

10/04/11/25

2002079580

**2001 NASA/ASEE SUMMER FACULTY FELLOWSHIP PROGRAM**

**JOHN F. KENNEDY SPACE CENTER  
UNIVERSITY OF CENTRAL FLORIDA**

**EVALUATION OF ELECTROCHEMICAL METHODS  
FOR ELECTROLYTE CHARACTERIZATION**

**Robert H. Heidersbach  
Professor of Materials Engineering and Department Chair  
California Polytechnic State University  
KSC Colleague: Luz Marina Calle**

**ABSTRACT**

This report documents summer research efforts in an attempt to develop an electrochemical method of characterizing electrolytes. The ultimate objective of the characterization would be to determine the composition and corrosivity of Martian soil. Results are presented using potentiodynamic scans, Tafel extrapolations, and resistivity tests in a variety of water-based electrolytes.

# EVALUATION OF ELECTROCHEMICAL METHODS FOR ELECTROLYTE CHARACTERIZATION

Robert H. Heidersbach

## 1. INTRODUCTION

Purpose of this project: This report documents the summer research efforts in an attempt to develop an electrochemical method of characterizing electrolytes. This summer's project had as its objectives the following tasks:

Design experiments to be done at KSC, then at an Arizona test site, and ultimately on a Mars mission in 2007 or later.

Validate that the experiments are relevant and reproducible.

Identify limitations and uses for the experiments developed.

The ultimate objective of the characterization would be to determine the composition and corrosivity of electrolytes, including Martian soil. Results are presented using potentiodynamic scans, Tafel extrapolations, and resistivity tests in a variety of water-based electrolytes.

The summer efforts are part of a multi-year project to develop electrochemical characterization techniques for a variety of NASA-related uses. Work will continue at Kennedy Space Center after the summer project.

Mars: The composition and other characteristics of Martian soil are controversial and not well documented. A number of probes have been sent to Mars, and the results have been publicized [1-3], but the interpretation of the data remains controversial. They can be summarized by stating that Mars has a variable climate with temperatures that range from very cold near the poles to temperatures that get above the freezing point of water during the day near the equator. This is summarized in Figure 1, adopted from a recent National Geographic article on Mars.

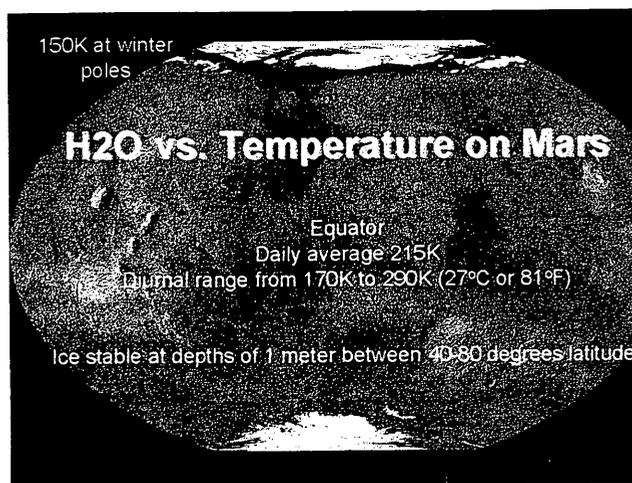


Figure 1: Temperatures and water on Mars [4].

While most of Mars is very cold and dry, it will be necessary to create habitats with moisture and warmer temperatures if manned missions ever go to Mars. The Mars Surveyor missions in the 1990's showed that Martian soil is ionic and will leach ions into any available water. Recent reports indicate that there may be natural brines on or near the surface. These brines would be corrosive at the temperatures where humans would function (approximately 25°C).

Table 1: Atmospheres on Earth and Mars [5]

	Earth	Mars
Pressure	760 mm Hg	7 mm Hg
N <sub>2</sub>	78%	2.7%
CO <sub>2</sub>	0.033%	95.3%
Ar	0.93%	1.6%
O <sub>2</sub>	21%	0.13%

The atmospheres on Earth and Mars are also very different. Table 1 shows that the Earth's atmosphere is primarily inert nitrogen and argon, whereas Mars has an atmosphere that is mostly carbon dioxide at a very low pressure. Experience on earth indicates that most corrosion and other chemical activity arises from the levels of dissolved atmospheric oxygen in electrolytes such as condensation, surface water, and soils. The presence of carbon dioxide serves to make waters corrosive on earth (Figure 2), unless there are also substantial amounts of dissolved metallic ions. If this happens, then scales can form which will cover metal surfaces and retard corrosion (Figure 3). This scale is normally somewhat protective and leads to the general conclusion that "hard" waters (those having high calcium or magnesium contents) are generally less corrosive than "soft" waters that have lower concentrations of these dissolved metals.

### CO<sub>2</sub> Channeling

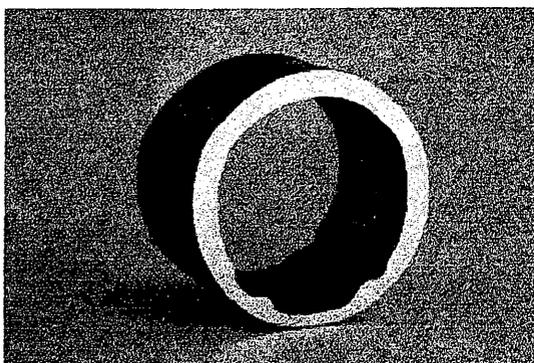


Figure 2: CO<sub>2</sub> channeling caused by high dissolved gases in unbuffered condensate soft water. [6]

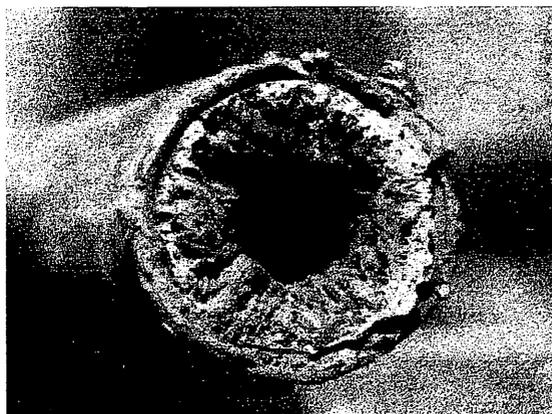


Figure 3: Calcium carbonate scale caused by high mineral content in hard water.

The effects of dissolved oxygen in water cause most corrosion on earth. Dissolved CO<sub>2</sub> is a secondary effect that leads to corrosion, but only if a reducible species such as dissolved oxygen is also available to promote corrosion. On Mars, the presence of CO<sub>2</sub> will insure that the pH and mineral scale formation on metal surfaces will tend to be different than on earth,

but the limited amount of atmospheric oxygen should make any brines that form less corrosive than they would be on the earth's surface.

Electrochemical characterization of soil and electrolytes: Pipelines and other structures exposed to soil on earth will corrode depending on a number of variables. The most important variables are recognized to be the conductivity of the soil, its compaction (permeability to moisture and air), and moisture content. Figure 4 shows the relationship between soil corrosivity and soil resistivity on earth. In general, low resistivity soils are more corrosive than high resistivity soils.

Characterization of the corrosivity of Martian soil should also depend on the conductivity of the soil. The NASA Kennedy Space Center already has a group working on the effects of conductive Martian soils on the reliability of equipment sent to Mars [8], and joint efforts are underway between the Electromagnetic Physics Laboratory and the Corrosion Technology Testbed groups. It is an obvious step to include conductivity measurements in the program at some time in the future.

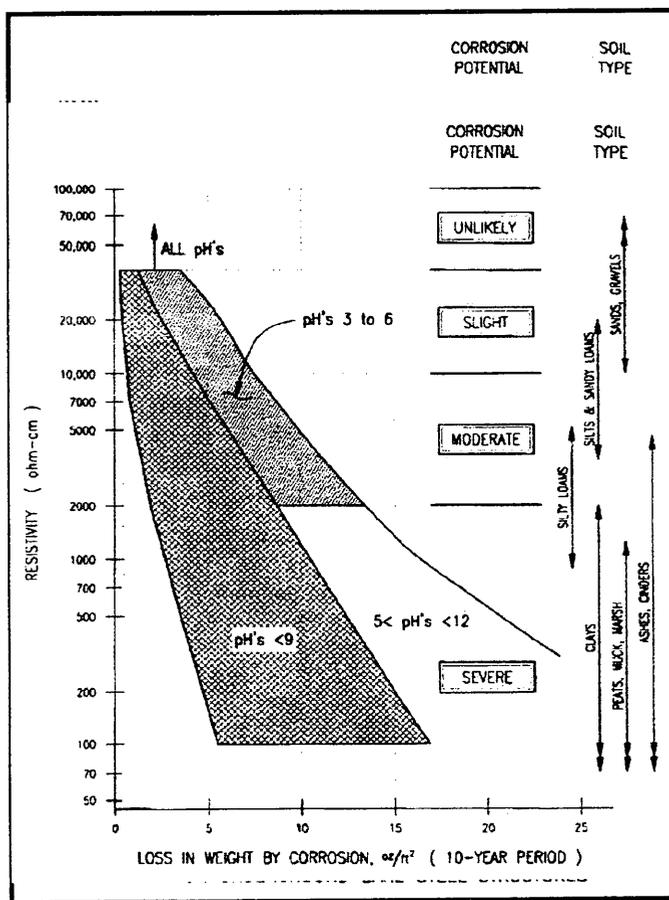


Figure 4: The effects of soil resistivity on soil corrosivity [7]

## 2. Experimental procedures

**Background efforts:** The incentive for this summer's work is a collaborative effort between NASA's Kennedy Space Center and the Jet Propulsion Laboratory (JPL) in Pasadena, California. The original idea on this project was to use a series of electrodes fabricated for a Mars mission to characterize Martian soil. JPL has experience in developing similar electrodes [9], and the electrode arrangement being developed by JPL is shown in Figure 5. The eight sensors labeled "galvanic cell array" in Figure 5 are the electrodes being fabricated for the Kennedy Space Center and will be used for electrochemical experiments designed to characterize electrolytes such as Martian soil.

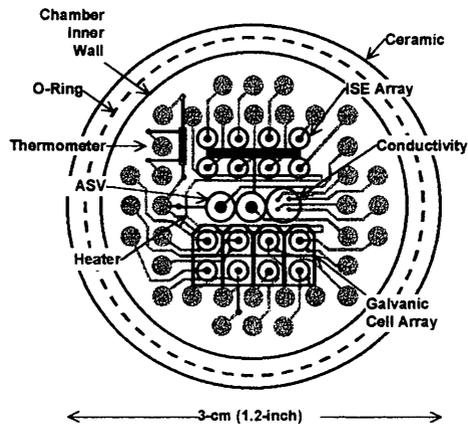


Figure 5: Mars soil characterization electrode schematic.

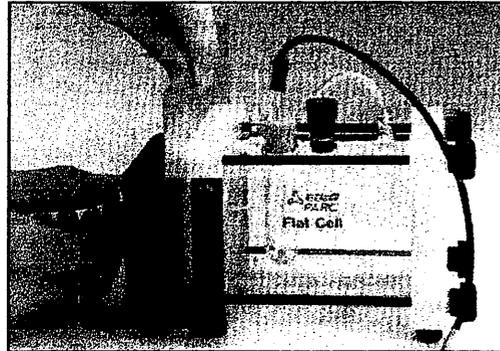


Figure 6: Electrochemical cell used for potentiodynamic scans

**Potentiodynamic experiments:** The original ideas that started this research were based on the results of a Master's thesis [10] cited in a standard corrosion textbook [11]. The idea was to use potentiodynamic scans of various metals to characterize electrolytes. Figure 6 shows a standard electrochemical cell used for this type of experiment.

Cells of this type are routinely used for corrosion electrochemistry tests around the world, and they can be purchased from a variety of commercial suppliers.

**Conductivity experiments:** Electrolyte conductivity is one of the controlling parameters that

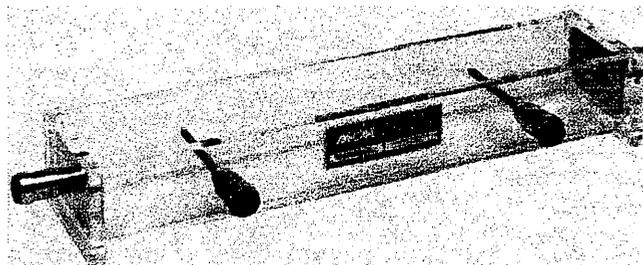


Figure 7: Soil resistivity test box

control corrosion. The test box shown in Figure 7 is one standard apparatus used for measuring resistivity. A test box similar to the one shown in Figure 7 was purchased for the purpose of the resistivity measurements conducted on this project.

Electrochemical control apparatus: The potentiodynamic scans measured in this project used a variety of potentiostats, and resistivity was determined using a standard resistivity meter. These instruments are commonly used in electrochemical testing [11] and will not be discussed in this report.

### 3. RESULTS

Potentiodynamic scans: Figure 8 shows representative potentiodynamic scans made using

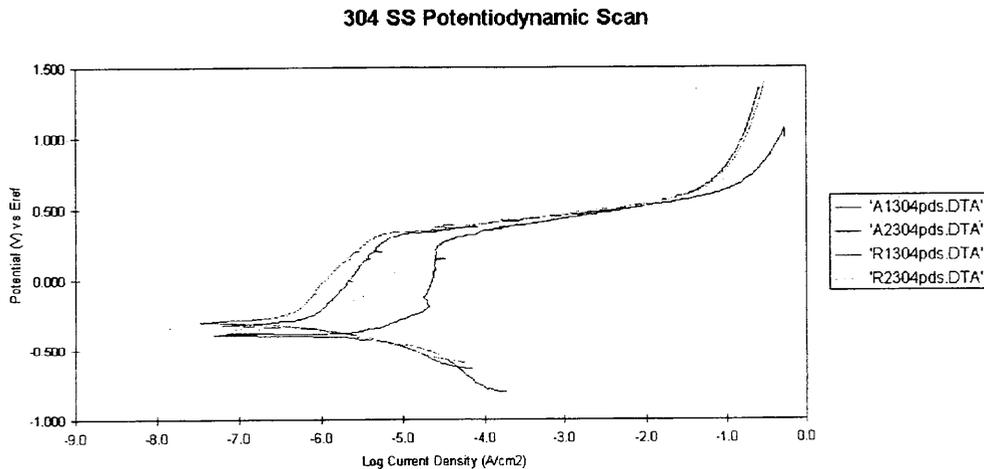


Figure 8: Typical potentiodynamic scans obtained at the KSC corrosion laboratory a laboratory potentiostat and following standard electrochemical procedures. The four scans shown in Figure 8 represent supposedly replicate experiments performed on the same piece of 304 stainless steel by two different electrochemists. Other potentiodynamic scans were performed in a variety of one-normal acid and base electrolytes using both 304 stainless steel and carbon steel samples.

The conclusions from this work were that the potentiodynamic scan technique could not be used to characterize electrolytes. While open circuit (rest or "corrosion") potentials could be reproduced within approximately 50 mv, the current densities were not reproducible. Thus these scans could not be used to predict corrosion rates or to identify electrolytes. A careful check of the electrochemical literature [12-17] shows that, since current density is highly dependent on potential, electrolyte resistivity, reduction reactions, and other parameters, electrochemical currents are unlikely to be useful for identifying or characterizing electrolytes.

Resistivity measurements: One of the more common methods of characterizing environments for their corrosivity is resistivity measurement. [18] The resistivity of 1 Normal solutions of the same electrolytes that were used for the potentiodynamic tests were determined using a resistivity "soil box" shown in Figure 7. While soil boxes are normally used for soil electrolytes, they can be used for liquids as well. Figure 9 compares the resistivity of diluted NaOH as measured by two different electrochemists using the same soil box and compares

these measurements with the results obtained using a single probe electrode meter.

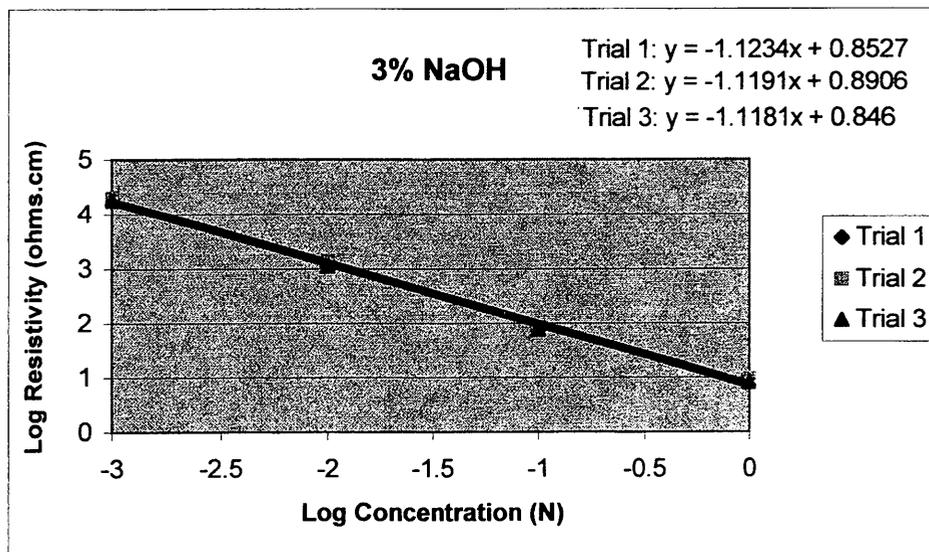


Figure 9: Results of resistivity measurements by two different electrochemists using a “soil box” compared with the resistivity determined by a single probe resistivity meter

The results of this work showed that resistivity is far more reproducible than potentiodynamic scanning and does not vary from experimenter to experimenter. Resistivity can also be duplicated using several standard resistivity techniques.

While resistivity measurements can be used to compare the corrosivity of various electrolytes, it is not specific to any given electrolyte and cannot be used to identify electrolytes. Any electrolyte with the same ionic concentration can be expected to show the same conductivity. The reason for the different conductivities for one normal electrolytes shown in Figure 9 is because the salts in these electrolytes have slightly different solubilities. This effect would be more apparent if divalent metallic salts (e.g., salts of calcium or magnesium) had been included in the experimental program.

Soil collection: Because the conductivities of various soils can be used to determine their relative corrosivities, a series of soils were collected from locations in Florida, Georgia, and South Carolina. Time restraints prevented the resistivities of these soils from being tested, but they were supplied to the KSC corrosion personnel for use in the future.

Tafel extrapolation: An examination of the “open circuit” or “corrosion” potentials obtained with the potentiodynamic scans (e.g., Figure 8) suggested that concentrating on the regions near the open circuit potentials would produce more reproducible data.

Table 2 shows that the Tafel slopes (Beta C and Beta A in Table 2) [13, 16] obtained using the standard potentiodynamic scan technique are not reproducible. A review of the literature suggested that if the potentials tested were limited to those nearer the open circuit potential, less damage to the sample might occur during testing, and the slopes, or at least the open circuit potentials, should be more reproducible. Figure 10 confirms this supposition.

Table 2: Tafel slope data from potentiodynamic scans

Trial	Electrochemist 1, trial 1	Electrochemist 1, trial 2	Electrochemist 2, trial 1	Electrochemist 2, trial 2
Environment	3.5% NaCl	3.5% NaCl	3.5% NaCl	3.5% NaCl
E <sub>corr</sub> (mV)	-403.5	-471.2	-414.6	-468.6
I <sub>corr</sub> (A/cm <sup>2</sup> )	3.83E-06	3.50E-06	6.61E-06	5.29E-07
BetaC (mV/decade)	72.9	43.2	84.9	11.9
Beta A (mV/decade)	34.9	33.7	34	14.5
R <sub>p</sub> (ohm-cm <sup>2</sup> )	2.68E+03	2.35E+03	1.60E+03	5.36E+03
Corrosion rate (mm/yr)	0.044	0.041	0.077	0.006

304 Stainless Steel Potentiodynamic Scans  
1N NaCl - No Stirring - No Gas

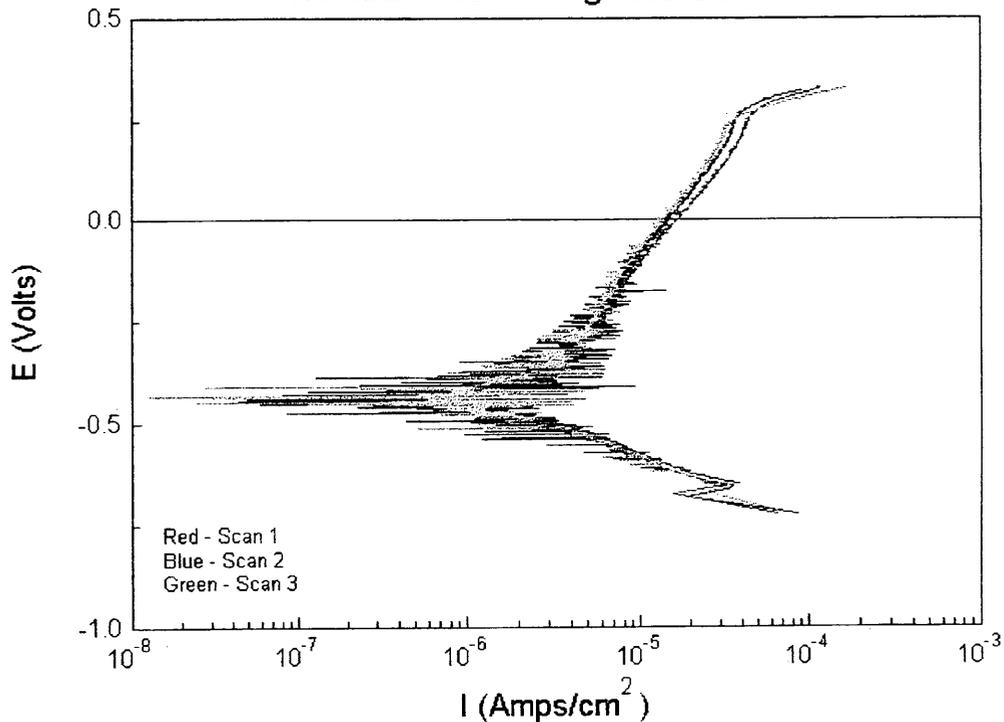


Figure 10: Reproducibility of open circuit potentials and Tafel extrapolation currents for 304 stainless steel in NaCl

A series of tests in various electrolytes was conducted using 304 stainless steel samples. The complete results of these tests have been provided to the NASA Kennedy Space Center colleagues. The results of this work conducted in August 2001 were that the potentials seem reproducible with approximately 50 mv, but the current data is noisy. This experimental noise could be due to metal/environment interactions, or it could be due to instrumental settings. This experimental approach seems worthy of continuing work.

when the potentials are limited to less than 100 mv from the open circuit potential

#### **4. CONCLUSIONS**

The purpose of this work was to determine an electrochemical means of characterizing electrolytes.

Potentiodynamic scans using techniques suggested by the work of Bennett at the University of Connecticut [10] did not yield useful results. The suggestion that this kind of experiment would prove useful in characterizing electrolytes [11] could not be confirmed.

Resistivity measurements were shown to be very reproducible. This would prove useful information for characterizing the corrosivity of electrolytes. Unfortunately, resistivity determinations cannot be used to identify the chemicals in an electrolyte.

Preliminary results indicate that further efforts on potentiodynamic experiments near the open circuit potential may prove useful in characterizing electrolytes. This may produce useful Tafel slope information that would be characteristic of various electrolytes. This work was not completed, but a complete set of the data necessary for continuation of this work has been provided to NASA Kennedy Space Center Corrosion Test Bed group.

#### **5. ACKNOWLEDGEMENTS**

Amanda Runciman, a summer student fellow from Cal Poly, and Ruby Vinje, Dynacs Inc., performed the laboratory experiments described in this report. Dr. Luz Marina Calle was the NASA colleague whose original ideas started this project. She also obtained funding for its continuation. We thank her for her insight, ideas, and thoughtful contributions and encouragement. Louis McDowell is the NASA researcher most responsible for the continuing vitality of the Corrosion Test Bed efforts at Kennedy Space Center, and we thank him for his foresight and determination in keeping Kennedy Space Center as a major source of government expertise in corrosion research, engineering, and testing. Joe Curran from Dynacs insured that support was available whenever necessary. This work could not have been done without all of their help.

#### **6. REFERENCES**

- [1] Allen, C.C., and J.L. Conca, "Weathering Of Basaltic Rocks Under Cold, Arid Conditions - Antarctica and Mars," Proceedings of Lunar and Planetary Science, 21, 711-717, 1991.
- [2] S. Clifford and T. Parker, "The evolution of the Martian Hydrosphere: Implications for the Fate of a Primordial Ocean and the Current State of the Northern Plains," [www.lpi.usra.edu/meetings/geomars2001/eleclogo.jpg](http://www.lpi.usra.edu/meetings/geomars2001/eleclogo.jpg)
- [3] G. Landis and P. Jenkins, "DUST ON MARS: Materials Adherence Experiment Results From Mars Pathfinder," Proceedings of the 26th IEEE Photovoltaic Specialists Conference - 1997, IEEE, NJ, 1997, pp. 865-869. ISBN 0-7803-3767-0. [http://powerweb.grc.nasa.gov/pvsee/publications/mars/Dust\\_97.html](http://powerweb.grc.nasa.gov/pvsee/publications/mars/Dust_97.html)

- [4] National Geographic Map of Mars Using MGS MOLA and MOC Data,  
<http://ftpwww.gsfc.nasa.gov/tharsis/ngs.html>
- [5] Jet Propulsion Laboratory, "Mars environmental compatibility assessment,"  
<http://mars.jpl.nasa.gov/2001/lander/meca/science.htm#Corrosion>
- [6] R. Heidersbach, Carbon dioxide channeling,  
<http://www.mate.calpoly.edu/mate425/powerpoint/forms/img164.gif>
- [7] M. Romanoff, "Underground Corrosion" (National Bureau of Standards Circular 579, April 1957), reprinted in 1989 by NACE, Houston.
- [8] Kennedy Space Center Electromagnetic Physics Laboratory,  
<http://empl.ksc.nasa.gov/index2.htm>
- [9] M. Buehler, S. Kounaves, D. Martin, S. West, and G. Kuhlman, "Designing a Water-Quality Monitor with Ion Selective Electrodes, 2001 IEEE Aerospace Conference Proceedings, Big Sky, Montana (March 2001).
- [10] D. Bennett, "The Application of Electrode Kinetics to Galvanic Corrosion: I. The Use of Polarization Curves for Predicting Galvanic Corrosion, II. The Galvanogram," MS Thesis, University of Connecticut, 1973.
- [11] D. Jones, Principles and Prevention of Corrosion, Macmillan, New York, 1992
- [12] M. Fontana, "Corrosion Engineering," McGraw-Hill, New York, 1986.
- [13] H. Hack, "Galvanic Corrosion Test Methods," NACE International, Houston, 1993, pp. 7-10.
- [14] H. Hack, private communication, July 2001.
- [15] F. Mansfeld, "Don't be afraid of electrochemical techniques, but use them with care," Corrosion, 1998, pp. 856-868.
- [16] J. Scully, "Electrochemical methods for laboratory corrosion testing," Corrosion Testing and Evaluation: Silver anniversary volume, ASTM STP 1000, R. Baboian and S. Dean, editors, American Society for Testing Materials, Philadelphia, 1990. pp. 351-378.
- [17] W. S. Tait, "Increase your confidence in corrosion test data," Materials Performance, March 2001, pp. 58-61.
- [18] "Standard method of Field Measurement of Soil Resistivity Using the Wenner Four-Electrode Method," ASTM G 57-95(a).
- [19] Mars Environmental Compatibility Assessment (MECA) Science,  
<http://mars.jpl.nasa.gov/2001/lander/meca/science.htm#Corrosion>