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OCRWM Office of Science and Technology and International

Center for Electrochemical Science and Engineering

University of Virginia

Coupled Multi-Electrode Investigation of Crevice Corrosion of 316 Stainless Steel

Presented to:
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Presented by:

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Acronym Table

- ZRA: zero resistance ammeter
- EIS: electrochemical impedance spectroscopy
- CE: counter electrode
- WE: working electrode
- SS: stainless steel
- OCP: open circuit potential
- G: crevice gap
- X_{crit}: critical distance from crevice mouth for initiation of crevice corrosion
- SCE: saturated calomel electrode
- MCA: multi-crevice assembly
- MEA: multi-electrode array
- MMA: multi-channel micro-electrode analyzer (trade name)

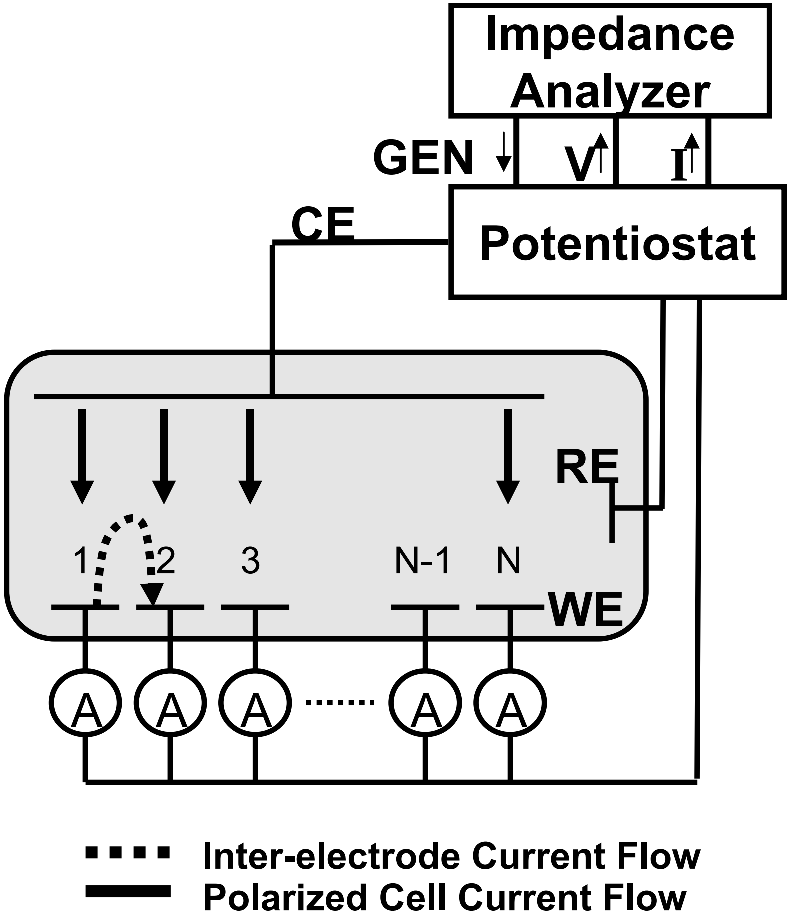
Mechanisms of Crevice Corrosion

- Critical concentration model
  - Crevice solution Cl^- and H^+ concentration must exceed a critical value for crevice corrosion to initiate
  - MnS inclusion dissolve producing S-based ions, which concentration must exceed a critical value to initiate crevice corrosion at the inclusions site
- IR drop model
  - Passive material becomes active in the crevice due to IR drop caused by high resistance of the crevice geometry
- Crevice corrosion initiates at the sites of metastable pitting under the crevice

- Unknown effects on initiation and propagation of some factors such as: proximate cathode, limited cathode and semi-permeable crevice former

Multi-Electrode Array (MEA)

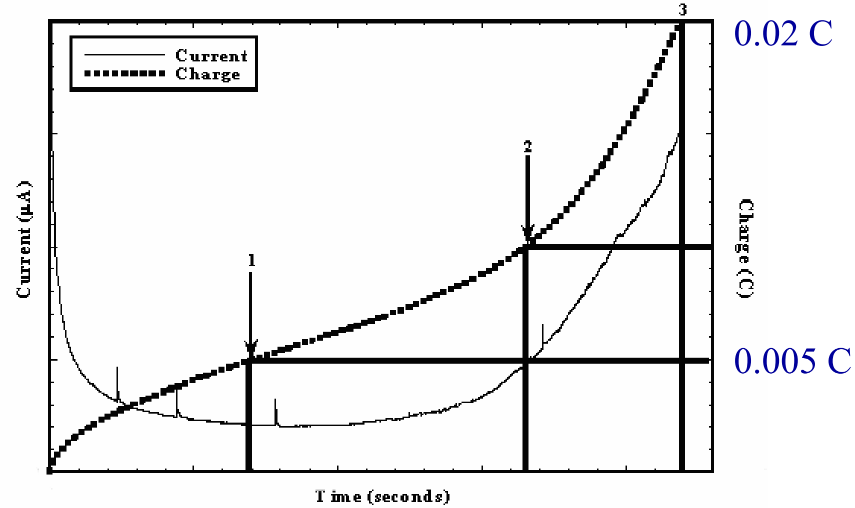
- Multi-electrode array is a system comprised of up to 100 coupled electrodes through ZRA
- Close packed array is made of 100 wires, 5 rows of 20. Each wire is polyimide coated to insure insulation
- The 100 electrodes are divided in 10 groups of 10
- The current is individually measured on each electrode
- Each group potential can be individually controlled
- EIS capable MEA system has been recently developed



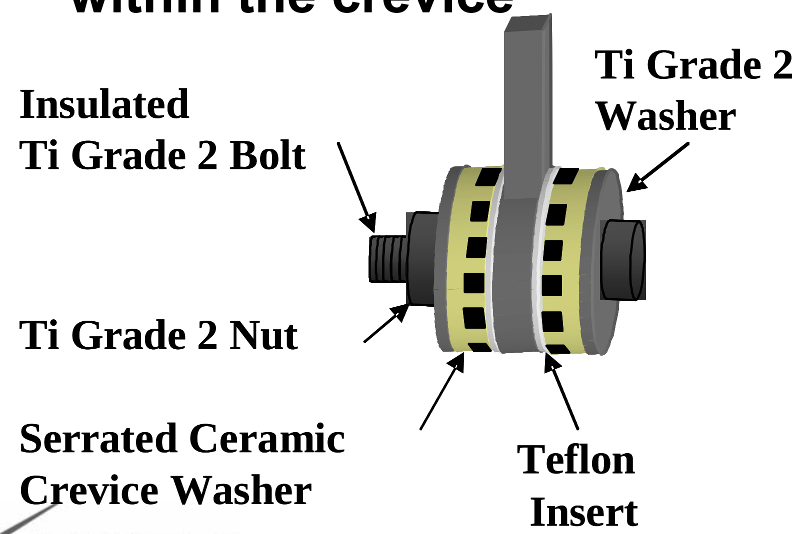
From **Development of a Multielectrode Array Impedance Analyzer for Corrosion Science and Sensors**, K.R. Cooper, M. Smith, J.R. Scully, N.D. Budiansky, NACExpo 2006, **06674**

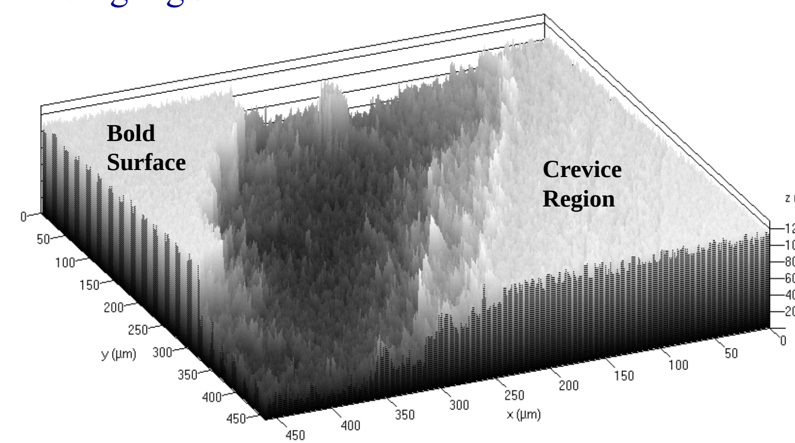
Uninstrumented Multi-Crevice Assembly (MCA)

- **Example of the current and charge data that can be obtained using MCA**
- **Does not provide detailed spatial-temporal resolution for electrochemical data**
- **Current measured cannot be related to a localized area within the crevice**



Ni-Cr-Mo based alloy in 5 M lithium chloride, 0.26 M sodium sulfate and 0.24 M sodium nitrate, pH=2.75 at 95 °C at 5 mVAg/AgCl



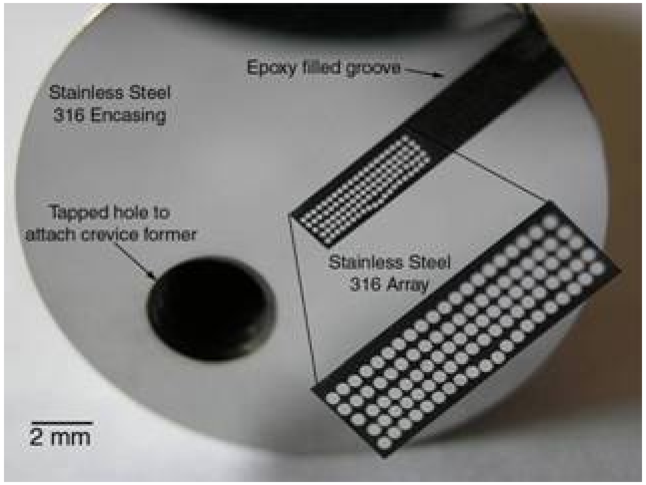


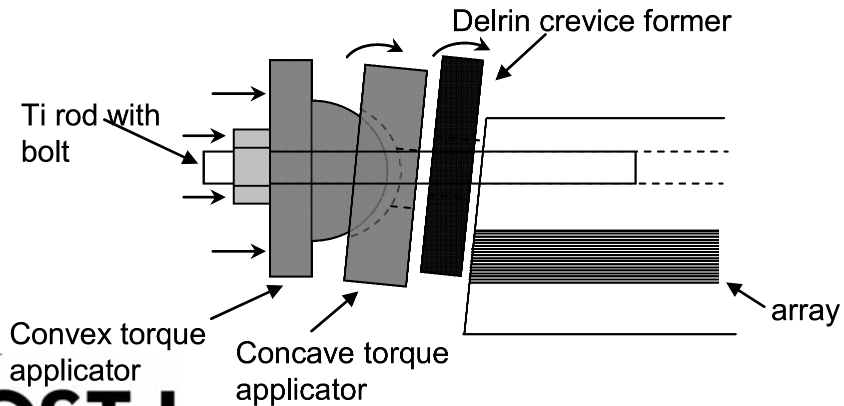
Post-test: Ni-Cr-Mo 625, after an accumulated charge of 4 C at 400 $mV_{Ag/AgCl}$ at 95 °C

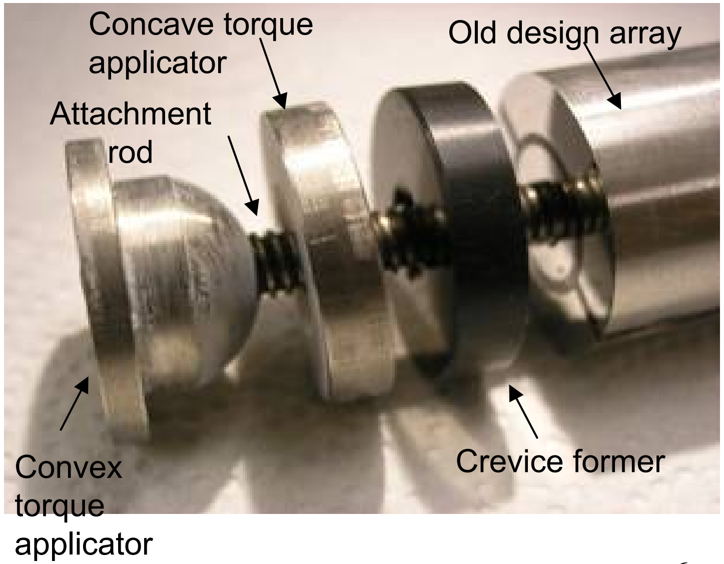
B.A. Kehler, J.R. Scully, Corrosion 61, (2005): p. 665.

Array in Practice

- The array is mounted in a metallic rod of similar composition to the wire to emulate a flush-mounted setup. This results in a surface-volume ratio similar to planar electrode crevice
- A crevice former setup as shown on the right is applied onto the array using a fixed torque
- Concave and convex applicators are used so the torque is homogeneous and the crevice gap is constant over the surface.
- Arrays are made of polyimide coated 316 Stainless Steel wires (0.25 mm diameter) and 1" diameter 316 SS rod.
- Crevice former is made from Delrin and the torque application setup is Titanium made

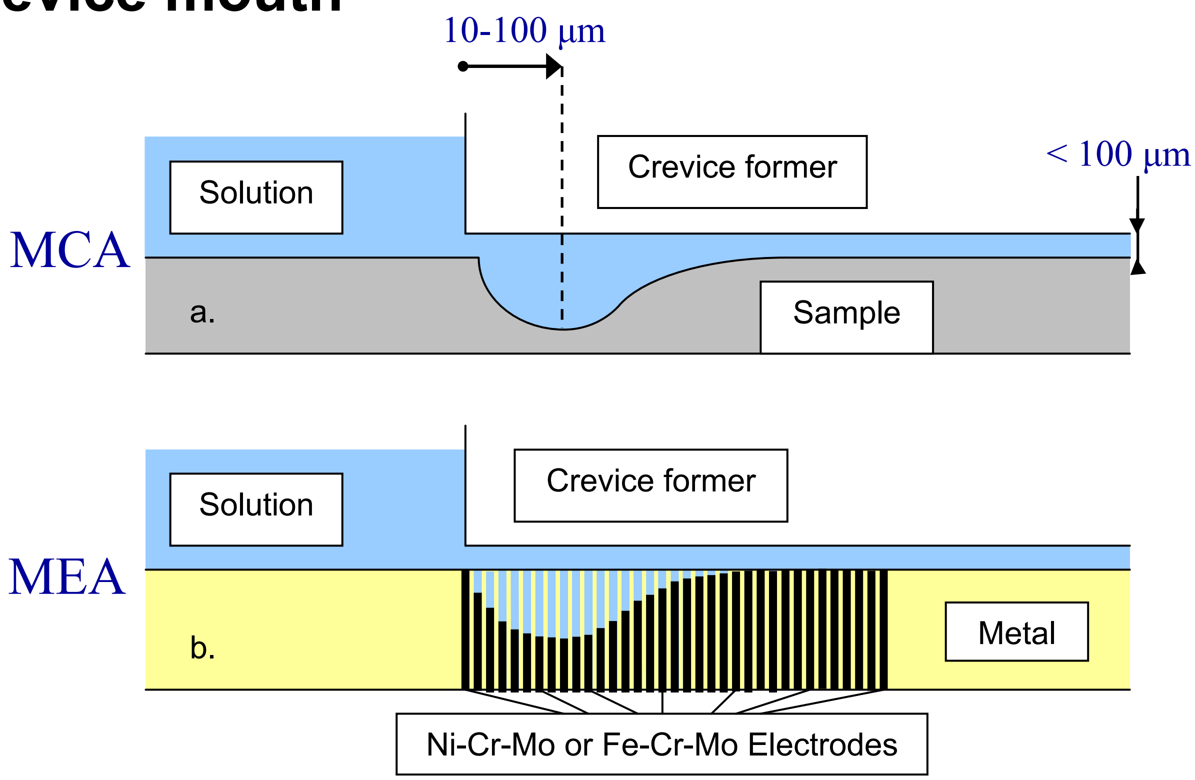






MCA vs. MEA

- **Schematic of the expected profile of attack for same test conditions**
- **Every electrode of the MEA provides the current at a certain distance from the crevice mouth**
- **Allow a discrete current measurement over the surface**
- **EIS enables examination of film breakdown /repair process through interpretation of capacitance**



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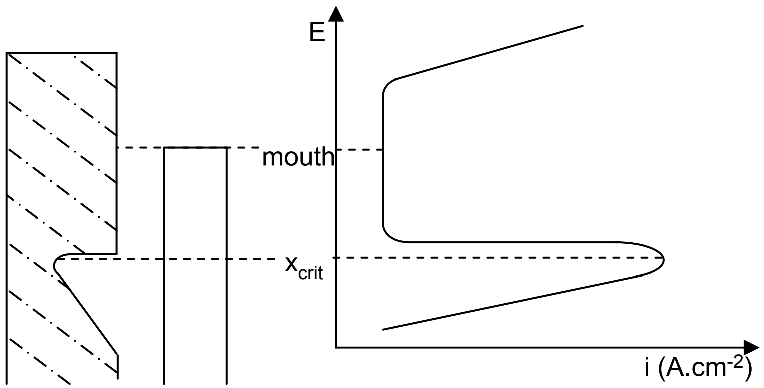
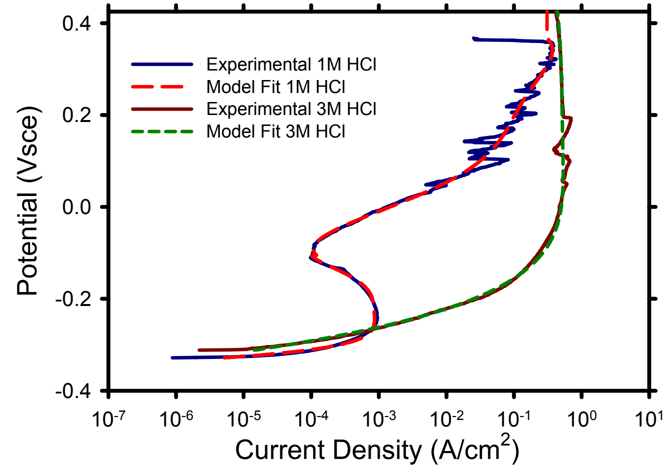
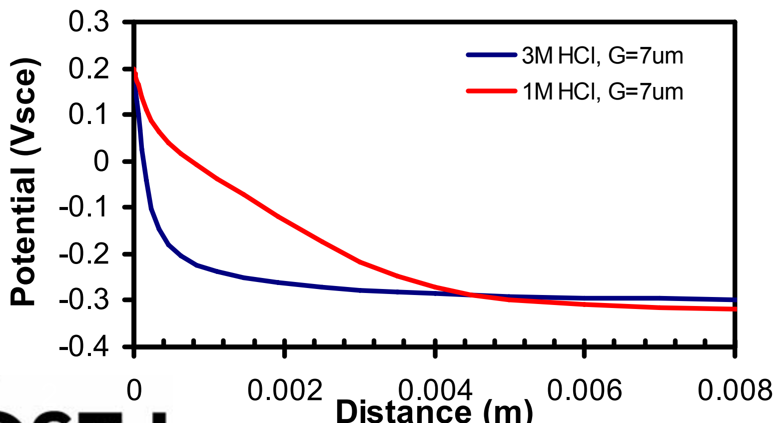
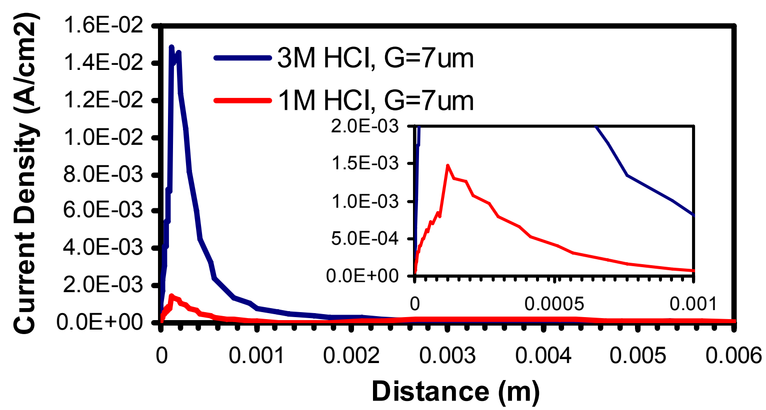
Scaling Laws – Definition and Derivation

- **Scaling laws are used to rescale crevice electrochemistry to a larger system, so larger electrodes using commercial alloys can be used (250 μm diameter)**
- **Current assumptions: constant critical concentration and pH inside the whole crevice**
- **Derived from micro-electrode anodic polarization data in acid solutions to simulate crevices**



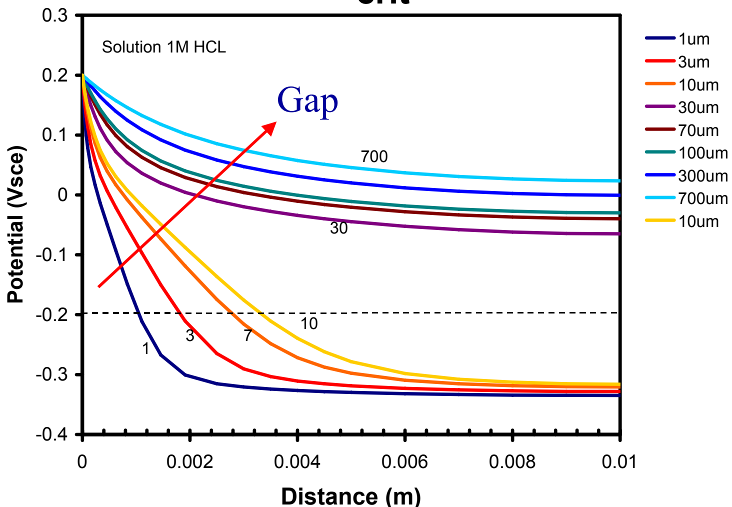


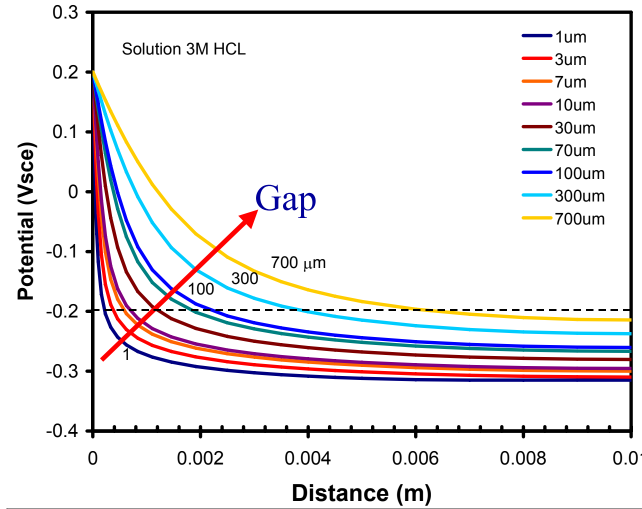


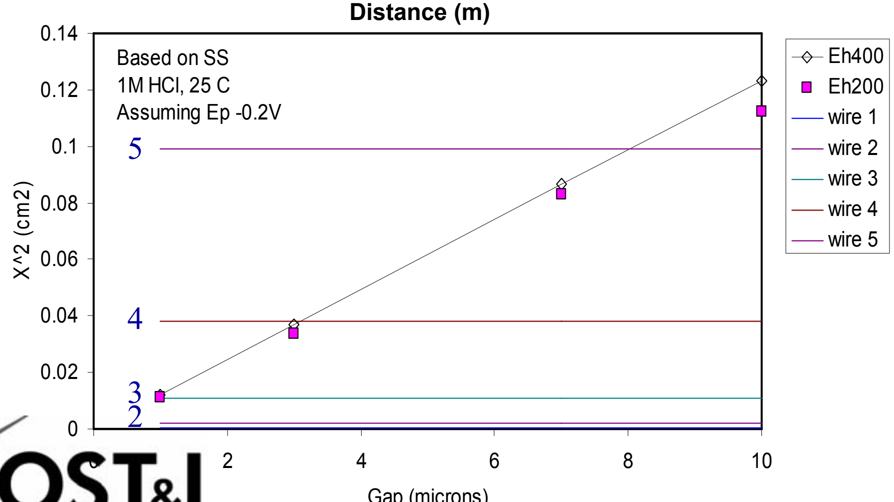


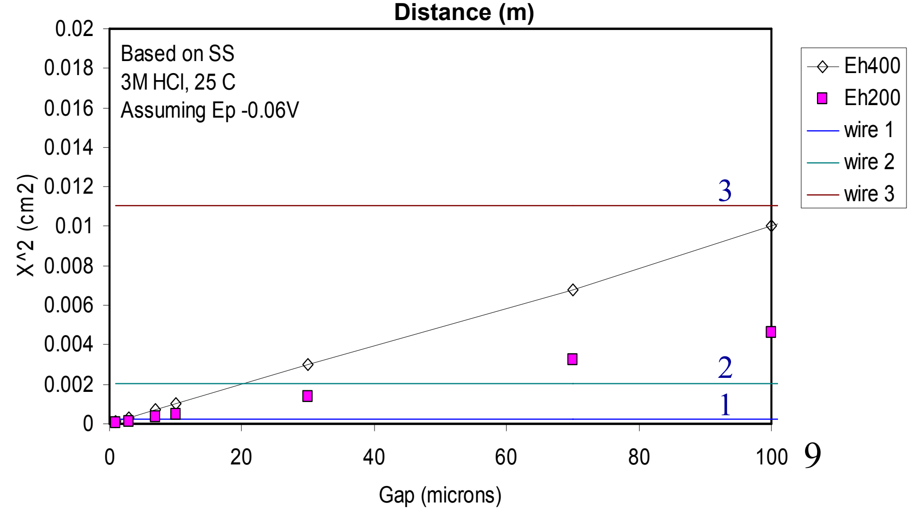
Scaling Laws – Application to MEA

- **Evolution of potential with distance inside crevice at different gap size**
- **From this the x_{crit}^2 vs. G scaling law is plotted**



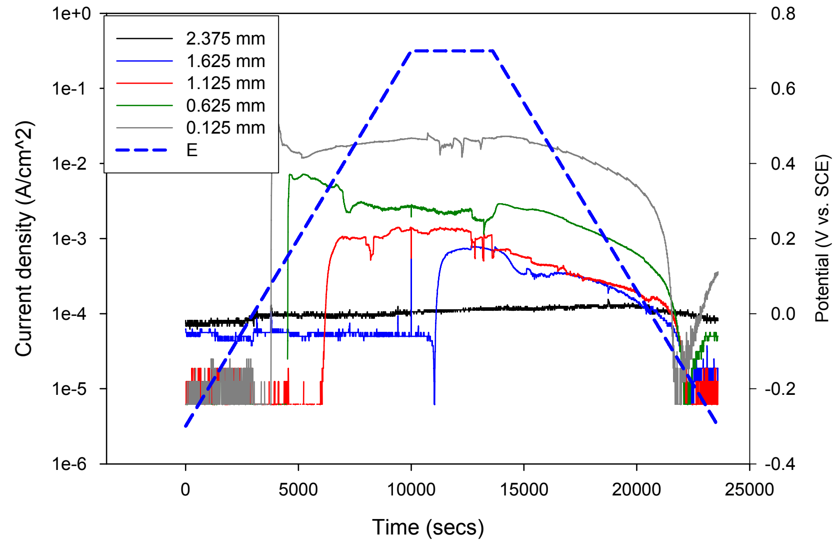


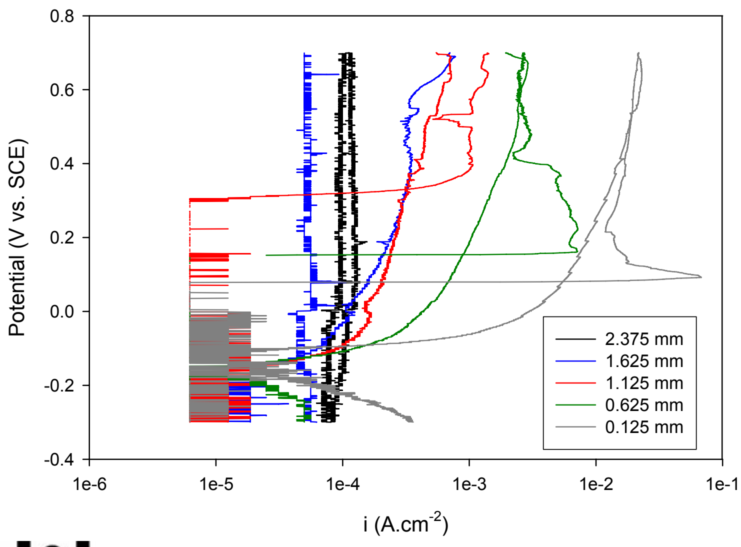


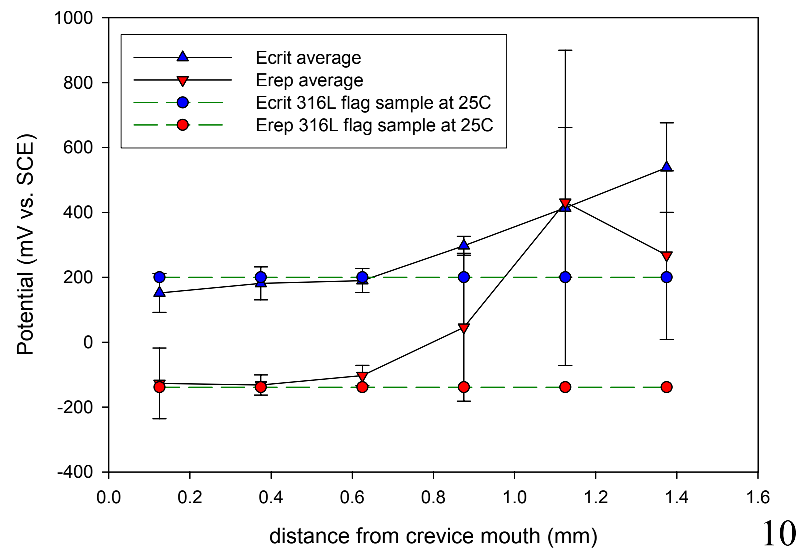


Polarization Curve Under crevice

- **Setup (316 SS array):**
  - **From -0.1 mV_{OCP} to 0.7 V_{SCE} @ 0.1667 $mV.sec^{-1}$**
  - **1 hr @ 0.7 V_{SCE}**
  - **From 0.7 mV_{SCE} to -0.1 V_{OCP} @ 0.1667 $mV.sec^{-1}$**
  - **0.6 M NaCl at 50 °C**
- **Potential at which the first wire initiates is E_{crit} for a conventional MCA test**
- **Potential at which the last wire repassivates is E_{rep} for a conventional MCA test**
- **The maximum current inside the crevice is ohmically controlled**

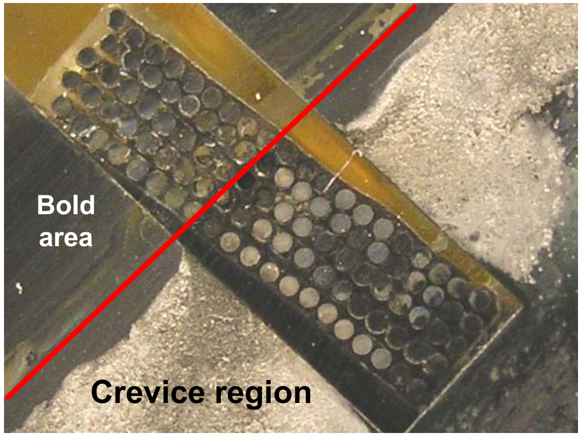




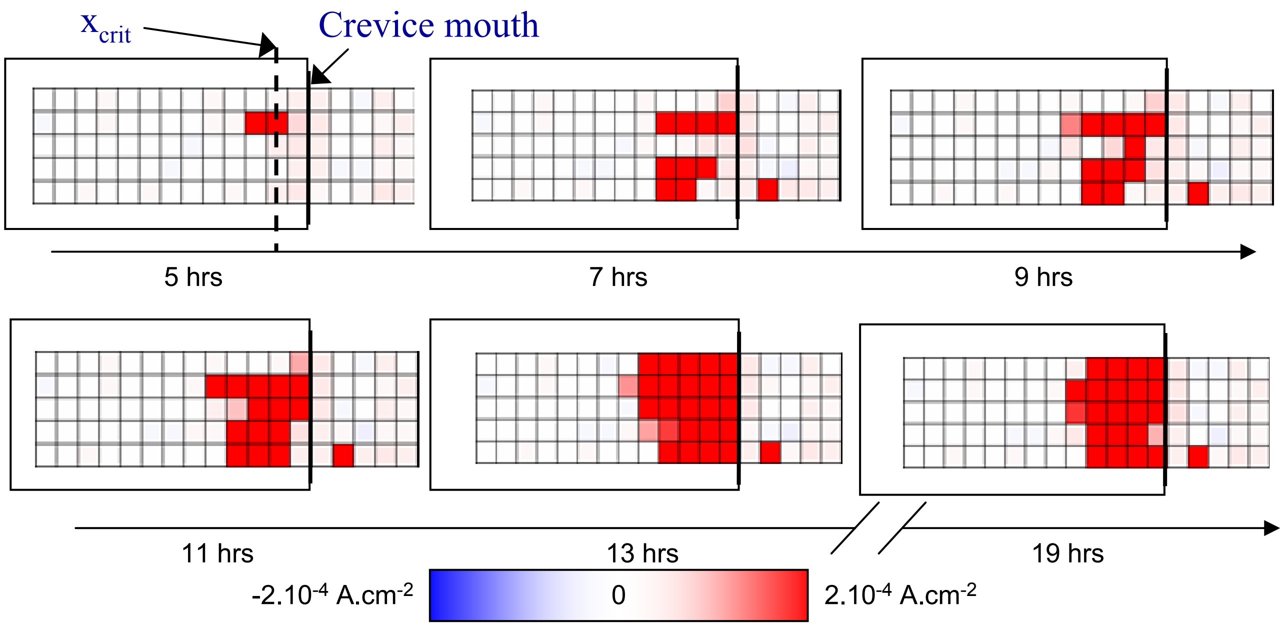


MEA Crevice Corrosion – Current Map

- **Setup (316 SS array):**
  - 0.6 M NaCl; aerated; 50 °C; 25 in-lbs torque
  - 2 days at OCP; 1 day at -25 mV_{SCE}; initiation at 0 mV_{SCE}
- **Initiation at the crevice mouth spreading inwards and sideway**
- x_{crit} **is located on the second row**

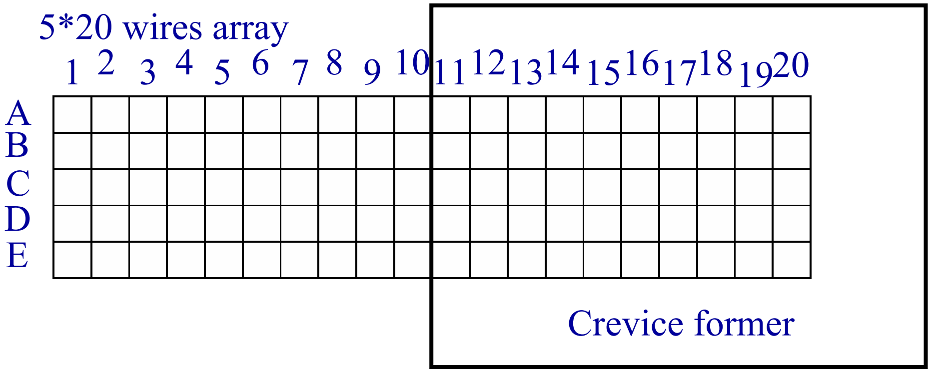


Initiation and propagation of crevice corrosion at 0 mV_{SCE}, current mapping

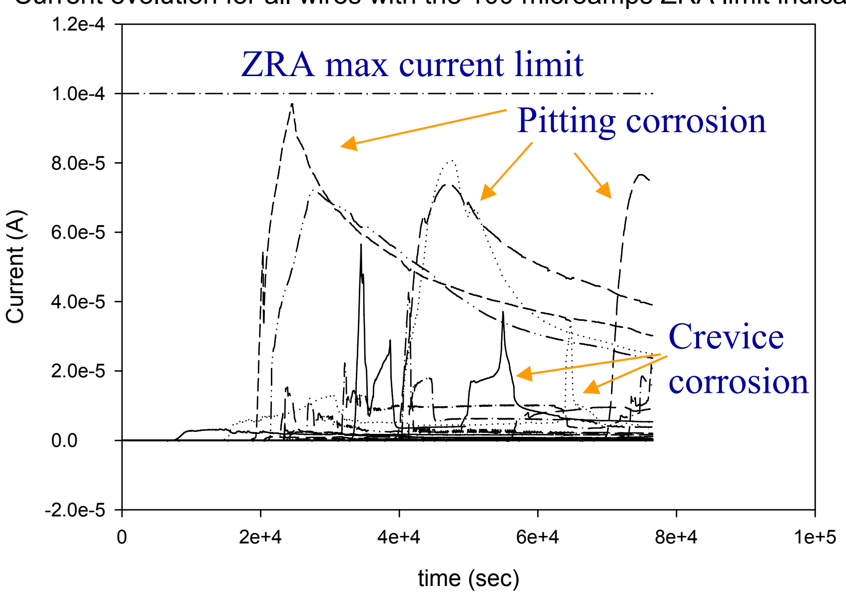


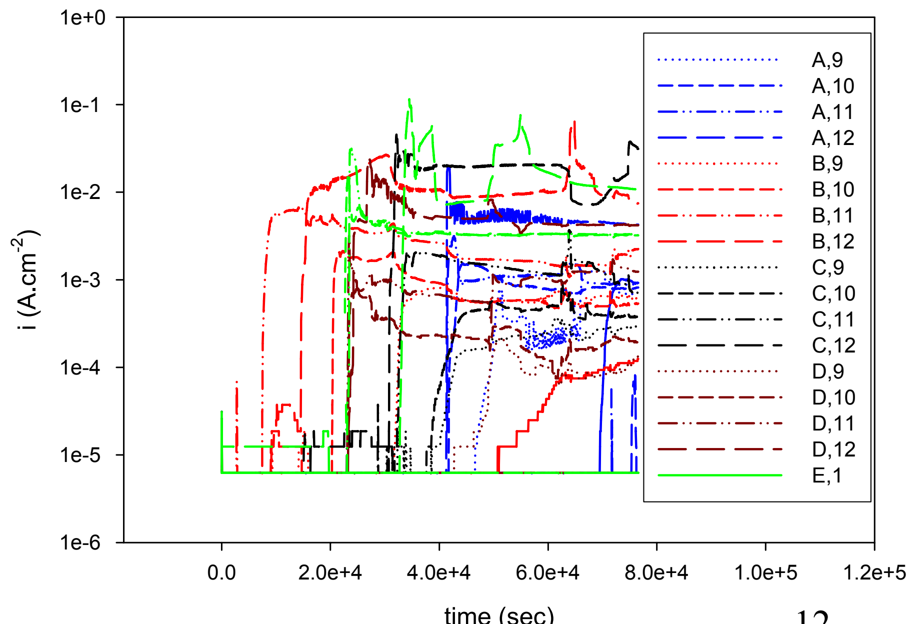
MEA Crevice Corrosion – General Data

- **MEA current measurement is below the ZRA maximum current**
- **Pitting and crevice corrosion display different current profile**



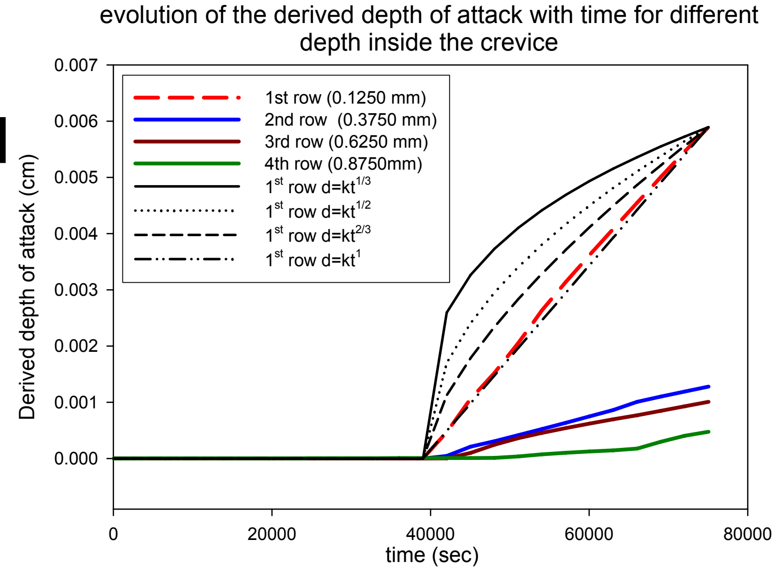
Current evolution for all wires with the 100 microamps ZRA limit indicated

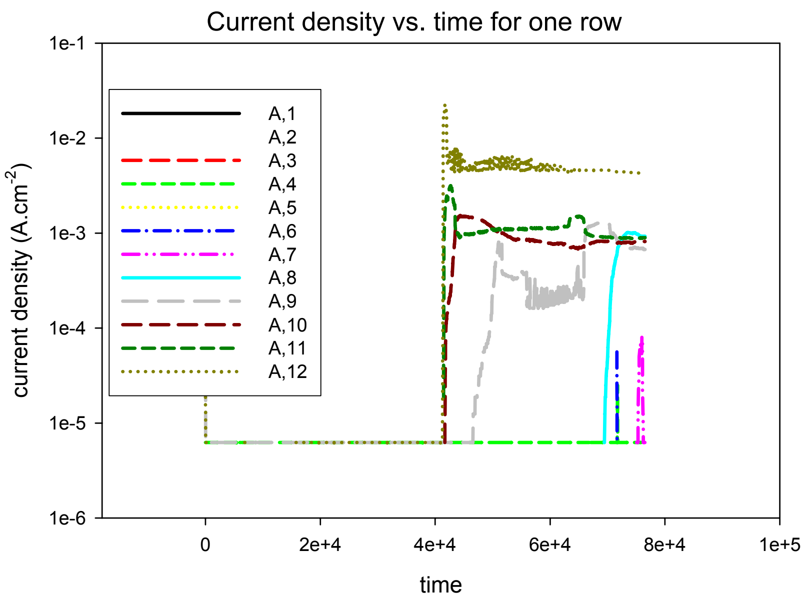


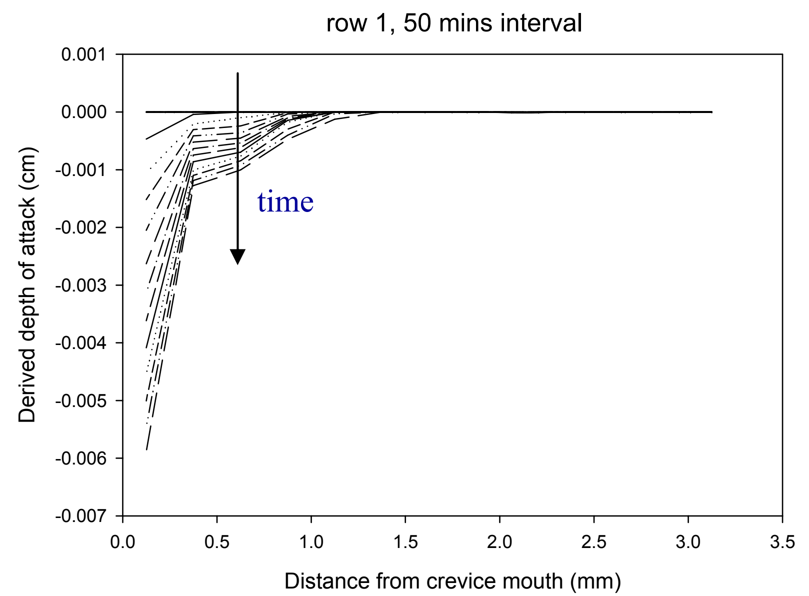


MEA Crevice Corrosion – Row A Analysis

- **From the current density at $0mV_{SCE}$, depth can be derived**
- **Current is net current, i.e. local cathodic current not accounted for here**
- **Derived results are realistic**

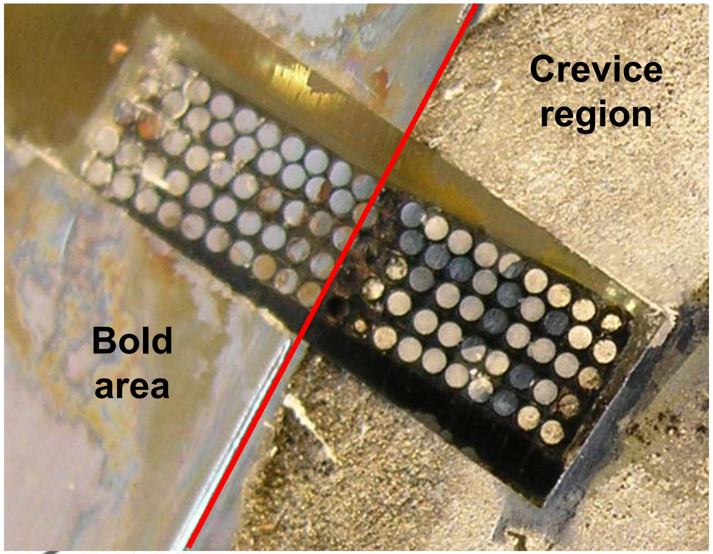


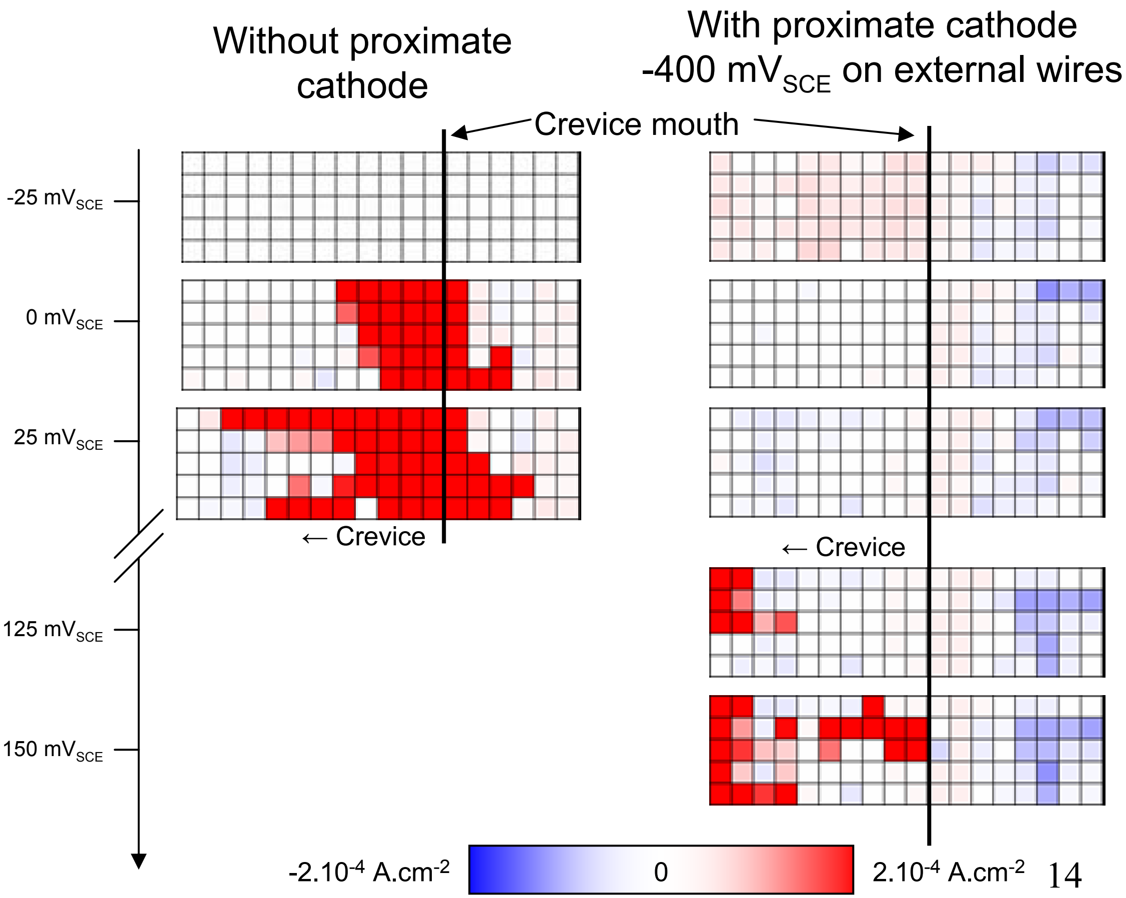




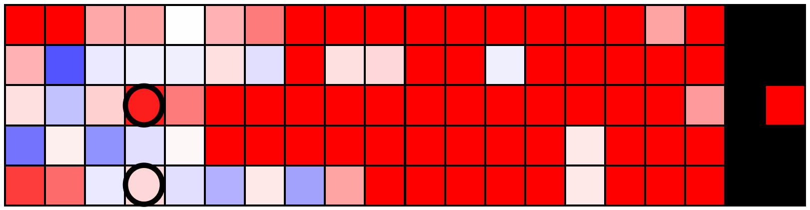
Proximate Cathode MEA

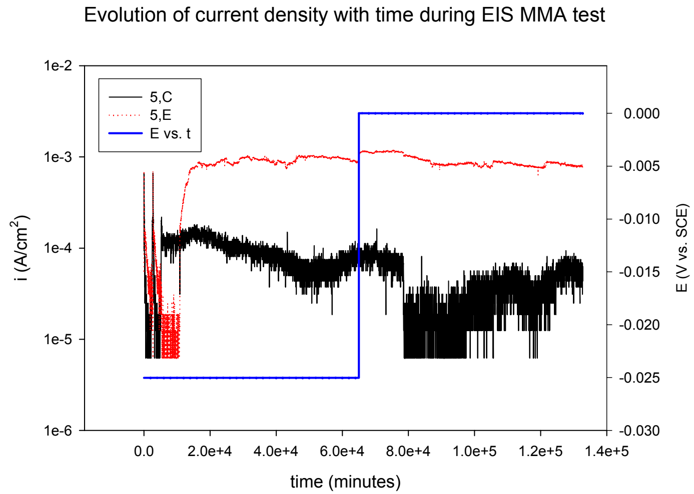
- Proximate limited cathode in the case of thin film solution Initiate at much higher E when external proximate cathode
- Initiate further inside and spread outwards
- Setup (316 SS array):
  - 0.6 M NaCl; aerated; 50 °C; 25 in-lbs torque
  - 2 days at OCP; 1 day increment of 25 mV up to 150 mV_{SCE}; initiation at 125 mV_{SCE}
  - Outside wires at -400 mV_{SCE}

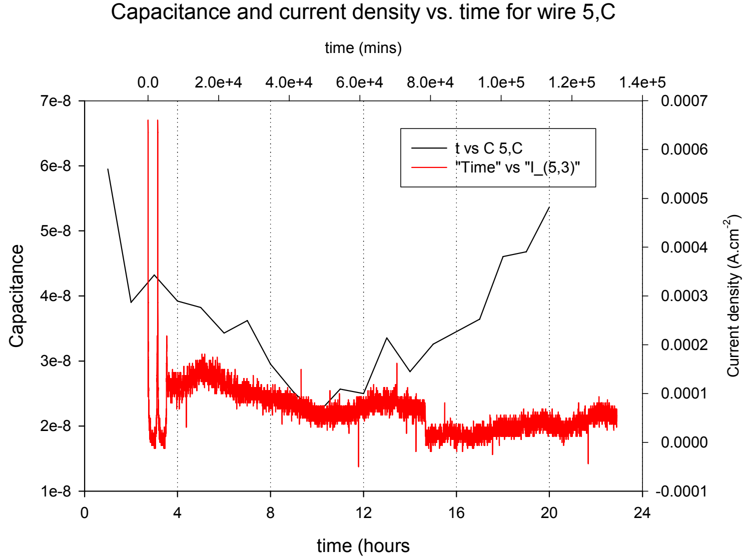




EIS MEA







More results to be announced

Conclusion

- MEA is a powerful instrument to study localized corrosion with spatial resolution and can easily be used to study crevice corrosion
- Use of scaling laws to increase spatial resolution up to the array dimension enable use of commercial electrodes and conduct spatially resolved crevice test
- The critical and repassivation potential found wit MEA are in agreement with previous MCA experiments
- The distance x_{crit} can be determined at the early stages of crevice corrosion
- Current density can be monitored relative to the distance from the crevice mouth and depth of attack can be derived
- With the presence of an external proximate cathode, initiation requires a much higher potential inside with an outwards growth. While growth is also slower

Acknowledgements

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