^{-15}	gram/cm ² -sec	for Fe ⁺²
$dm/Adt = iM/zF$	6.6×10^{-10}	gram/cm ² -day	
$dm/Adt = iM/zF$ (T=0°C)	4.3×10^{-9}	gram/in ² -day	AC/EIS
$dm/Adt = iM/zF$ (T=25°C)	1.4×10^{-8}	gram/in ² -day	Rel. CR=3.35
$dm/Adt = iM/zF$ (T=43°C)	$\approx 1 \times 10^{-7}$	gram/in ² -day	WSTF

TABLE 4. Preliminary Results for Al6061/MON-1 System
(T = 0° Celsius; A = 0.06 cm²; pretest exposure time ≤7 hours)

Quantity	Approximate Value	Units	Comments
Experimental			
b_a (anodic Tafel slope)	(347.93)	millivolts	Analogy; CRES430
b_c (cathodic Tafel slope)	(260.54)	millivolts	Analogy; CRES430
$B = b_a b_c / 2.303 (b_a + b_c)$	(64.689)	millivolts	Analogy; CRES430
R_p (polarization resistance)	9.5×10^7	ohm - cm ²	
$i_{corr} = B/R_p$	6.8×10^{-10}	amperes/cm ²	
Derived			
$dm/Adt = iM/zF$	6.4×10^{-14}	gram/cm ² -sec	for Al ⁺³
$dm/Adt = iM/zF$	5.5×10^{-9}	gram/cm ² -day	
$dm/Adt = iM/zF$ (T=0°C)	3.6×10^{-8}	gram/in ² -day	AC/EIS
$dm/Adt = iM/zF$ (T=25°C)	1.4×10^{-7}	gram/in ² -day	Assume T depend.
$dm/Adt = iM/zF$ (T=43°C)	$>1 \times 10^{-7}$	gram/in ² -day	JPL/EF (long-term)

TABLE 5. Computer Printout for Tafel Measurements on 304L/N₂H₄

RUN PARAMETERS

TECHNIQUE	TAFEL
ORIGINAL NAME	N2H4/3040
INITIAL E (MV)	-250 VS E
FINAL E (MV)	250 VS E
SCAN RATE (MV/S)	.2
CONDITION E (MV)	PASS
CONDITION T (S)	PASS
INIT DELAY (MV/S OR S)	PASS

SAMPLE PARAMETERS

AREA (CMS ²)	.06
EQ WT (GM)	27.9
DENSITY (GM/CM ³)	7.86
CATHODIC TAFEL (MV)	PASS
ANODIC TAFEL (MV)	PASS

DATA SCALE

ECORR	-219
MV/PT	2
DATA MAX	.404
DATA MIN	-1
ABS MIN	0
ABS MAX	1

RESULTS

E(I-0) (MV)	-222.44
CATHODIC TAFEL (MV)	181.64
ANODIC TAFEL (MV)	191.83
I-CORR (UA/CM ²)	.5
CORR RATE (MPY)	.25
E(I-0) (MV)	
POL RESIST. (K-OHMS)	
I-CORR (UA/CM ²)	
CORR RATE (MPY)	

LEGEND

N2H4/304 PT REF STIRRING

TABLE 6. Computer Printout for Tafel Measurement on 430/MON-1

RUN PARAMETERS

TECHNIQUE	TAFEL
ORIGINAL NAME	NTO
INITIAL E (MV)	-100 VS E
FINAL E (MV)	100 VS E
SCAN RATE (MV/S)	.2
CONDITION E (MV)	PASS
CONDITION T (S)	PASS
INIT DELAY (MV/S OR S)	PASS

SAMPLE PARAMETERS

AREA (CMS ²)	1
EQ WT (GM)	PASS
DENSITY (GM/CM ³)	PASS
CATHODIC TAFEL (IV)	PASS
ANODIC TAFEL (MV)	PASS

DATA SCALE

ECORR	-5
MV/PT	1
DATA MAX	9E-03
DATA MIN	-8E-03
ABS MIN	0
ABS MAX	9E-03

RESULTS

E(I-0) (MV)	-5.94
CATHODIC TAFEL (MV)	260.54
ANODIC TAFEL (MV)	347.93
I-CORR (UA/CM ²)	0
CORR RATE (MPY)	UNKNOWN
E (I-0) (MV)	
POL RESIST. (K-OHMS)	
I-CORR (UA/CM ²)	
CORR RATE (MPY)	

TABLE 7. Conductivities of Different Electrolytes

Electrolyte	Conductivity (mho/cm)	Resistivity (ohm-cm)
Pure Ethanol	8.5×10^{-7}	1.18×10^6
0.0001 N HCl/EtOH	5.69×10^{-6}	1.76×10^5
0.001 N HCl/EtOH	5.69×10^{-5}	1.76×10^4
0.01 N HCl/EtOH	4.69×10^{-4}	2.13×10^3
0.1 N HCl/EtOH	2.50×10^{-3}	4.00×10^2
1.0 N KCl (water)	1.31×10^{-1}	7.63×10^0
0.01 N KCl (water)	1.34×10^{-3}	7.48×10^2
Deionized Water	$\approx 1.0 \times 10^{-6}$	$\approx 1.0 \times 10^6$
Hydrazine (99%)	6.0×10^{-7}	1.80×10^6

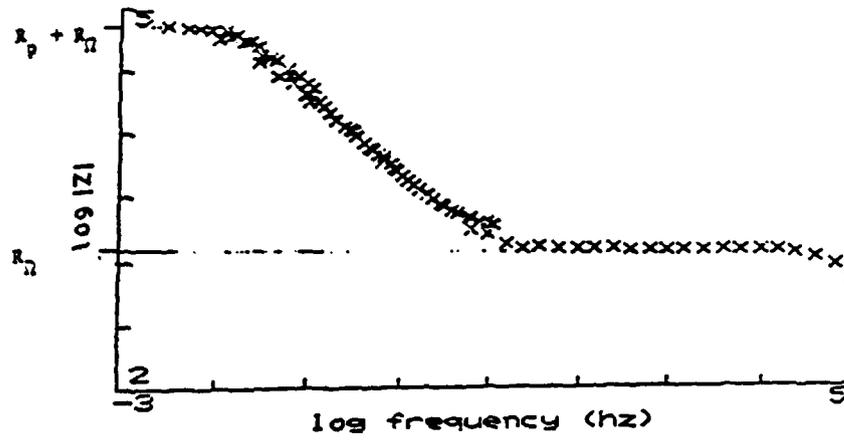


Figure 1. Bode Plot for 304L/N₂H₄

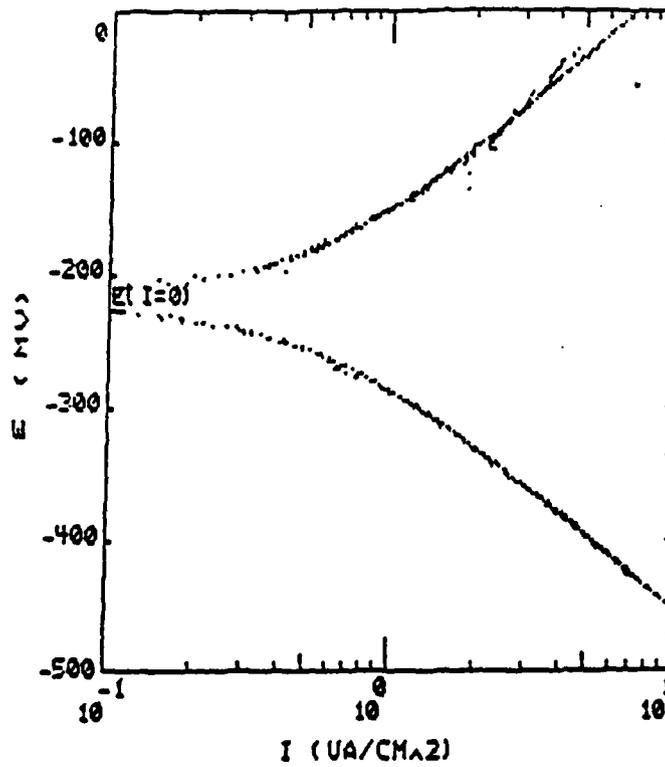


Figure 2. Tafel Plot for 304L/N₂H₄

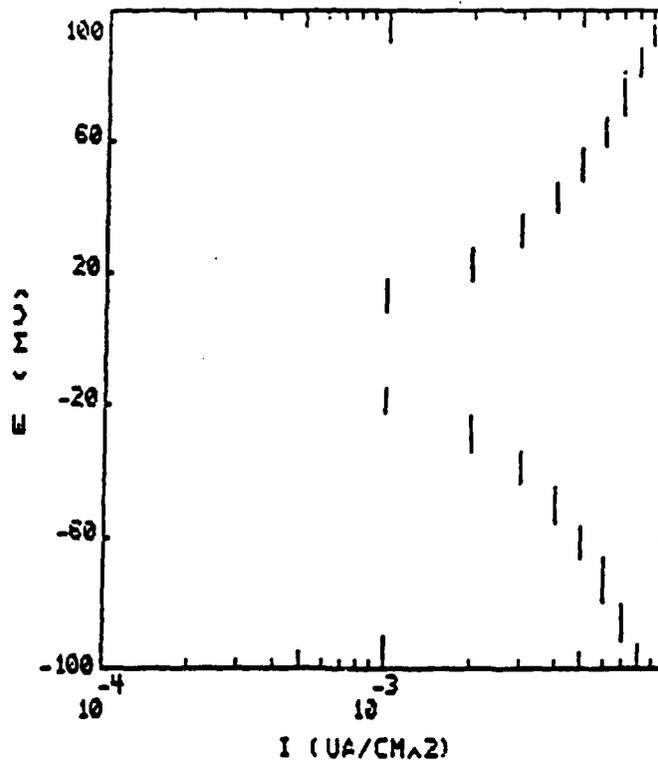
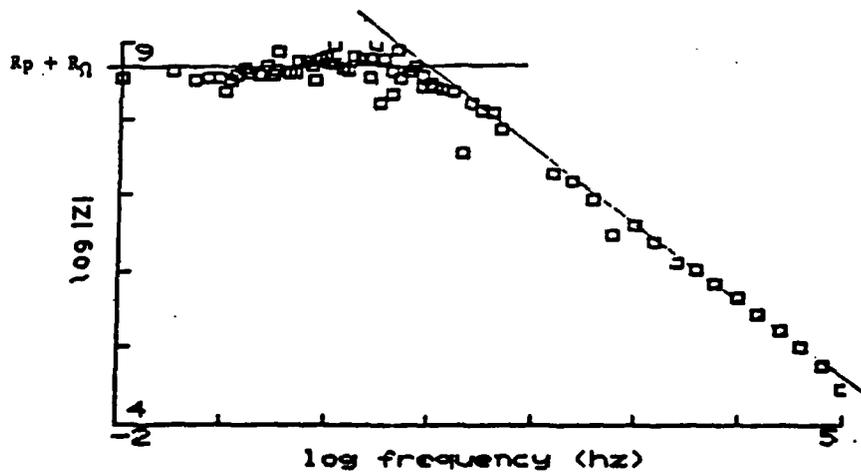
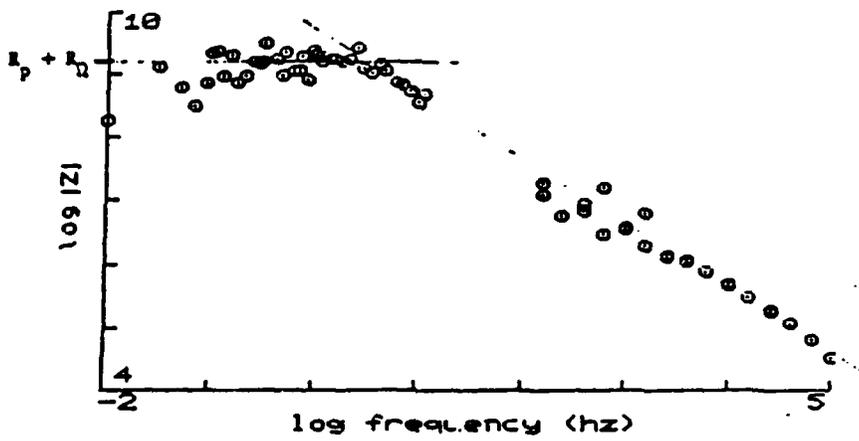


Figure 3. Tafel Plot for 430/MON-1



*Z not normalized for $A = 3.48 \text{ cm}^2$

Figure 4. Bode Plot for 304L/MON-1.6



*Z not normalized for $A = 3.48 \text{ cm}^2$

Figure 5. Bode Plot for A16061/MON-1.6

KCl COND

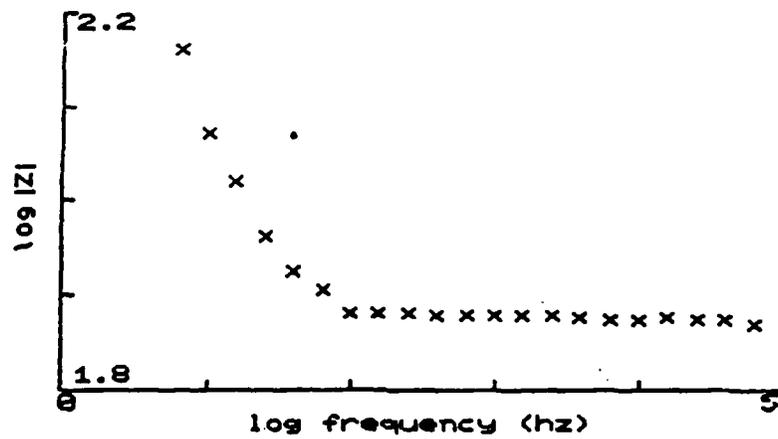


Figure 6. Bode Plot for KCl (0.01m) Solution

DIH2O

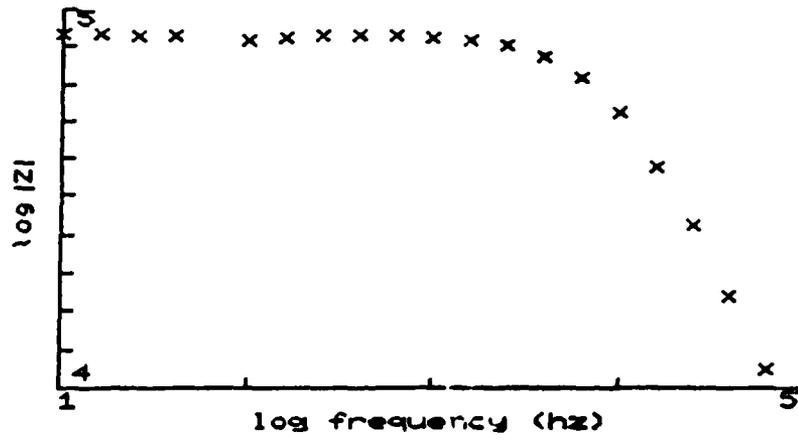


Figure 7. Bode Plot for Deionized H₂O

DIH2O

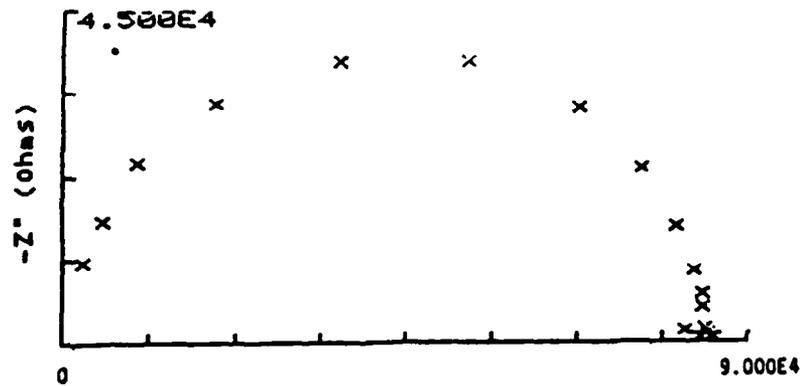


Figure 8. Nyquist Plot for Deionized H₂O

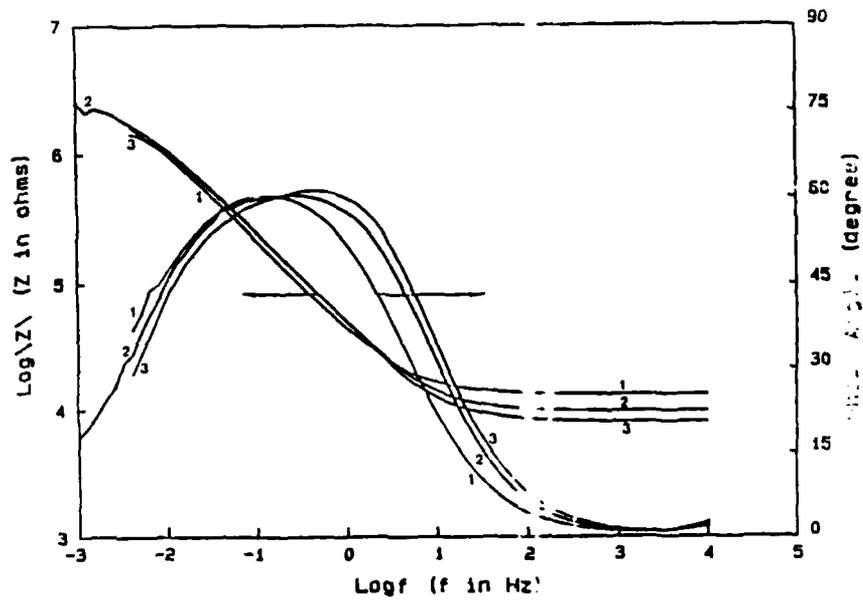


Figure 9. Bode Plots for 304L as Function of Exposure Time to N_2H_4
 (1) 1 day, (2) 5 days, (3) 12 days

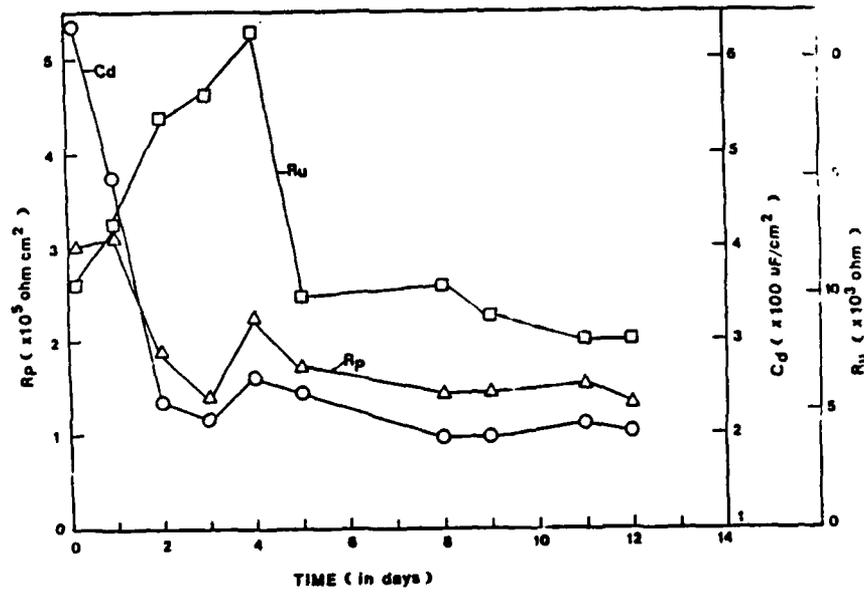


Figure 10. Time Dependence of R_p , C_d , R_u for 304L in N_2H_4

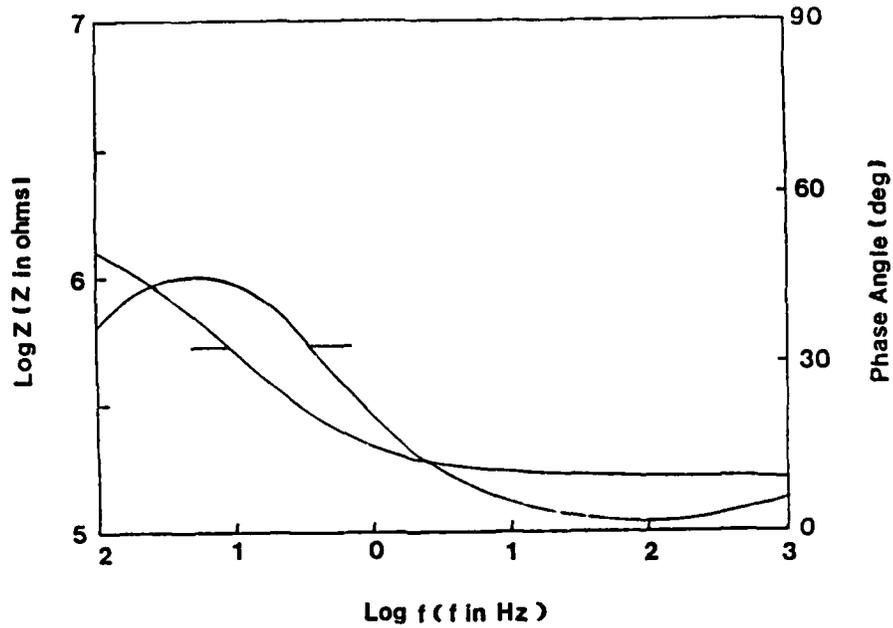


Figure 11. Bode Plots for 304L in 10^{-4} N HCl in Ethanol

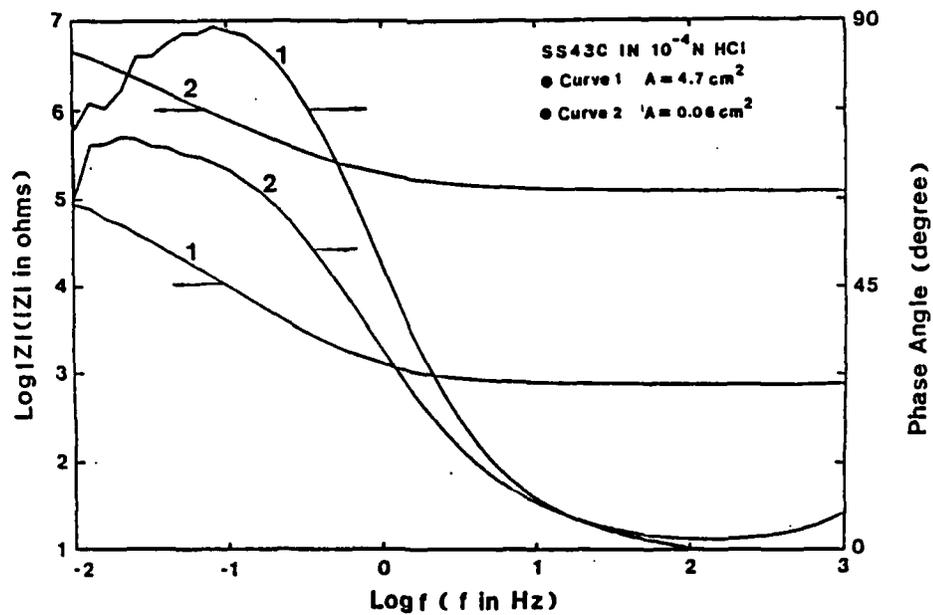


Figure 12. Effect of Electrode Area on the Values of Uncompensated Resistance

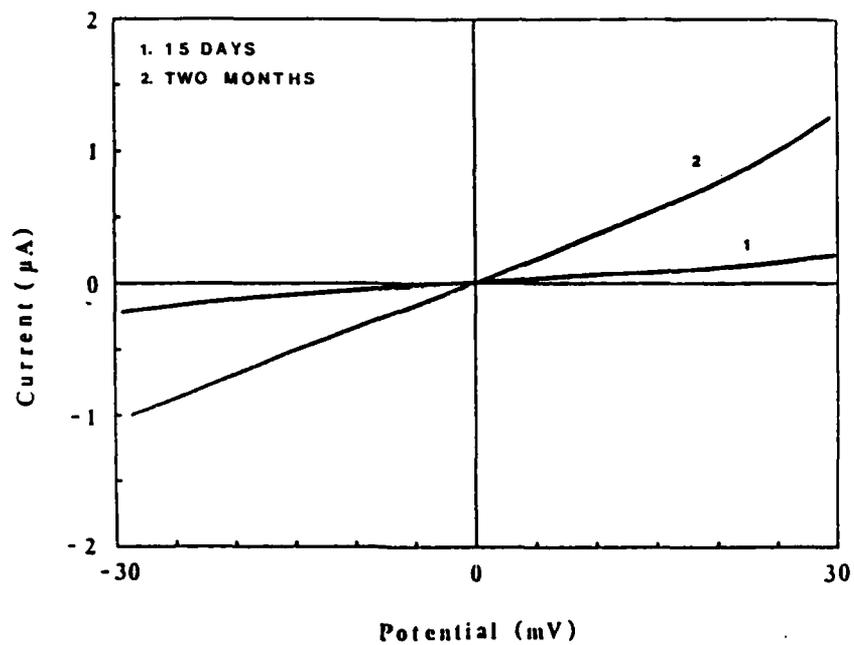


Figure 13. Polarization Resistance Measurements for 304L/N₂H₂

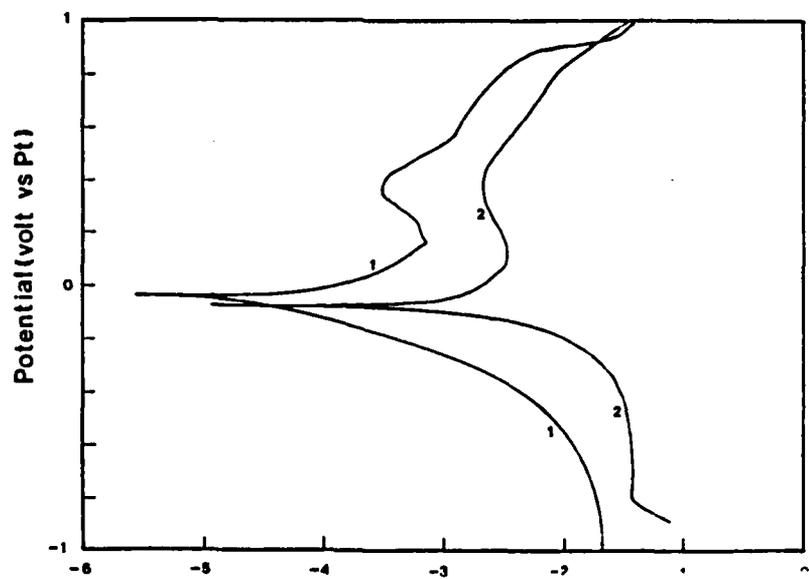


Figure 14. Potentiodynamic Polarization Curves for 304L/N₂H₄
(1) 23 days, (2) 60 days