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Relationship between electrochemical reaction processes and environment-assisted crack growth under static and dynamic atmospheric conditions

Fritz Friedersdorf
Luna Innovations, friedersdorf@lunainc.com

Carlos Hangarter
Excet Inc.

Nate Brown
Luna Innovations

Steve Policastro
Naval Research Laboratory

Matt Merrill
Luna Innovations

Relationship Between Electrochemical Processes and Environment-assisted Crack Growth Under Static and Dynamic Atmospheric Conditions

Patrick Kramer, Carlos Hangarter, *Fritz Friedersdorf*, Steve Policastro,
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Luna Innovations, Naval Research Laboratory, and Excet Inc.

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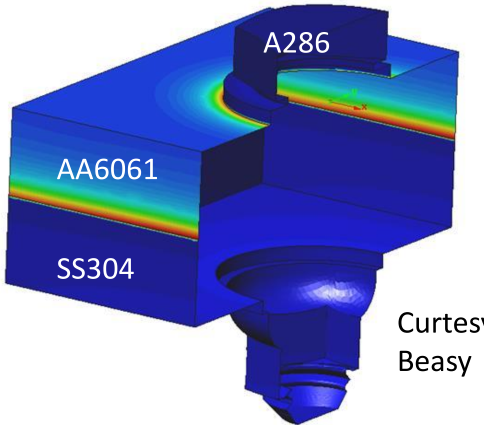
Objective

- Advance atmospheric corrosion measurements to support the Sea-based Aviation (SBA) corrosion theory and degradation modeling activities
  - Initial focus on galvanic coupling and corrosion of boldly exposed surfaces
    - FEA Models
    - Corrosion data library (PDS)
  - Longer term goal to extend modeling to localized corrosion and lifetime damage accumulation
    - Corrosion cracking and crevice corrosion
    - Service life prediction
- Our efforts are to use measurements to inform and verify multi-physics finite element analysis models
- This presentation focuses on relating electrochemical data for occluded cells to cracking processes



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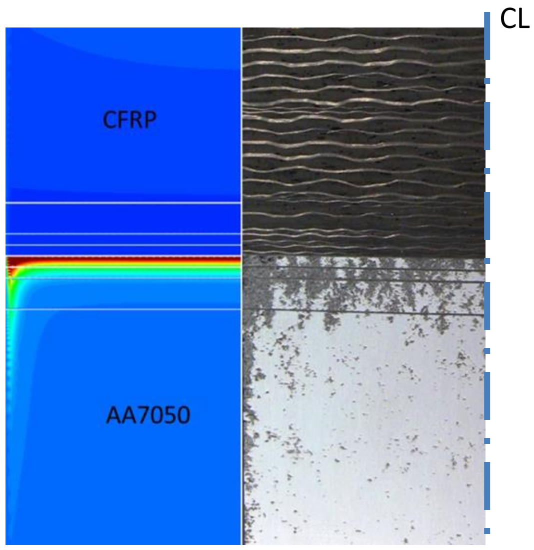
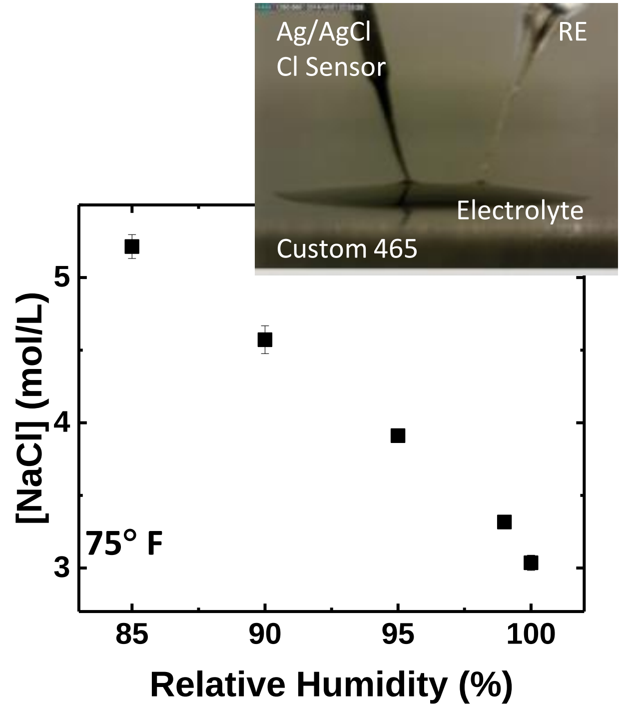
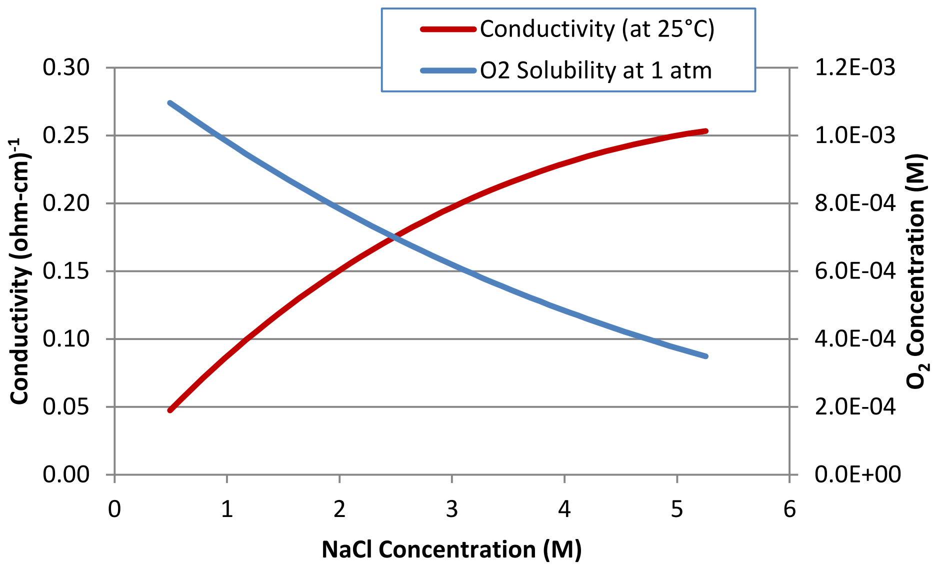


Model and experimental results for CFRP and AA7050 butt joint (Air Force FA8650-14-M-5062)

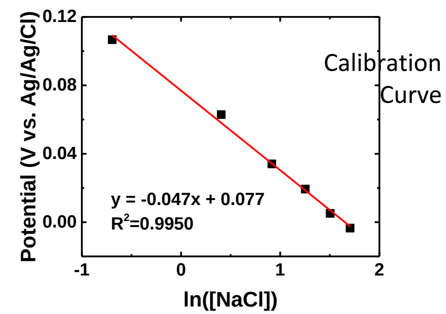
Environmental Conditions

- Environmental conditions relevant to atmospheric corrosion
  - Air and surface temperature
  - Relative humidity
  - Contaminant loading and composition
- These environmental parameters determine the properties and spatial distribution of thin film electrolytes
  - Salt concentration and film thickness
  - Conductivity
  - Oxygen concentration and diffusion rates





Shedd M. E., Master of Science Thesis, University of Virginia, 2012.



Measurements for Model Development and Verification

- Model development requires the use of appropriate material and environmental inputs
  - Solution properties (salt loading, film thickness, and conductivity)
  - Material performance data (potentiodynamic scans)
- Present work focuses on AA7075-T6 corrosion in sodium chloride solutions
- Reactions that are of primary importance to atmospheric corrosion, crevice corrosion, and cracking in chloride solutions:
  - Oxygen reduction
  - Alloy dissolution
  - Hydrolysis
  - Hydrogen reduction

$$O_2 + H_2O + 4e^- \rightarrow 4OH^-$$

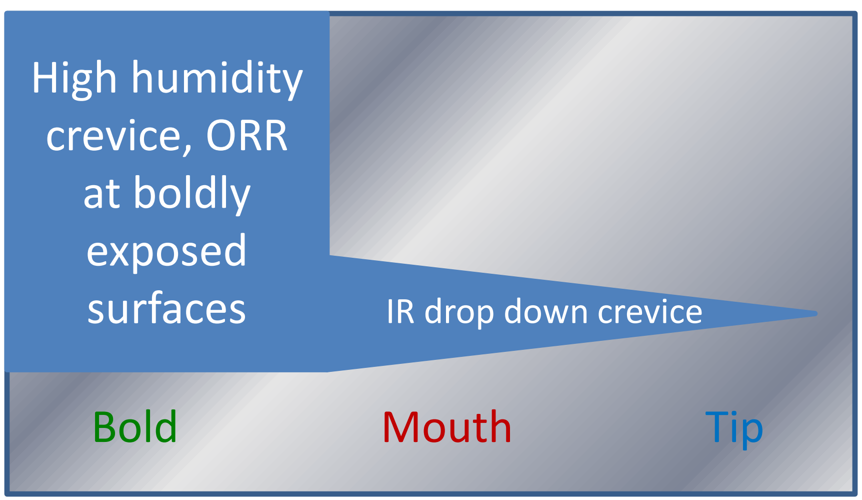
$$M \rightarrow M^{n+} + ne^-$$

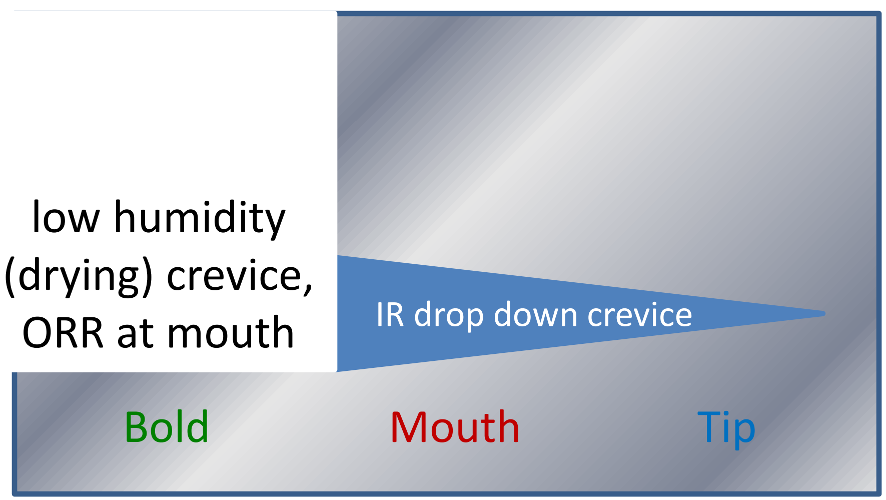
$$M^{n+} + zH_2O \rightarrow M(OH)_z^{(n-z)+} + zH^+$$

$$H^+ + e^- \rightarrow H_{ads}$$

Environmental Conditions

- The surface electrochemistry over a component varies based on atmospheric parameters and geometry
- Conditions expected for atmospheric corrosion:
  - Salt concentrations varying from 2.6 M to 4.6 M NaCl
  - Boldly exposed surface and crevice mouth - oxygenated at near neutral pH
    - Bulk electrolyte and thin films
  - Occluded cells - deoxygenated at low pH (pH 2 – 4)



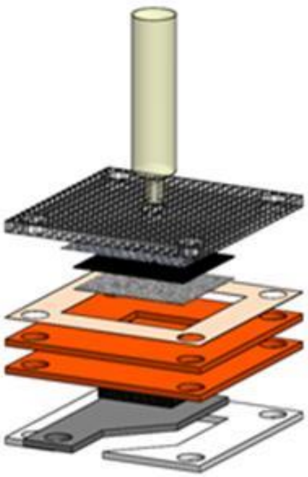


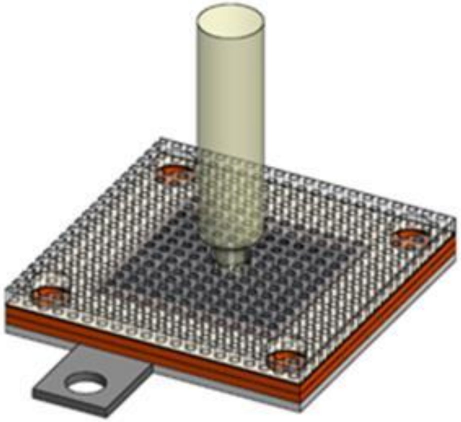
Potentiodynamic Scans

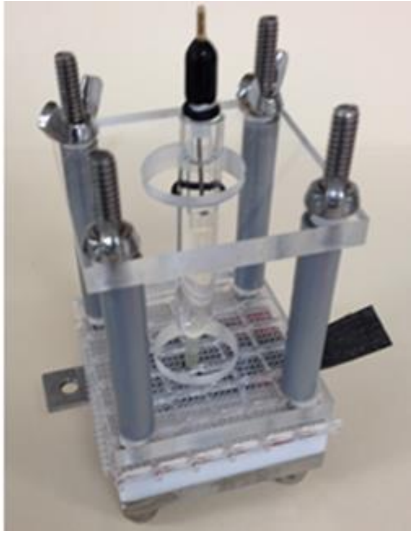
Bulk Electrolyte and Thin Film PDS Testing

- PDS tests were performed in a flat cell (bulk solution) and in a thin film test cell
- The three electrode thin film cell uses a porous, hydrophilic membrane (fiberglass fabric) to support the electrolyte over a surface with thicknesses in the range of 30 – 120 µm
  - A specific volume (4 µL/cm^2) of salt solution is applied to the membrane
    - The solution equilibrates based on the relative humidity
  - Working electrode – one inch square sample of AA7075-T6
  - Counter electrode – carbon cloth counter electrode with hydrophobic surface treatment
  - Reference electrode – Ag/AgCl reference electrode, Luggin probe with glass frit

Test type	Flat cell			Atm cell	
RH (%)	(40-70)	(80)	(90)	80%	90%
Salt Conc [M NaCl]	5.4	4.6	2.6	4.6	2.6
Temperature (°C)	25	25	25	35	35
OCP hold	30 to 60 minutes				
Scan Rate	0.2 mV/second				
Ref Electrode	SCE			Ag/AgCl	

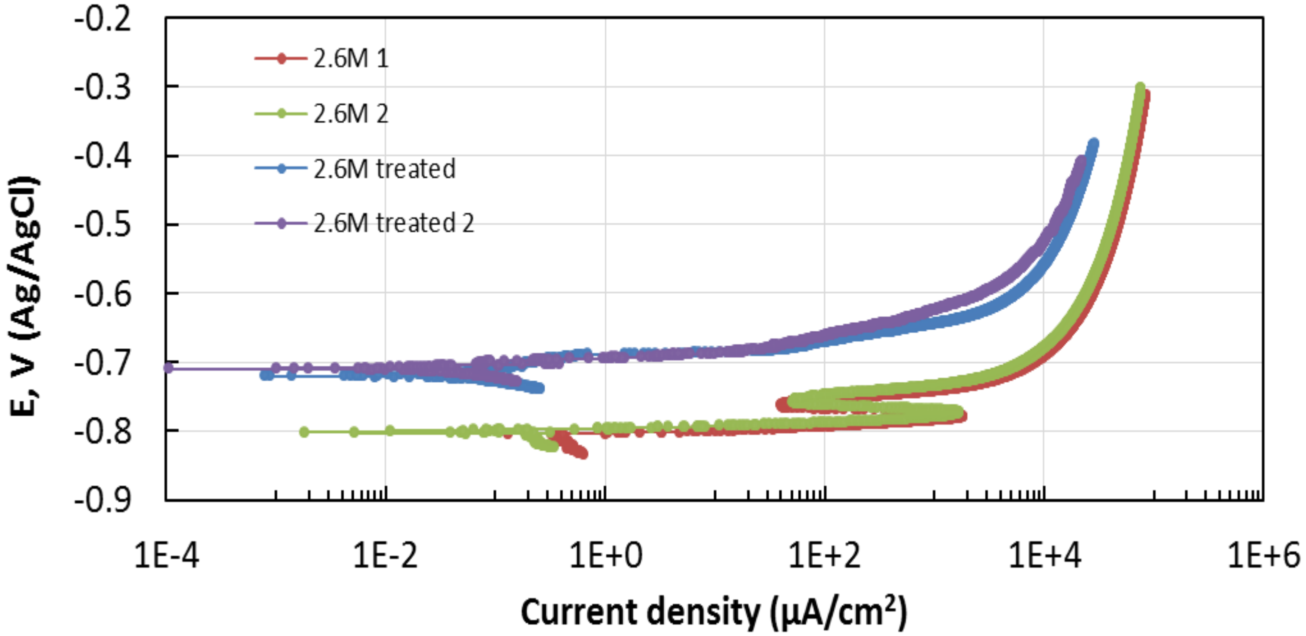






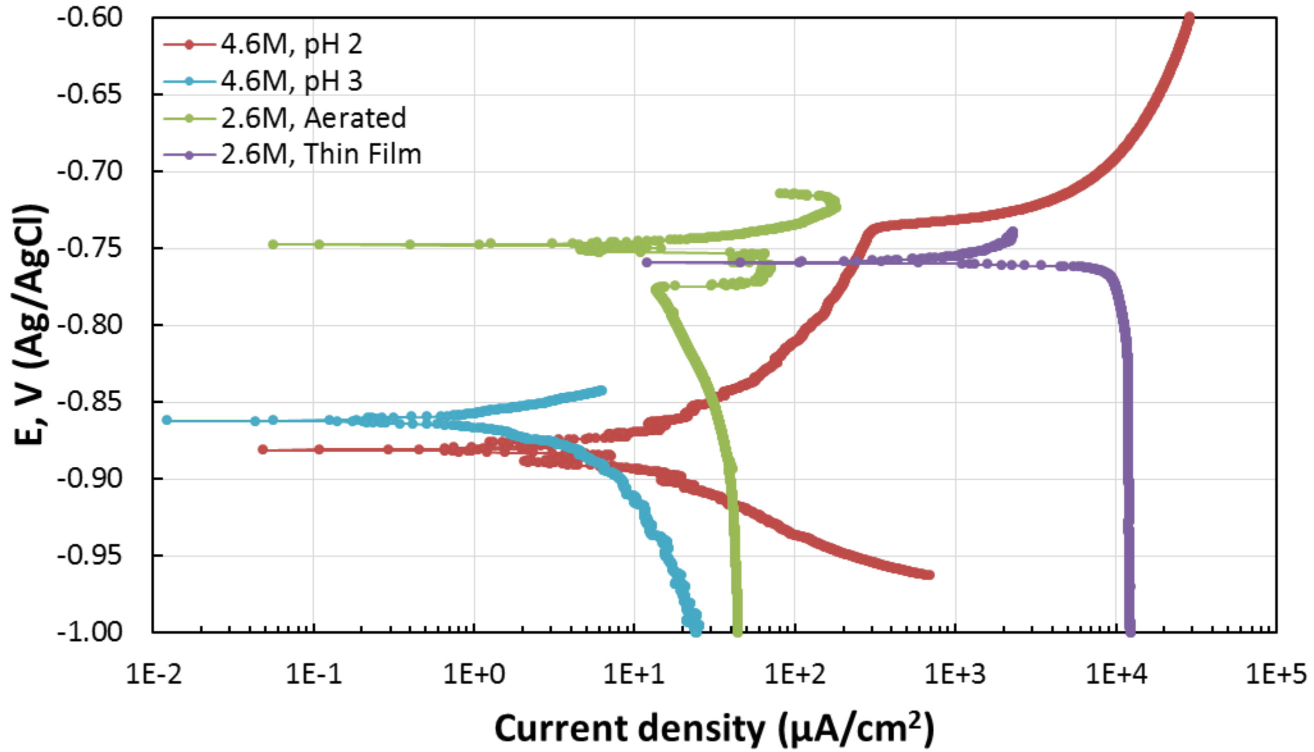
AA7075-T6 Surface Treatment

- Polishing creates thin Zn/Mg enriched layer at surface that alters polarization/corrosion behavior of AA7075-T6
- Chemical etching with NaOH was used to remove layer to obtain more representative corrosion properties



PDS Results

- PDS results can be used to estimated galvanic (concentration cell) currents using mixed potential theory
  - PDS data are used as FEA model inputs that provide area dependent responses for given electrolyte conditions (conductivity / IR drop in the thin film electrolytes)
- Aluminum alloy pits at E_{corr} for oxygenated bulk and thin film electrolyte
  - AA7075-T6 is essentially a non-polarizable electrode
  - Extremely high ORR and free corrosion rates (i_{corr}) are measured with thin film electrolytes
  - Deaerated low pH solutions decrease E_{corr} of A7075-T6

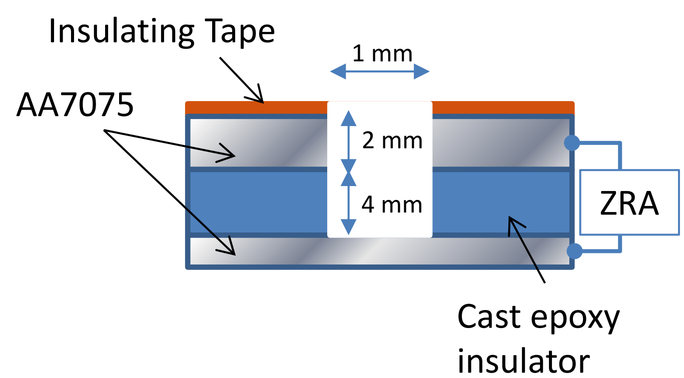


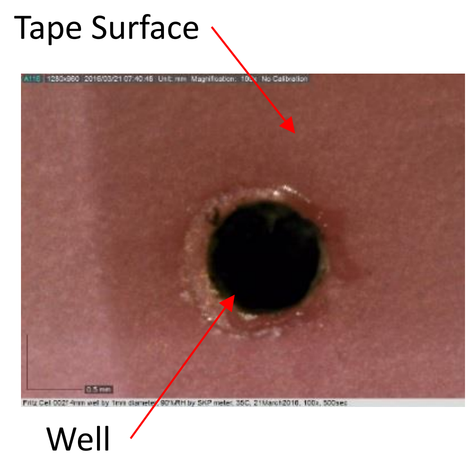
Coupled Electrode Testing

Coupled Electrodes – Hole Geometry

- Coupled electrodes with a hole geometry were used to measure galvanic currents between hole wall and bottom surface
  - Hole diameter 1 mm
  - Two electrodes separated by 4 mm thick cast epoxy
  - Tape used to mask boldly exposed surface
  - AA7075-T6 coupon thickness 2 mm
  - Occluded cell aspect ratio of 6:1

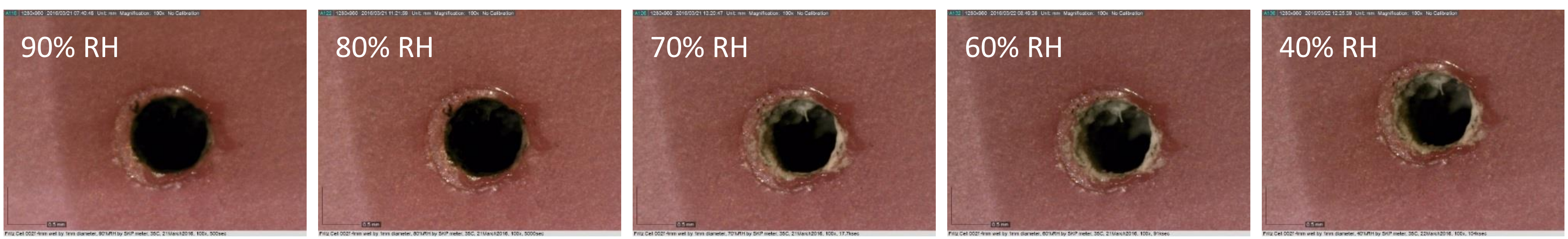
Hole electrode





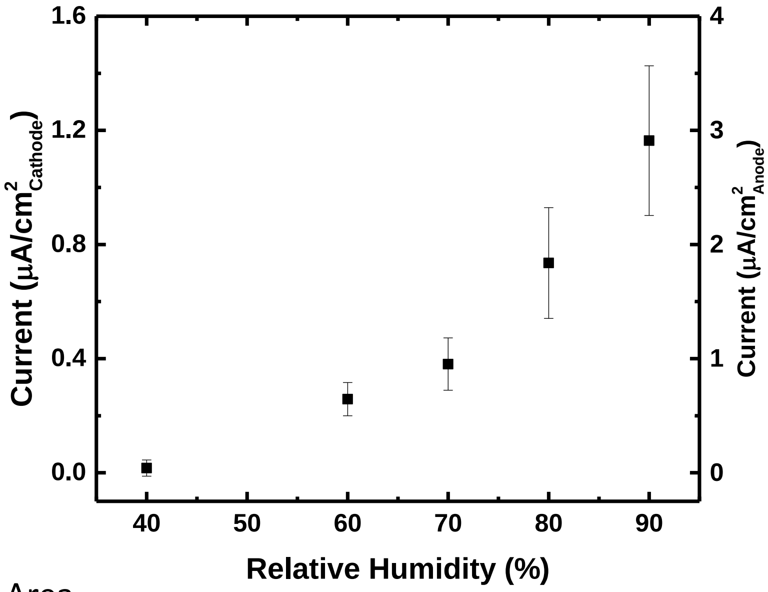
LUNA | Coupled Electrodes – Hole Geometry

- Environmental testing with coupled electrode and occluded cell geometries
  - Hole was filled with saturated NaCl solution (≈6 M NaCl)
  - RH was cycled using steps of 80, 70, 60, 40, 60, 70, 80, 90%
  - Salt precipitates were visible at and below 70% RH
    - Deliquescence RH approximately 76% for NaCl

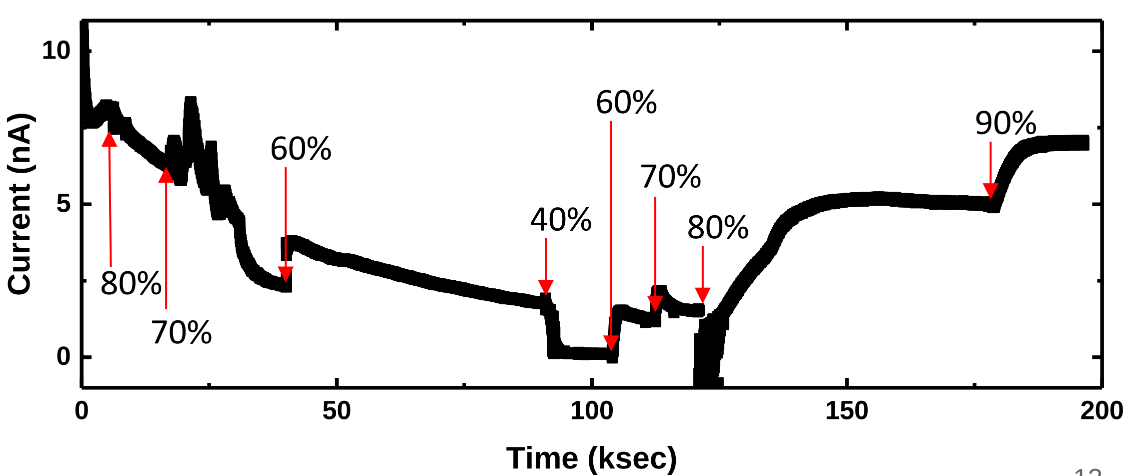


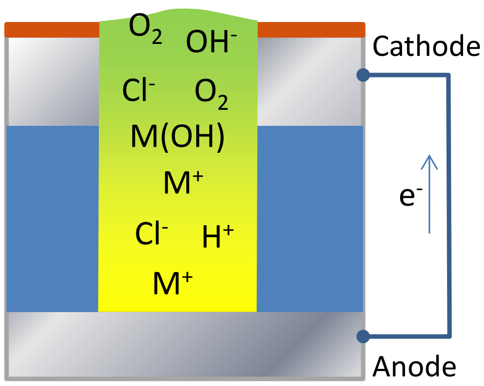
Hole Electrode Current

- Galvanic current increased with RH
  - Average current for the last hour of each RH step was used to estimate galvanic current
- Hole bottom was anodic to the hole wall
  - ↑RH: ↑i_{cell} (↓[Cl], ↑O_2 activity, ↑Volume, ↓IR)
- Currents are very low, but consistent with oxygen concentration cell



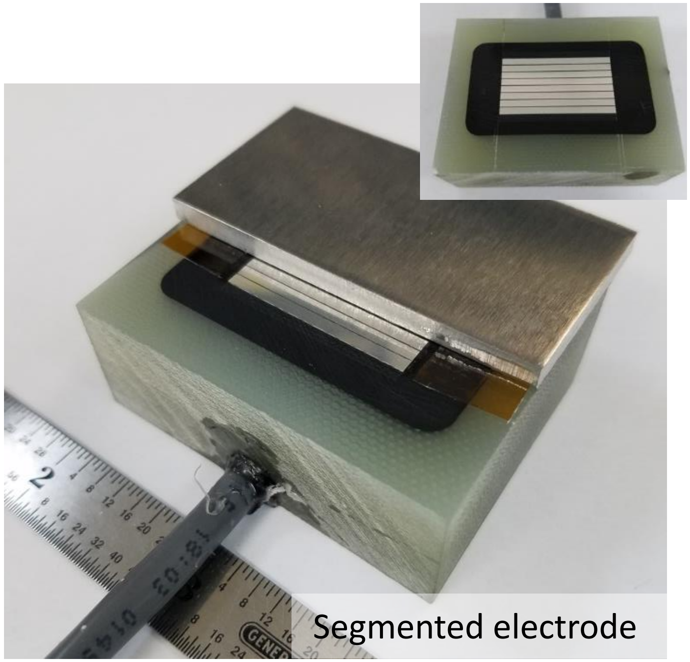
Area$_{Cathode}$ = 2.44 Area$_{Anode}$



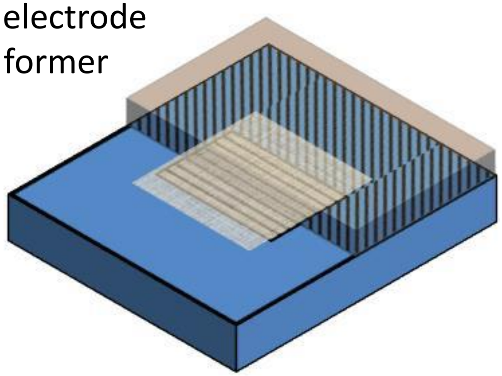


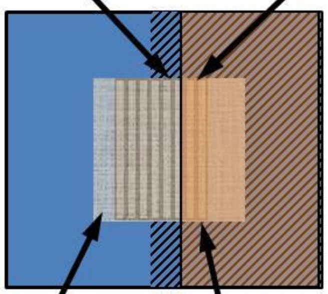
LUNA | Crevice Cell Measurements

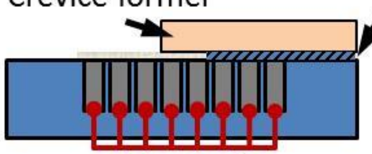
- Segmented electrodes are used to measure spatial distribution of current
  - Sectioned aluminum alloy sheets bonded with GRP prepreg to form multi-electrode array
  - Eight electrodes connected via multichannel ZRA
    - Tests were done using only three or two electrodes
  - Occluded cell aspect ratio of 12.7 : 0.08 (160)


Segmented electrode

Segmented electrode and crevice former

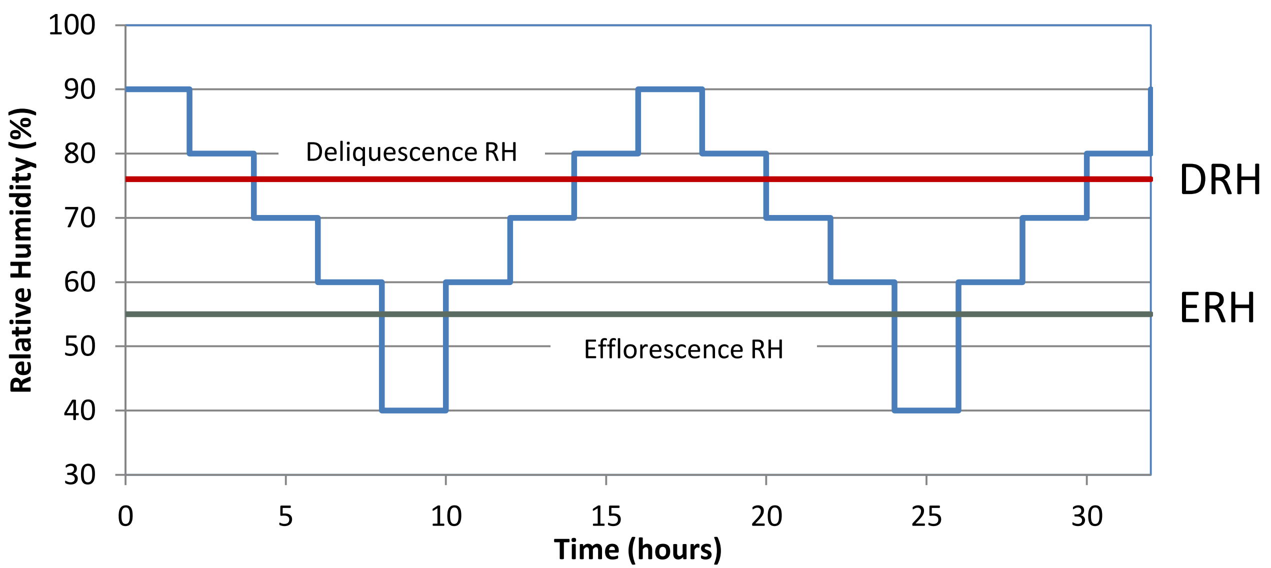






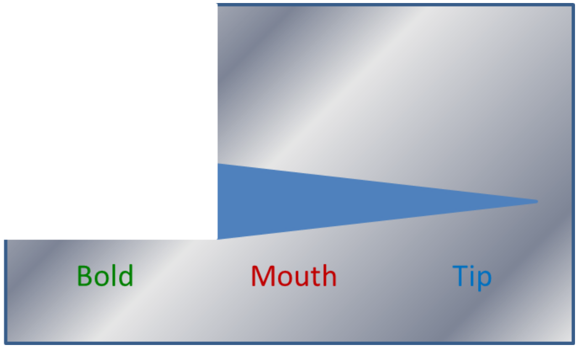
LUNA | Segmented Electrode Testing

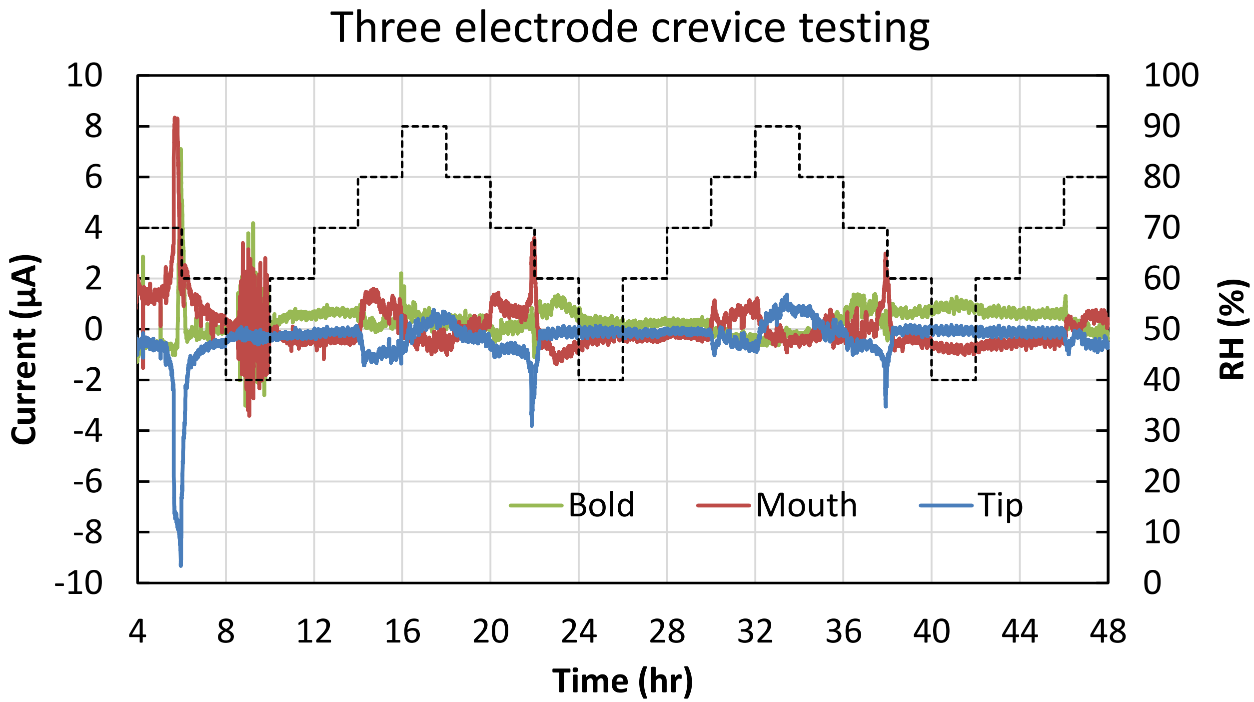
- Tests were done in a programmable RH and temperature cabinet
- The segmented electrodes were exposed to saturated NaCl solution (≈ 6 M NaCl) prior to testing
  - Three-electrode: membrane fully saturated
  - Two-electrode: crevice filled solution
- The segmented electrodes were then subjected to cyclic humidity testing
  - Two hour hold at each RH, three cycles, constant temperature of 35°C



LUNA | Crevice Measurements – Three Electrodes

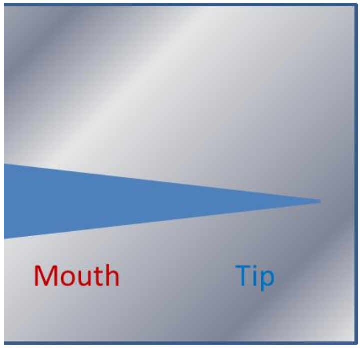
- Cathodic currents at the crevice tip peak during:
  - wetting above the DRH
  - drying between the DRH and ERH
- The largest cathodic currents at the crevice tip occurred during drying

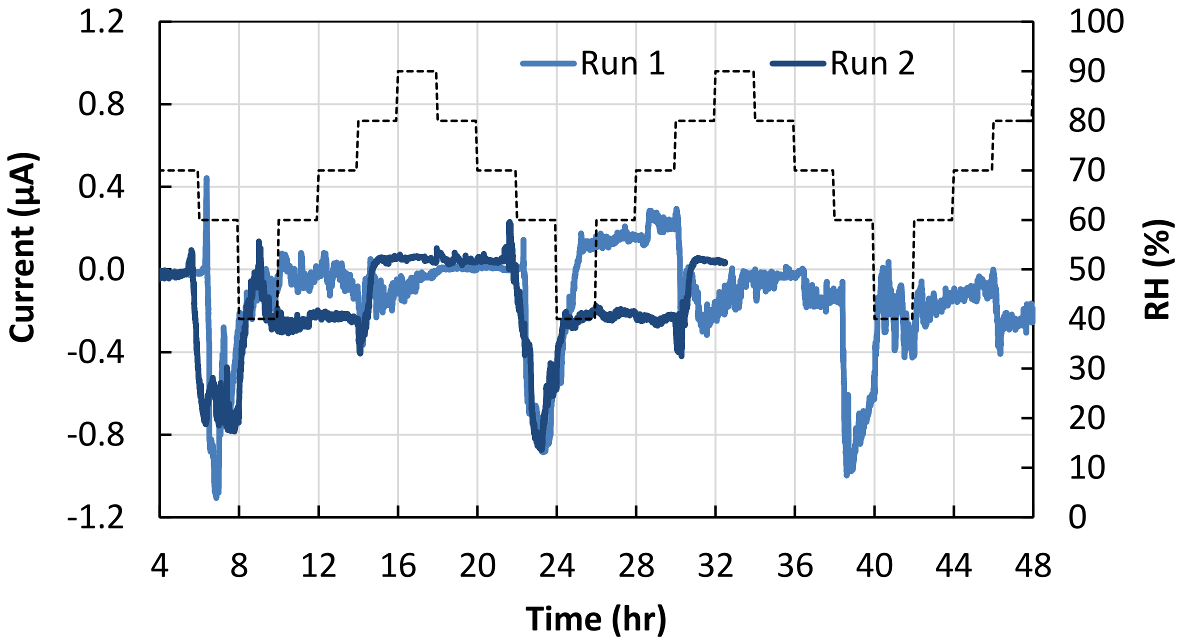




Crevice Measurements - Two Electrodes

- The two-electrode response to RH variation also had high crevice tip cathodic current densities during drying when RH decreased from 70% to 60%
  - Gamry Interface 1000 was used to make two-electrode ZRA measurements



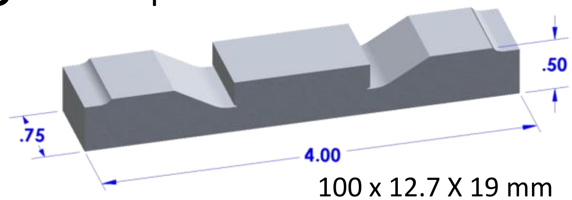


Environment Assisted Cracking

Environmental Cracking

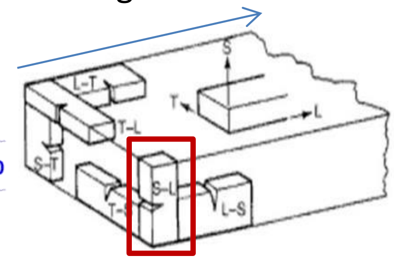
- An instrumented four point bend test sample is used to measure crack growth during atmospheric corrosion tests
- Four point bend test produces S-L cracks in thin plate/sheet materials
  - Don’t need thick plate material to obtain Mode I loading for S-L cracking
  - Useful only for alloys with anisotropic SCC susceptibility

Four Point Bend Test Sample

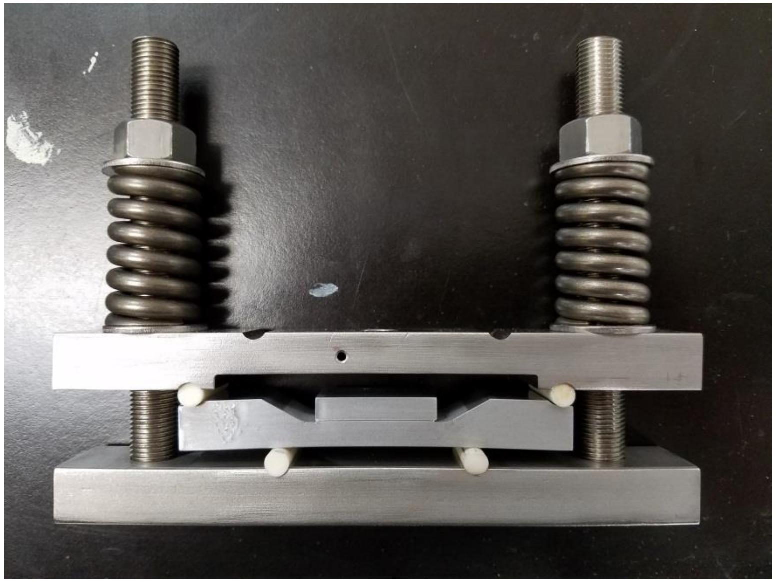


100 x 12.7 X 19 mm

Rolling Direction

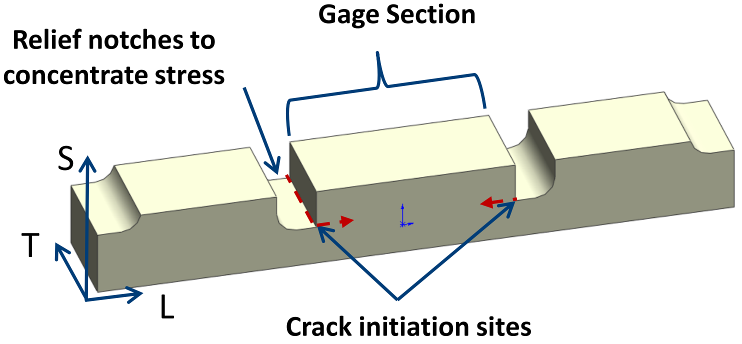


Crack Orientation

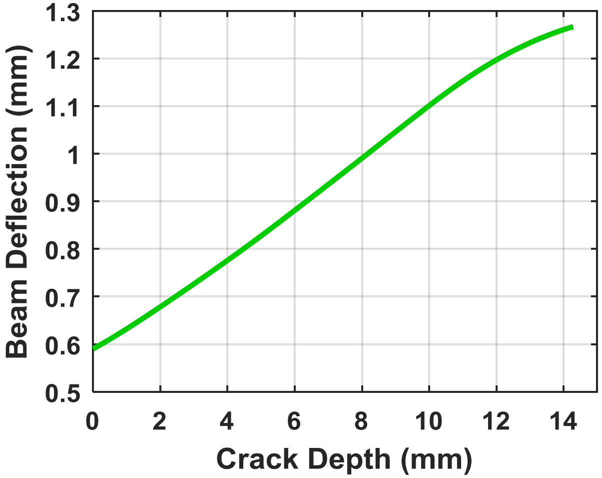


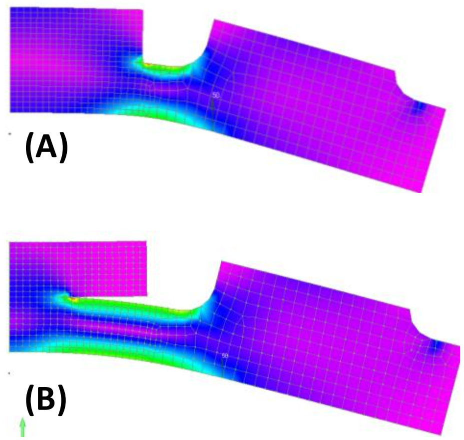
Beam Fracture Sample

- Loading of the beam sample results in mixed mode loading (Mode I and II)
- Crack initiates at relief notches
  - Four point bending promotes balanced cracking from each notch
- Stress intensity decreases with crack length
  - Estimate K_{ISCC}
- Under constant load, beam deflection can be used to estimate crack length

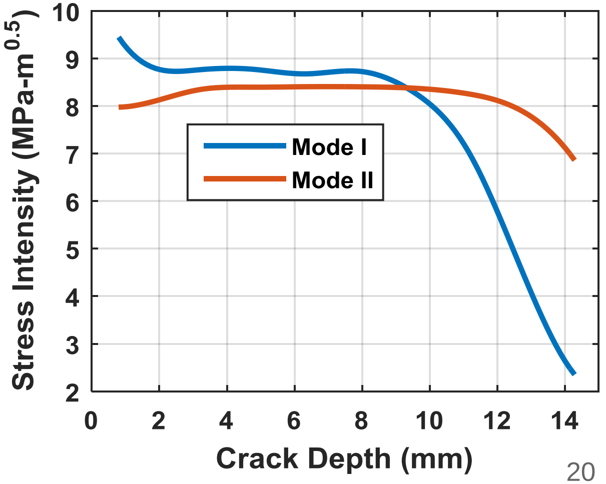


Beam deflection as a function of crack depth





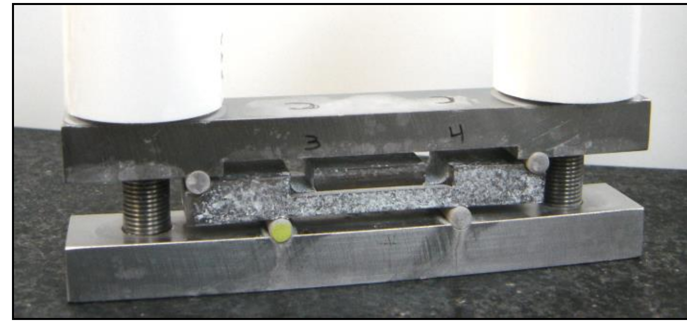
Mode I and II loading as a function of crack depth



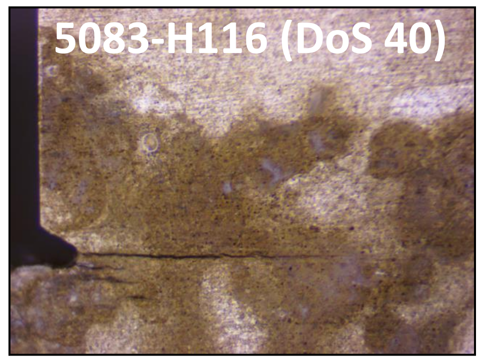
LUNA | Atmospheric Corrosion Bend Tests

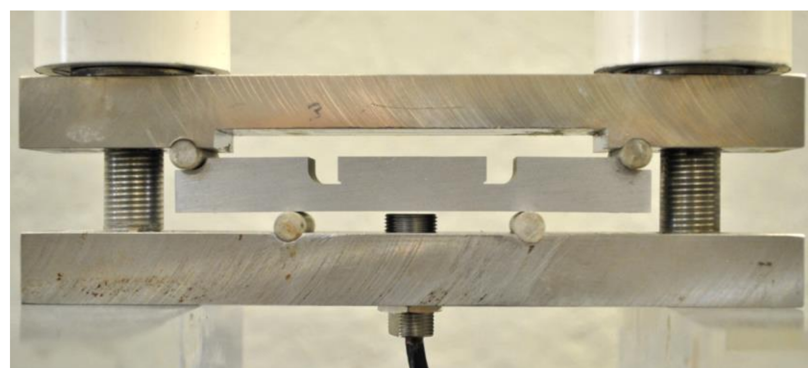
- S-L cracking along the sample mid-plane has been demonstrated using AA5083 and AA7075 alloys
- Cracking lengths of 10 to 15 mm achieved without ductile overload
- Inductive displacement transducer can be used to measure crack length *in situ*

SCC bend fixture following GM9540P salt spray exposure



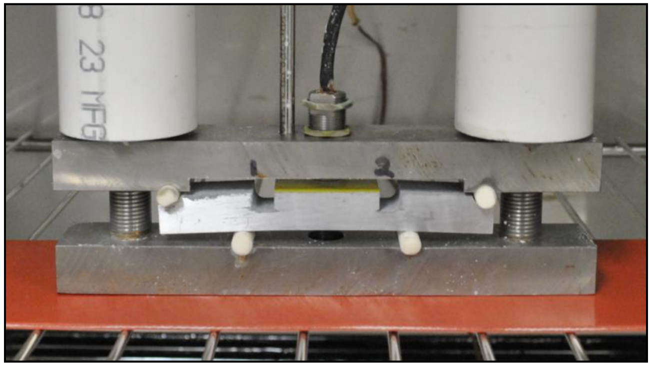
S-L cracks in thin plate



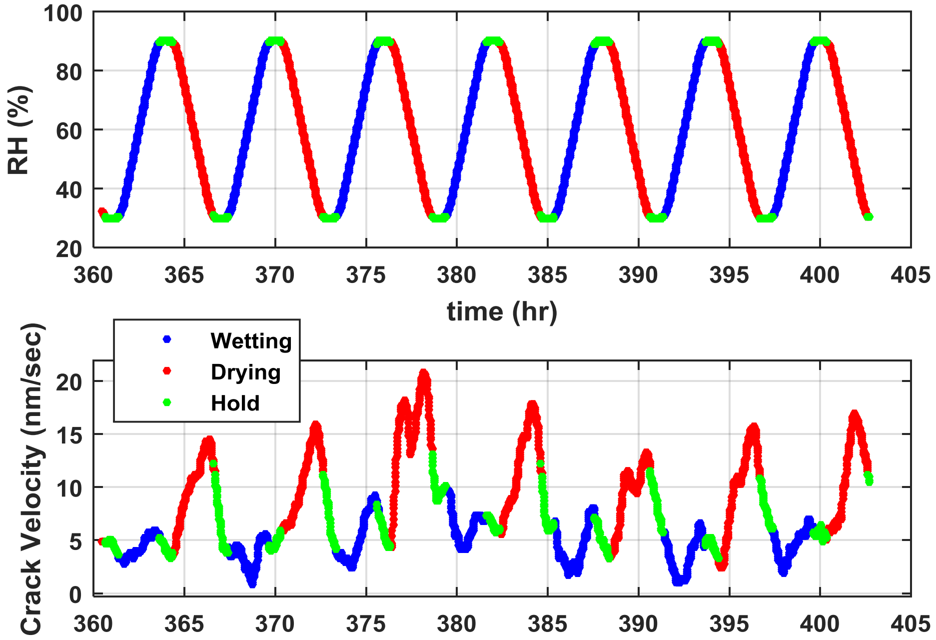


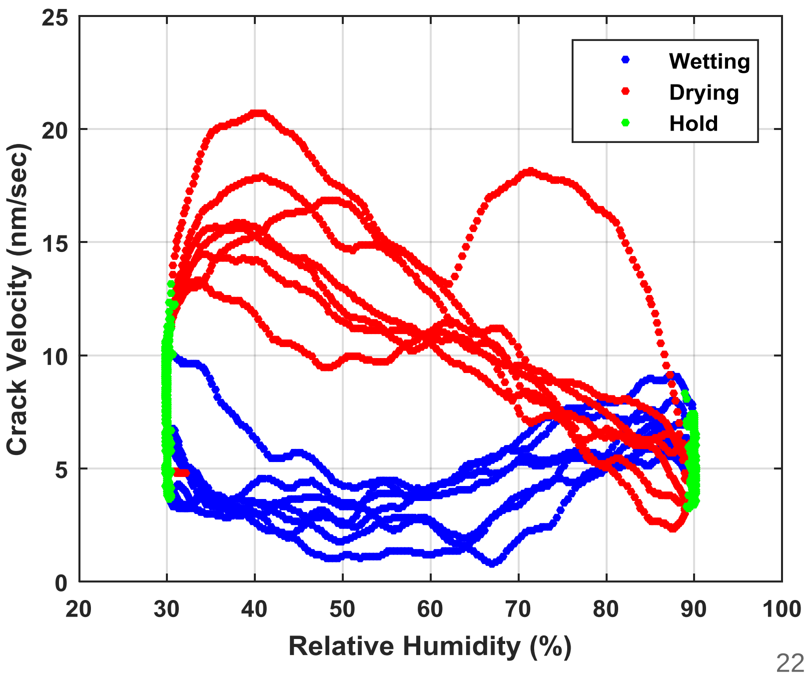
LUNA | Initial Crack Test Results

- Preliminary testing using the instrumented bend test was done with AA7075-T651
  - Spring loaded to KI = 10 MPa-m0.5
  - ASTM G85-A5 for 300 hours for salt loading and initiation
- Measurements then performed in cyclic humidity (RH 30 – 90%) at 35°C
- Peak velocities during drying, around 40% RH



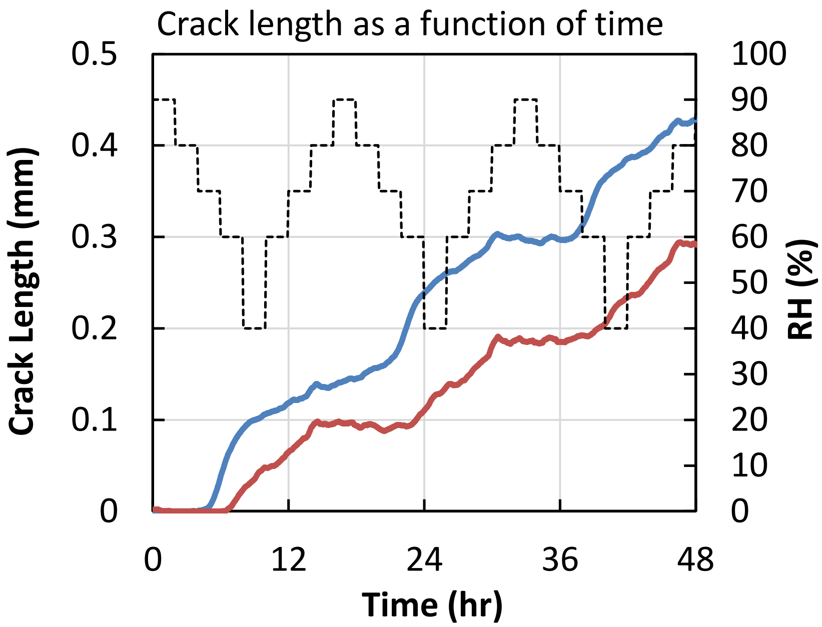
Instrumented Bend Test (AA7075)

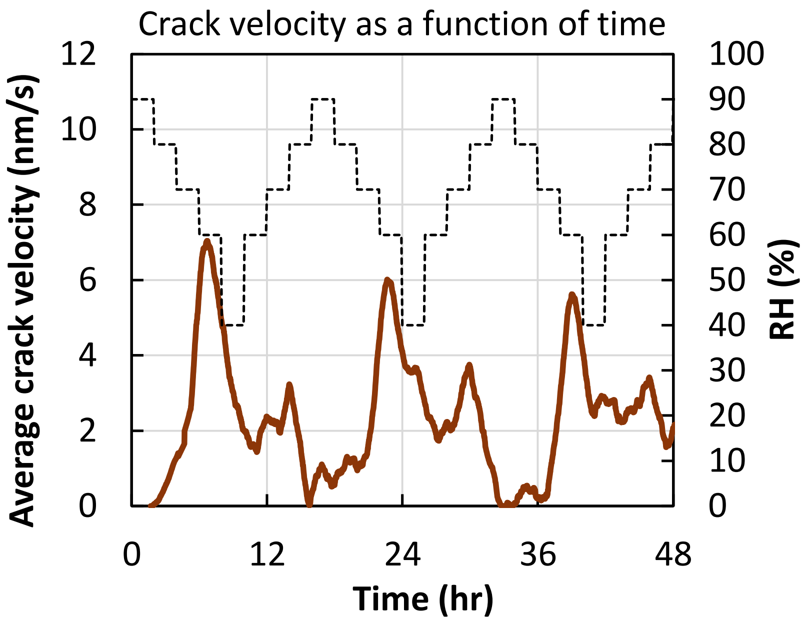




Environment Assisted Cracking Tests

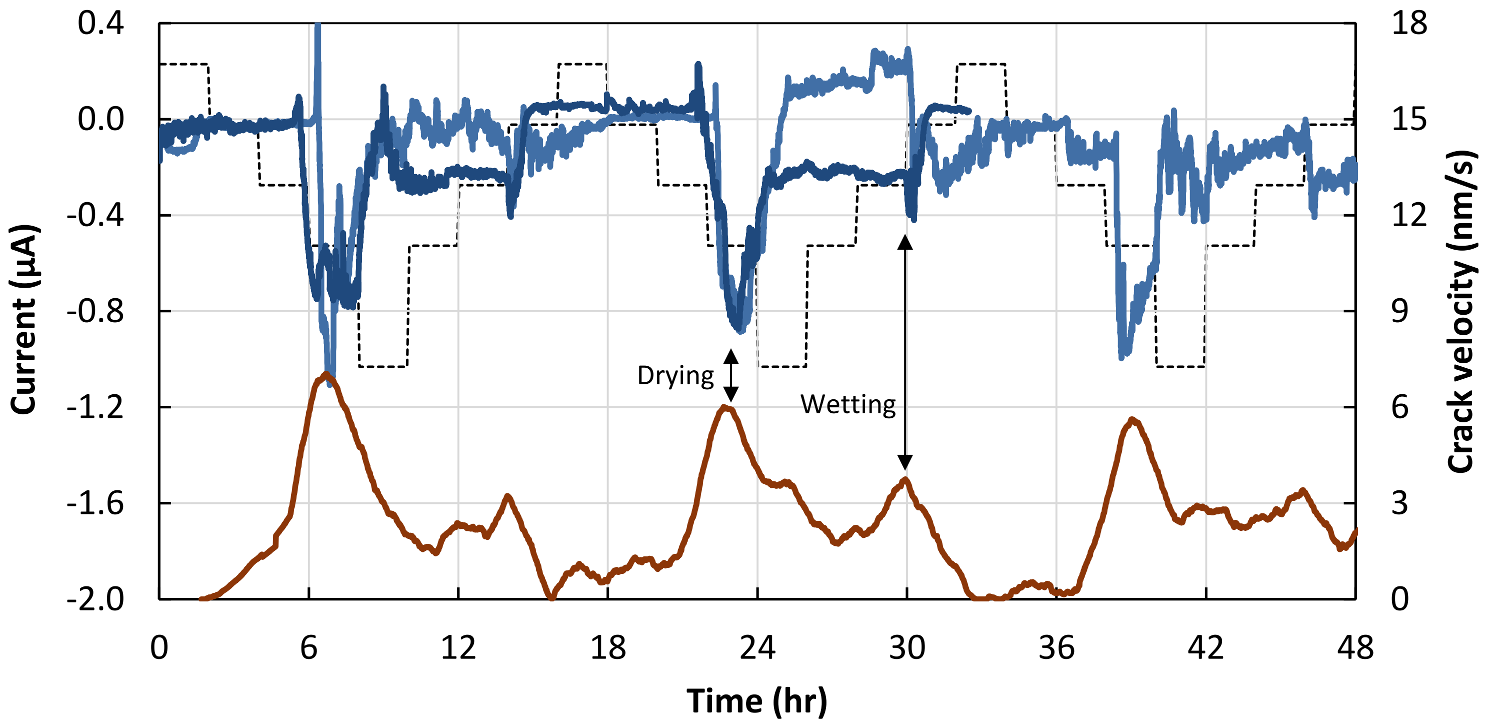
- Bend tests were done using AA7075-T6 samples exposed to the same humidity cycles used for the crevice testing
  - Samples were pre-cracked using cathodic polarization in salt solution
  - Bend test load frames with samples were salted and then placed in humidity cabinet
- Sample displacement was continuously monitored to estimate crack length as a function of time
  - Crack velocity was calculated as average da/dt for the two tests





LUNA | Cracking and Crevice Electrode Data

- Maxima in the crack velocities corresponded to cathodic current peaks at the crevice tip during wetting and drying transitions
  - For wetting, peak above the DRH
  - For drying, peak below DRH and above ERH



LUNA | Discussion

- For high humidity and contaminant (salt loading):
  - Boldly exposed surfaces with thin electrolytes have high corrosion currents
    - Aluminum alloy acts as a non-polarizable electrode and can support high cathodic current densities under thin film electrolyte conditions
  - Crevices with IR drop may not be strongly coupled to boldly exposed surfaces
    - Minimal driving force for aluminum dissolution and acidification within crevices and cracks
- For intermediate humidities
  - Boldly exposed surface may be dry, have poor connectivity to mouth, with high IR drop over surface
  - Crevice mouth supports both ORR and anodic dissolution, with some coupling to the crevice tip
  - Anodic dissolution within the crevice, near the crack mouth, supports acidification of the occluded cell
    - Occluded cell geometry may restrict diffusion / ionic mobility
      - Important difference between hole electrode results versus crevice data
  - Crevice tip may become acidified, deoxygenated, and support both anodic and cathodic reactions
    - Acidification makes hydrogen reduction more favorable
      - Hydrogen reduction at crevice tip may increase pH

LUNA | Discussion

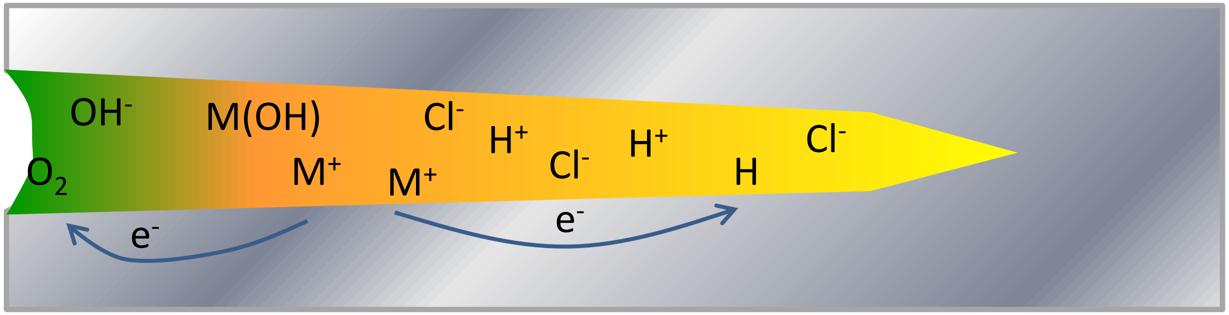
- Cracks or tight crevices may have three zones of activity
  - ORR at mouth
  - Anodic dissolution near the ORR mouth area
    - Hydrolysis lowers pH and promotes hydrogen ion reduction
  - At the crack tip hydrogen ion reduction may be favored
    - Proton reduction may increase pH at crack tip
- Results consistent with known importance of hydrogen in SCC of high strength aluminum alloys

$$O_2 + H_2O + 4e^- \rightarrow 4OH^-$$

$$M \rightarrow M^{n+} + ne^-$$

$$M^{n+} + zH_2O \rightarrow M(OH)_z^{(n-z)+} + zH^+$$

$$H^+ + e^- \rightarrow H_{ads}$$



LUNA | End