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Applications Of Multi-electrode Techniques To Aqueous And Atmospheric Corrosion Testing

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Benefits of using multielectrode measurements in corrosion and electrochemical research.

Increased data density vs. serial experimentation

⇒ pitting studies on pure aluminum & electronics degradation

Reduced sample cost and improved reproducibility

⇒ pitting under atmospheric conditions

Access to local corrosion behavior

⇒ pitting of Al-Cu at open circuit

Combinatorial discovery

⇒ Pt-Ru electrodes for glucose oxidation

Viability of a multielectrode approach is dependent on:

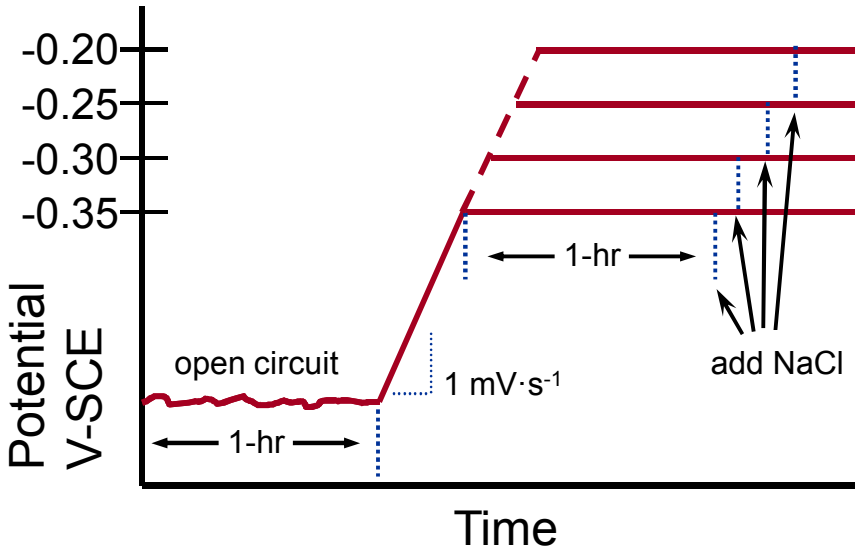
- Time or monetary savings
- Availability of otherwise inaccessible data
- Cost and availability of suitable test equipment and samples

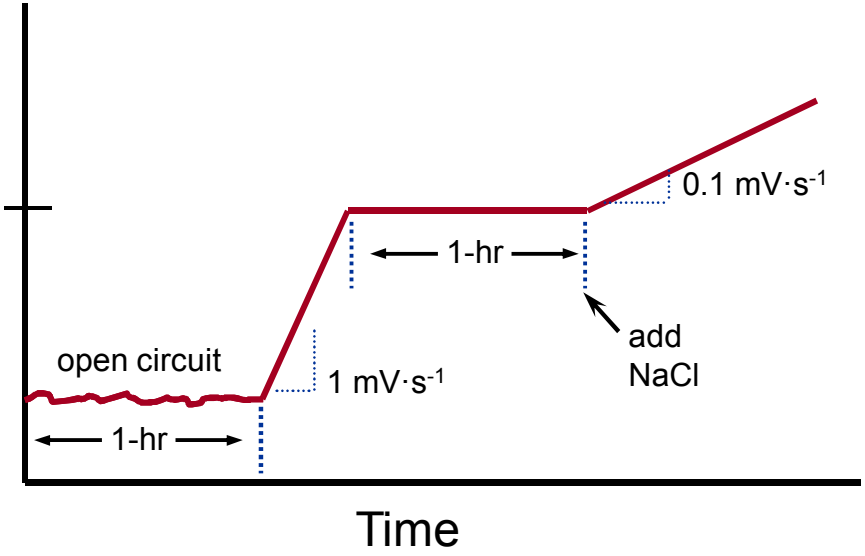
Case 1: high data density is required to establish distributions of pitting behavior for fundamental studies.

Linking pitting potential distribution to induction time data

$$\lambda(E) = A\,\beta\,\exp(E\,\gamma) \quad \Rightarrow ? \Rightarrow \quad CDF(E) = 1 - \exp\left\{-\frac{A\beta}{\nu\,\gamma}\left[\exp(\gamma\,E) - \exp(\gamma\,E_1)\right]\right\}$$

$$\lambda = -\left.\frac{d\log(P_s)}{d\tau}\right|_E$$





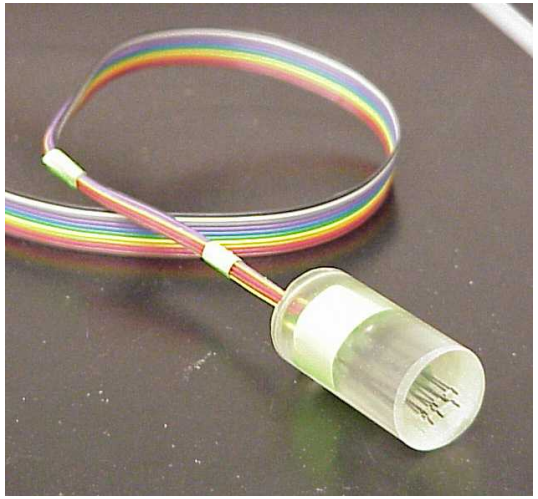
Mutliple potentiostatic experiments required at each potential to construct survivability plot.

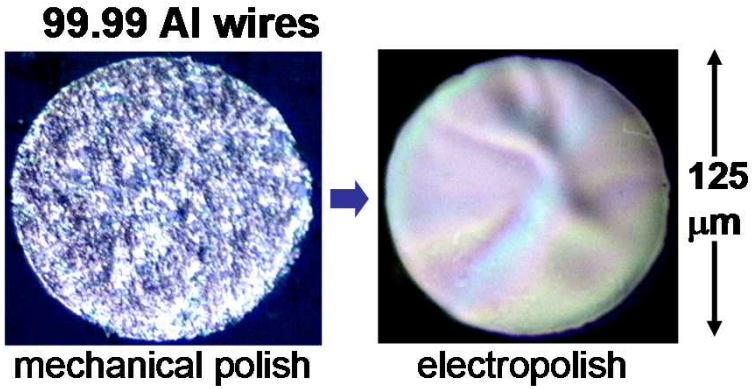
Multiple polarization curves required to construct E_{PIT} CDF.

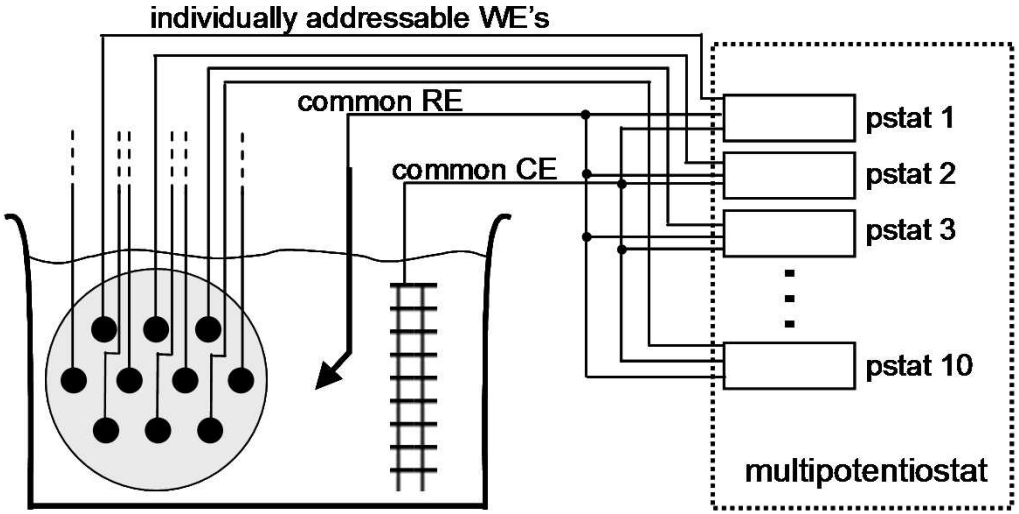
Sample configuration and experimental conditions for multielectrode pitting studies.

Material:
- 99.99 Al

Electrode Preparation:
- Coat with electrophoretic paint (77°C Cure)
- Attach ribbon cable
- Mount in epoxy
- Mechanical polish to 4000 grit SiC
- Electropolish in 75%MeOH, 20% perchloric acid, 5% glycerol



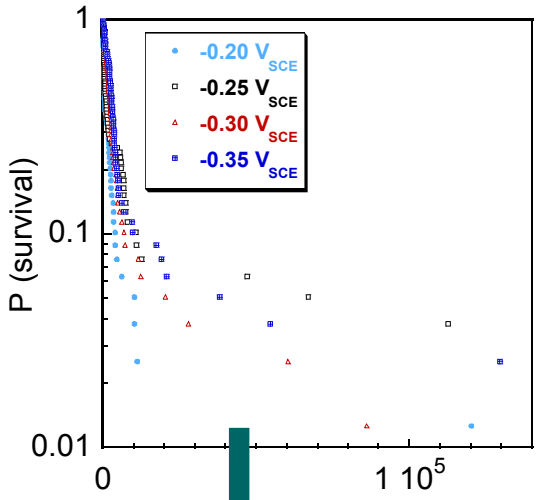


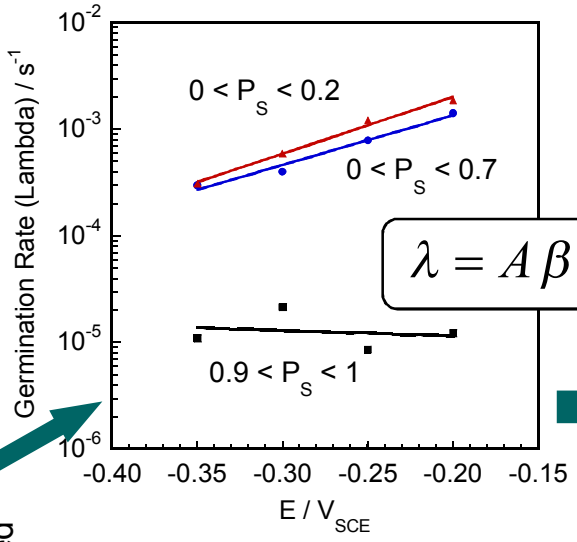


Test environment:
- 50 mM NaCl (pH 6.5)
- 25°C

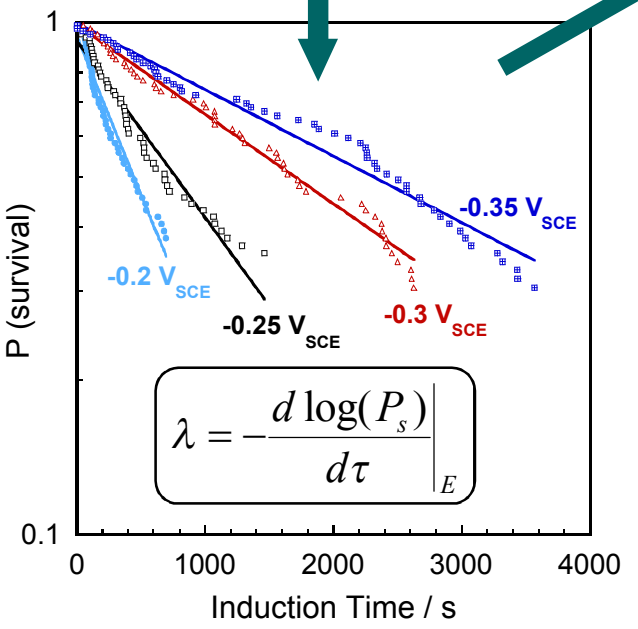
Multielectrode testing generated sufficient data to demonstrate the relationship between τ and E_{PIT}.

99.99 Al
125 μm ϕ
50mM NaCl
25°C

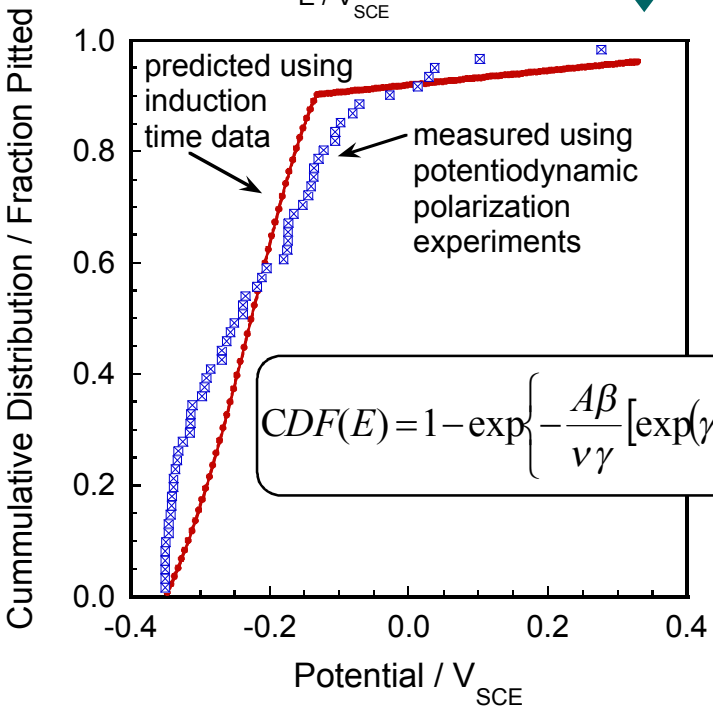




$$\lambda = A\,\beta\exp(E\,\gamma)$$

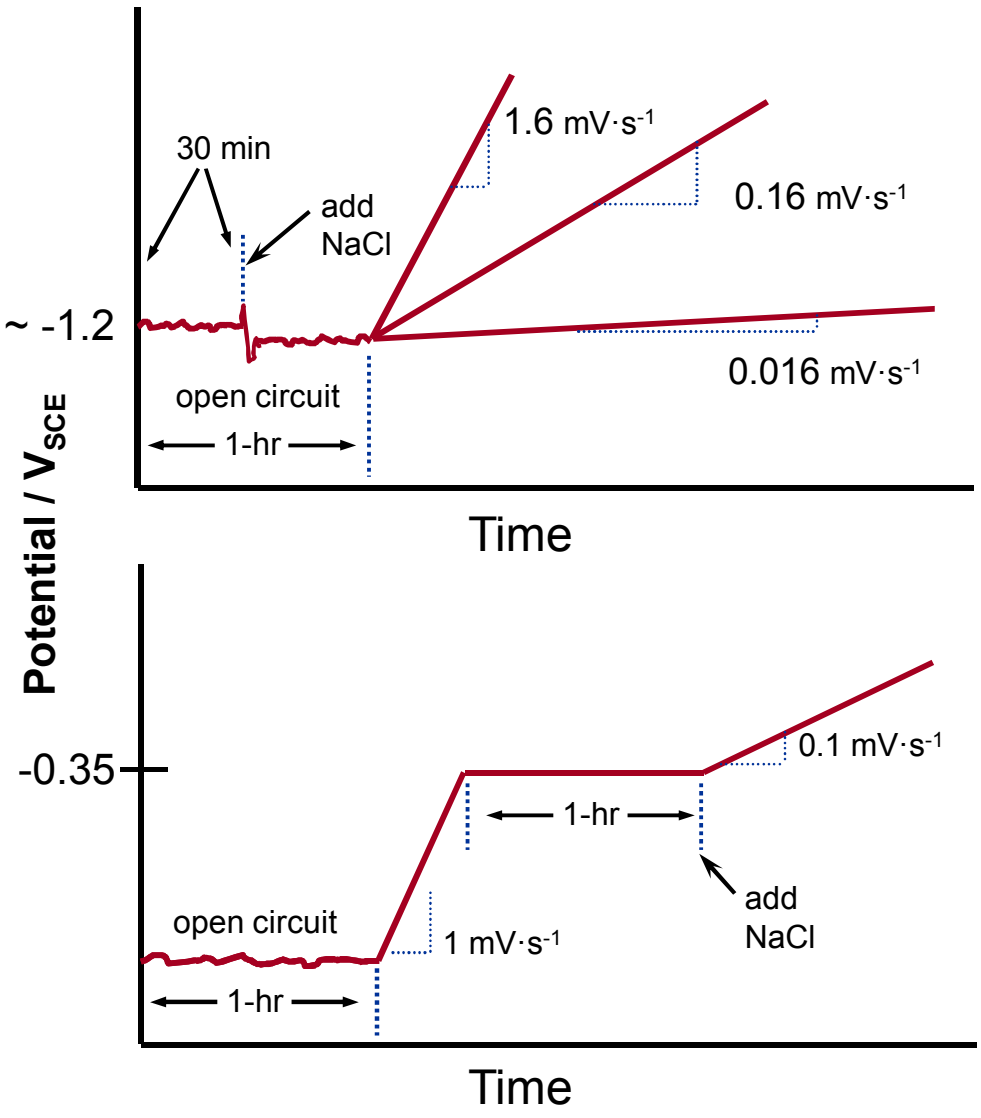


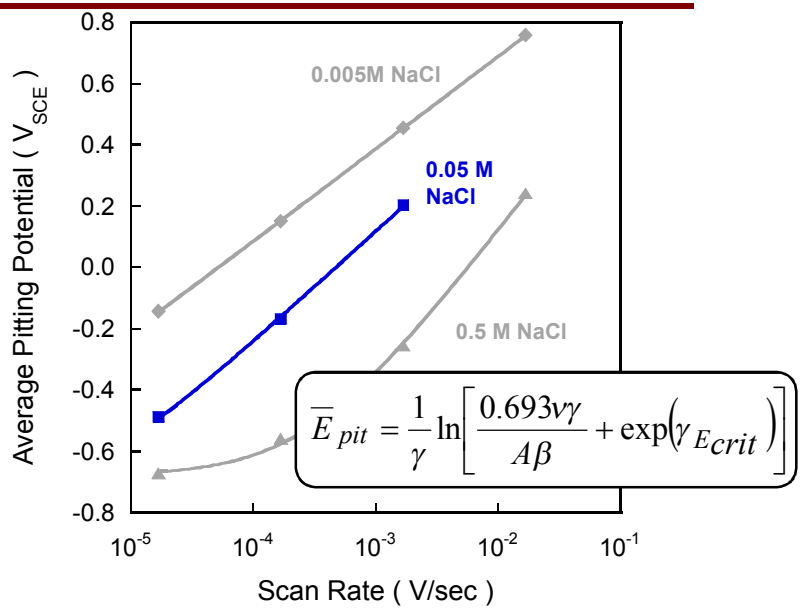
$$\lambda = -\left.\frac{d\log(P_s)}{d\tau}\right|_E$$

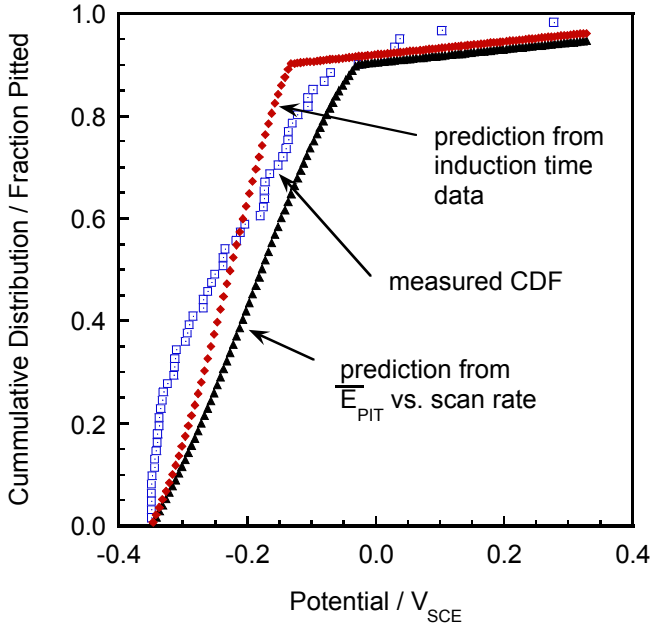


$$CDF(E) = 1 - \exp\left\{-\frac{A\beta}{\nu\gamma}\left[\exp(\gamma E) - \exp(\gamma E_1)\right]\right\}$$

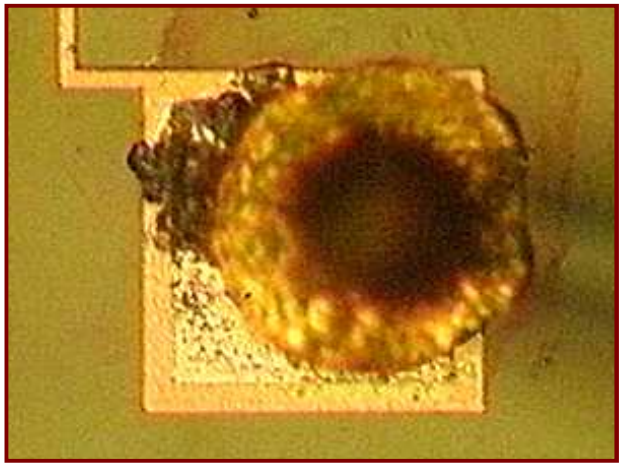
The relationship between τ and E_{PIT} can also be indirectly demonstrated using additional data sets.

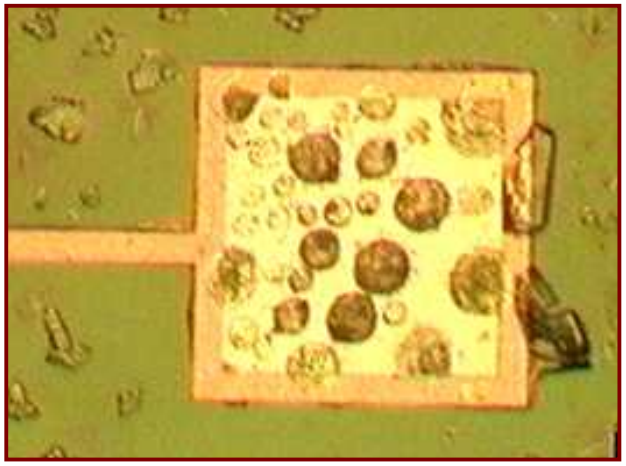






Case 2: Multiplexed sampling is required to build understanding of microelectronics degradation (R. Sorensen).



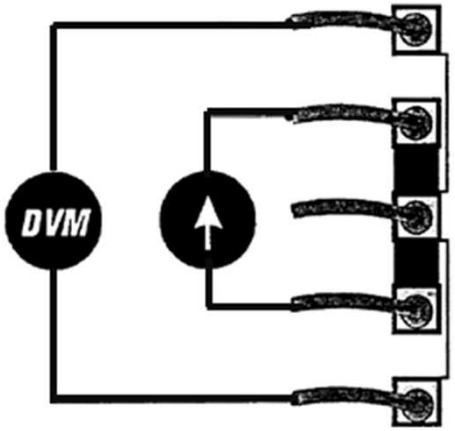


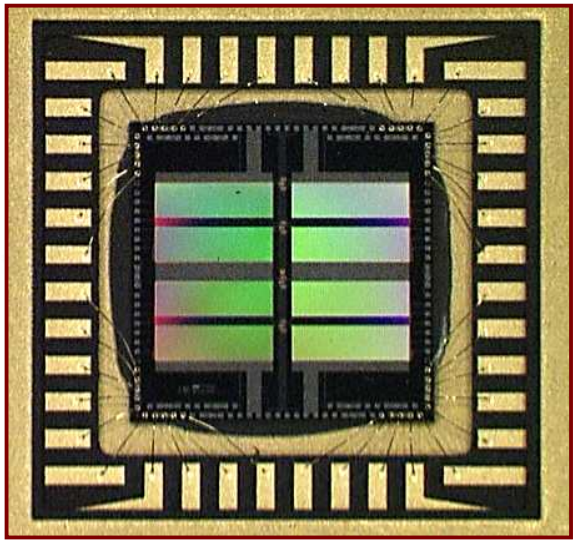
Au wirebonds form a galvanic couple with the Al pad, resulting in accelerated corrosion of the Al.

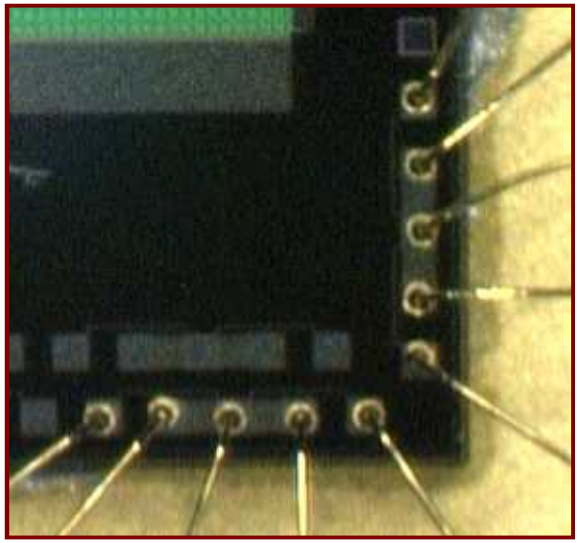
The corrosion process is sensitive to RH and contaminant concentration (i.e., $[Cl_{2(g)}]$).

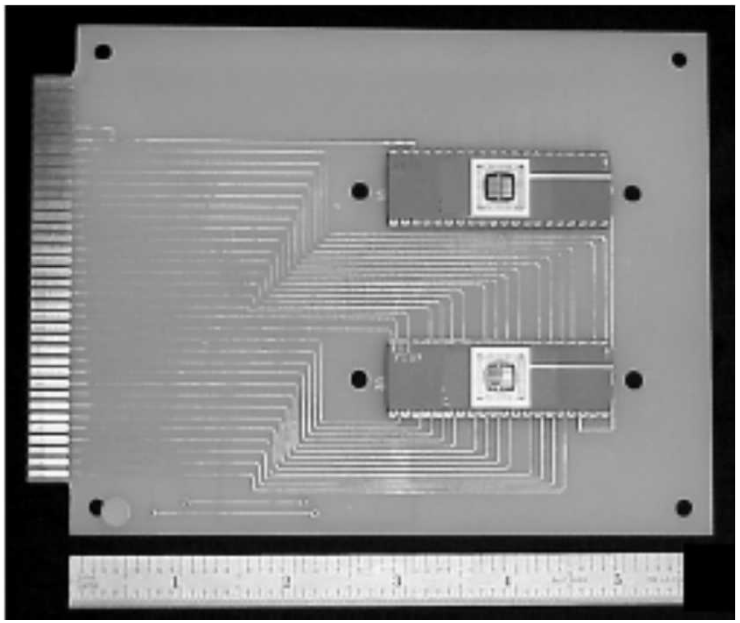
Variability in the response and length of experiments (hours up to weeks) precludes serial experimentation.

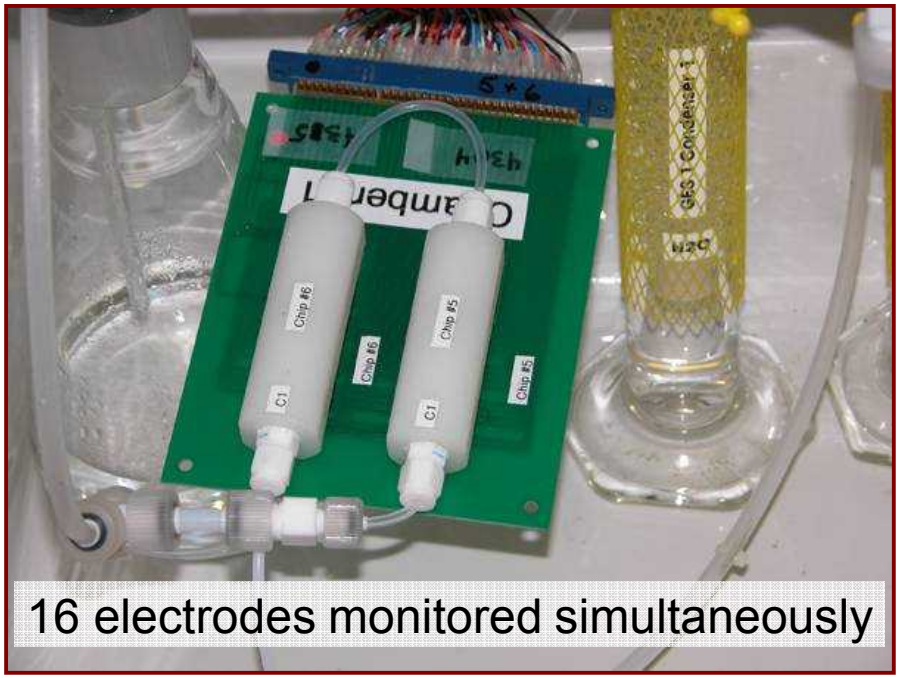
The extent of corrosion is quantified by monitoring sheet resistance during exposure to gaseous environments.





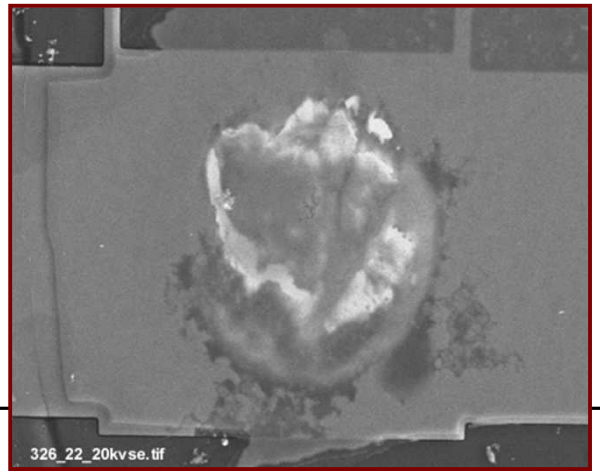


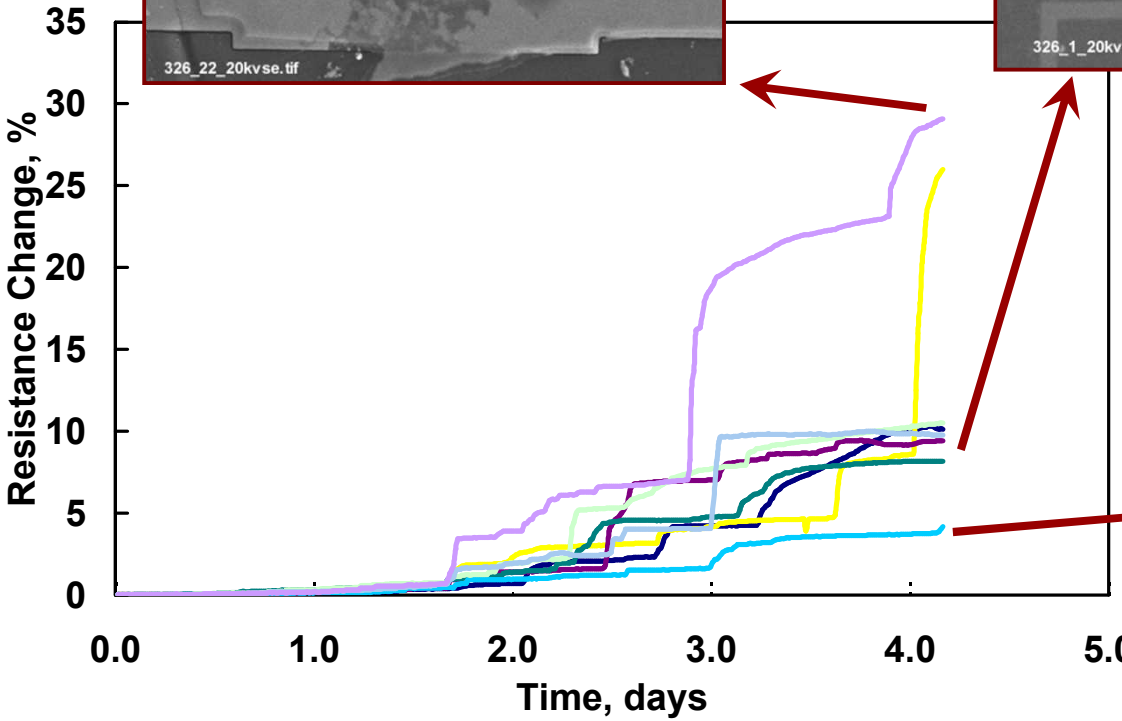


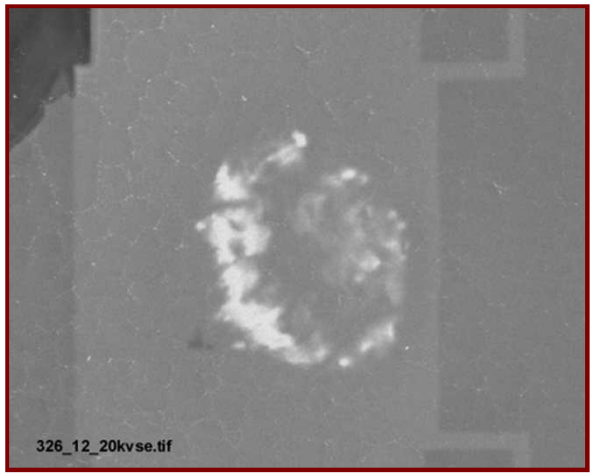


16 electrodes monitored simultaneously

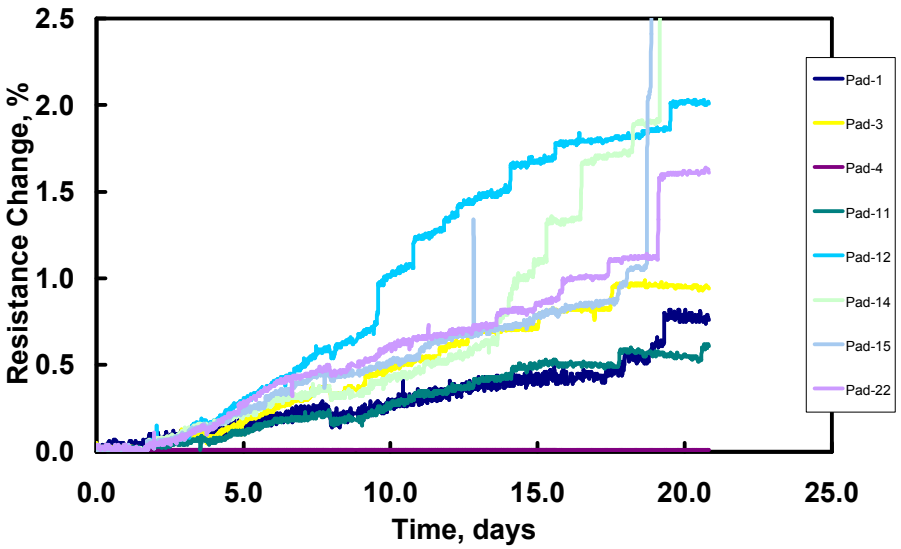
Correlating resistance changes with Z-contrast SEM enables visualization of extent of damage.



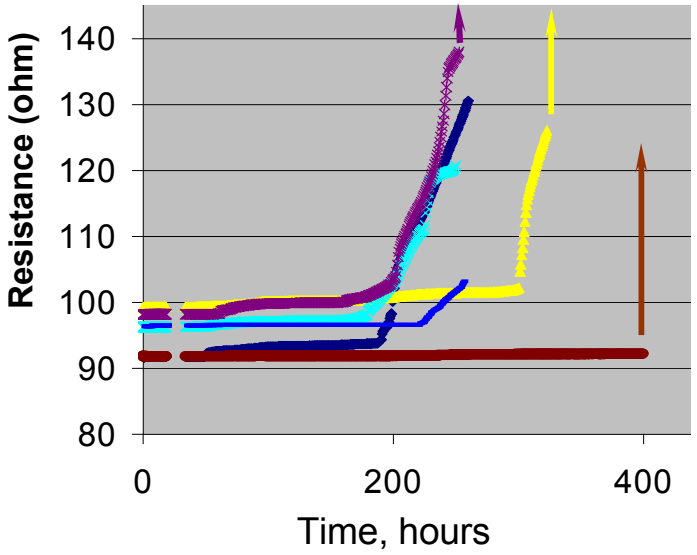




Multielectrode data reveal the effects of RH and contamination and the variability in response for each condition.

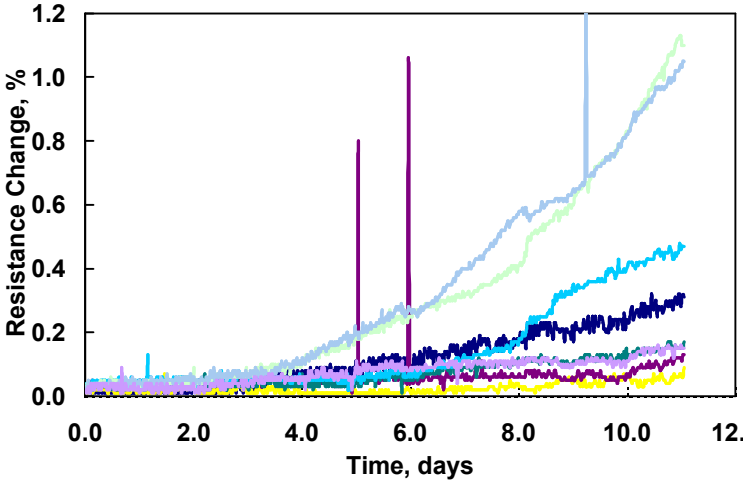


10 ppb Cl_2, 70%RH, 24C



200 ppb Cl_2, 85%RH, 30C

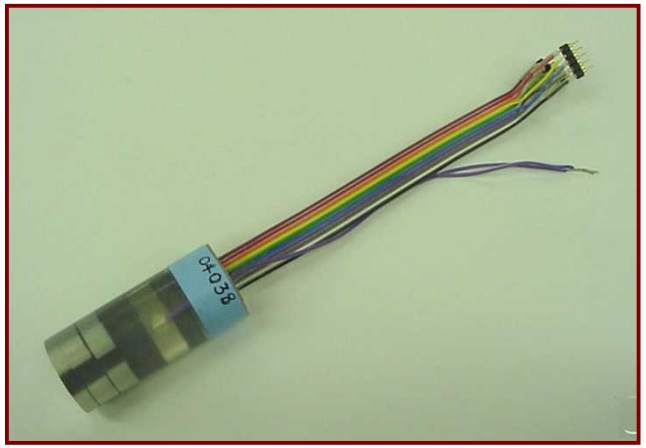
100 ppb Cl_2, 30%RH, 24C

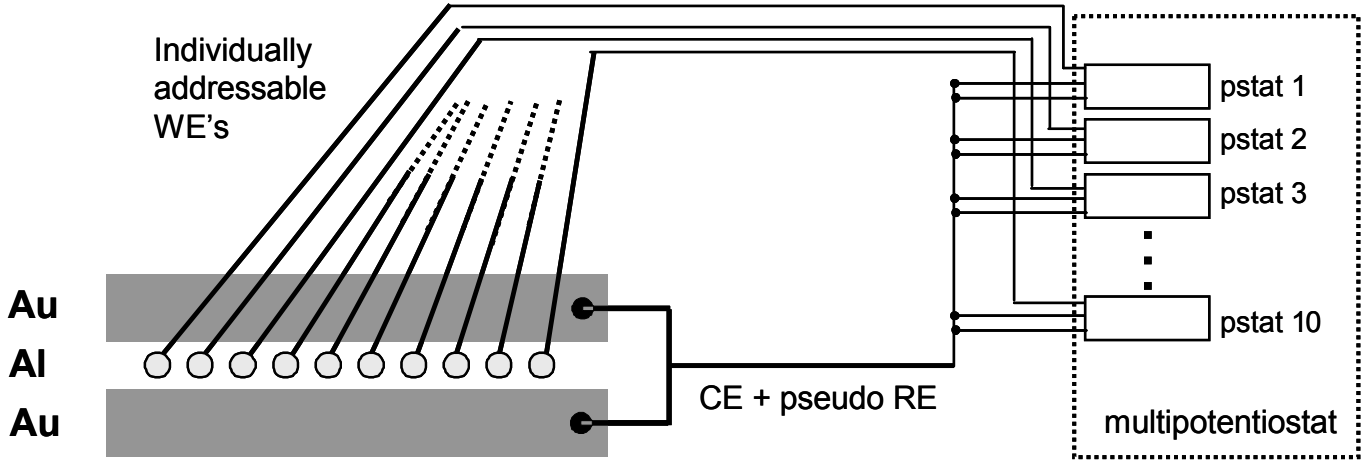


Case 3: reduced materials cost, assembly time and sample preparation needed for atmospheric pitting studies.

Can electrochemical measurements be used to quantify pit induction times under atmospheric conditions?

$$\lambda = -\frac{d\log(P_s)}{d\tau}\bigg|_E$$

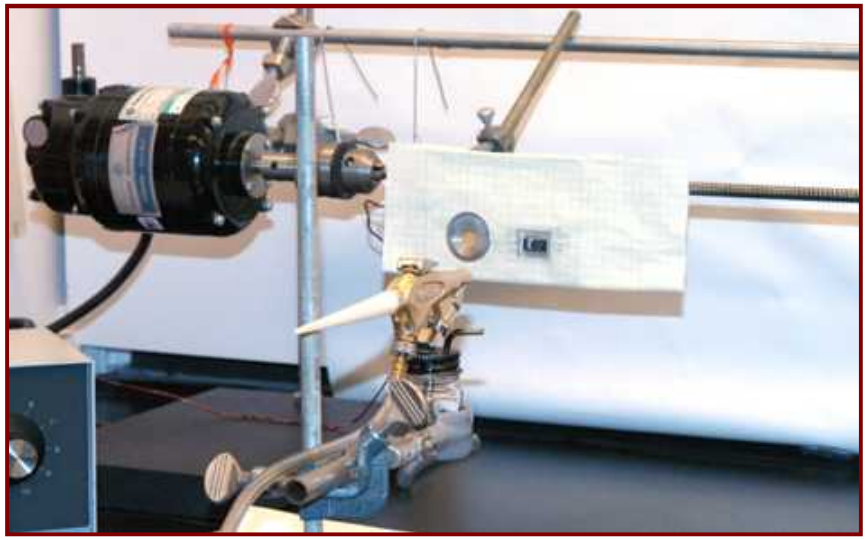


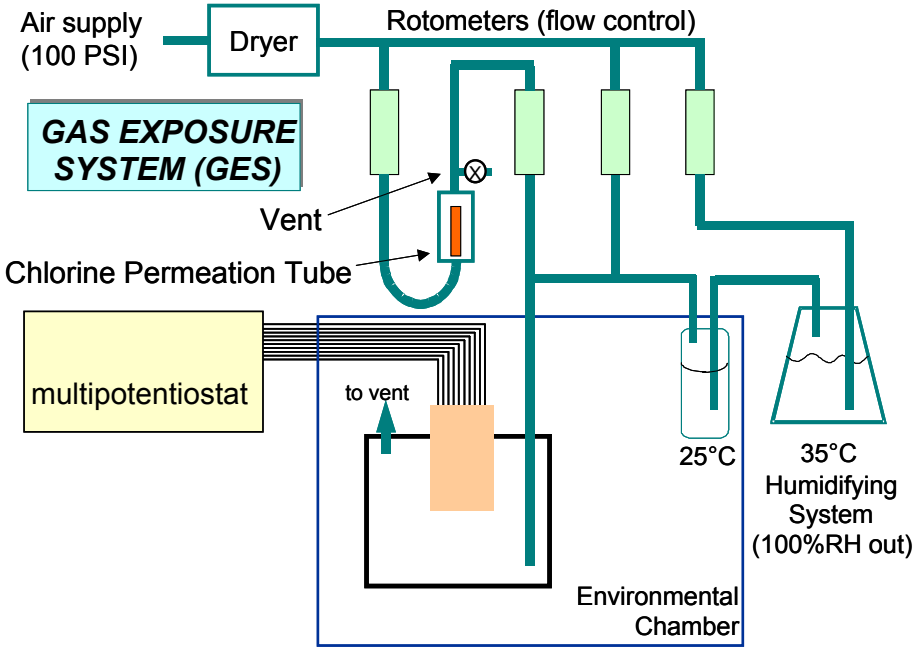


Sample configuration and experimental conditions for atmospheric pitting studies.

Materials:
- 99.99 Al (125μm ϕ)
- 99.95 Au (500μm thickness)

Electrode Preparation:
- Coat with electrophoretic paint (77°C Cure)
- Attach ribbon cable
- Mount in epoxy
- Mechanical polish to 1μm alumina

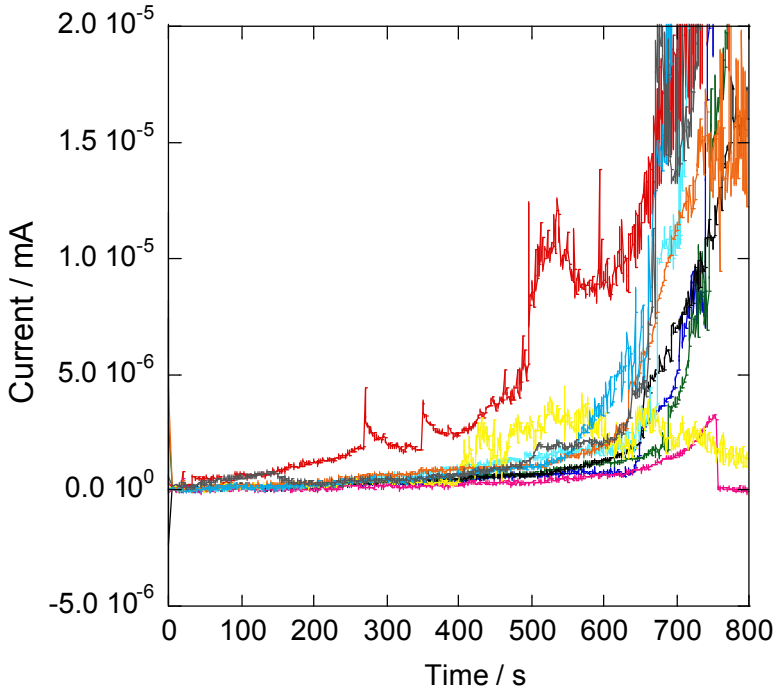




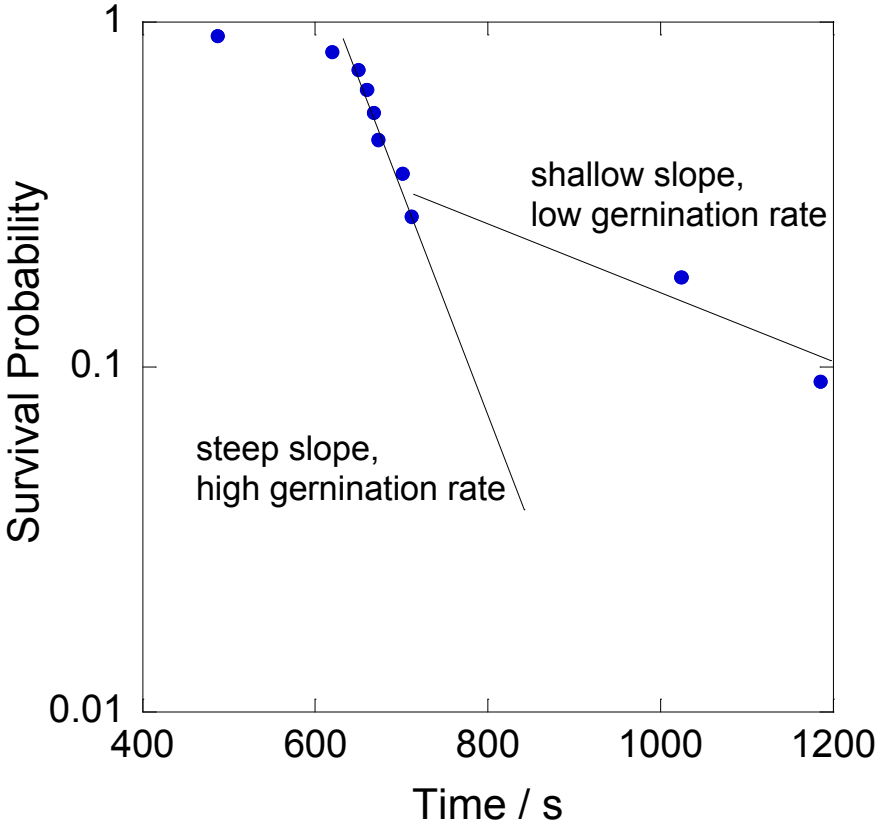
Pre-exposure contamination:
- spray with NaCl dissolved in methanol
- QCM located on traveler measures amount of contaminant applied.
- Sample coated with 100μg·cm^{-2}

Exposure environment:
- 25°C
- 80% RH
- Al-Au galvanic couple, monitor current

Pit induction time behavior under the atmospheric conditions tested appears similar to that under aqueous conditions.

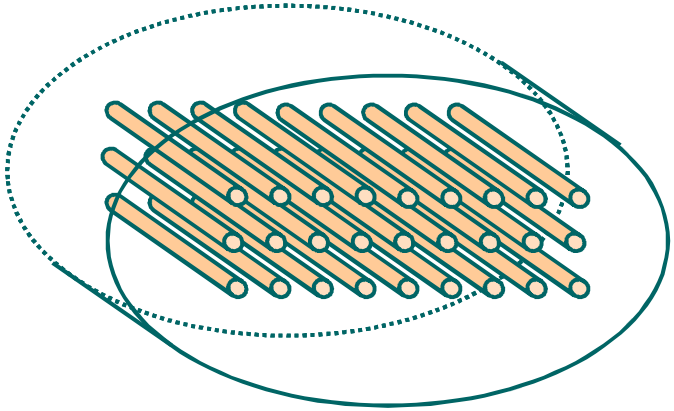


Current traces for 10 Al electrodes coupled to Au electrodes.

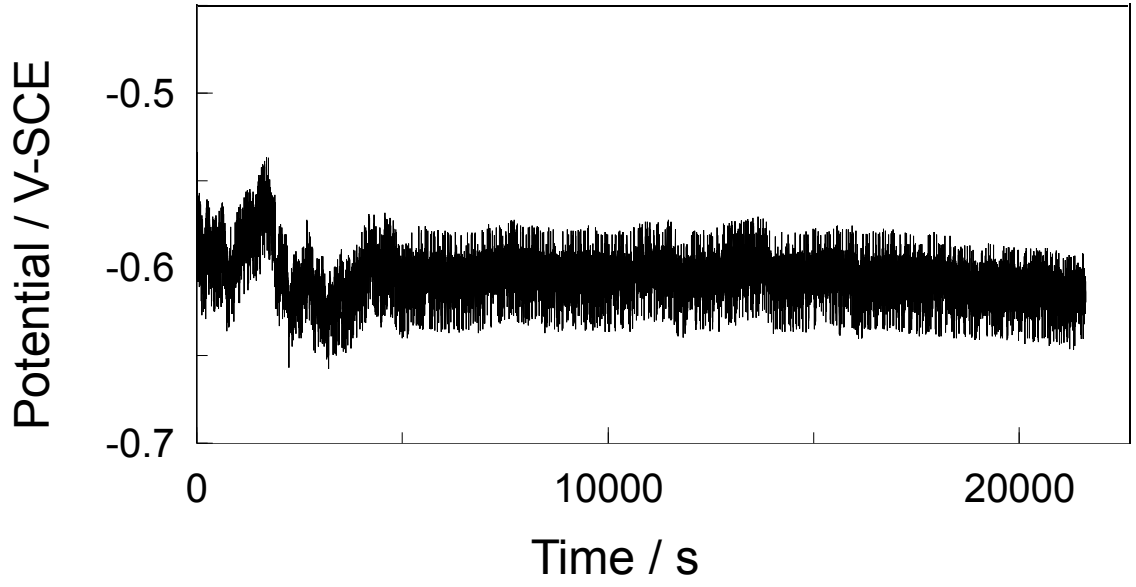


Two slopes in plot of P_S vs τ is similar to the response measured for electrodes in aqueous NaCl.

Case 4: local electrochemical measurements are needed to relate open circuit behavior to damage morphology.

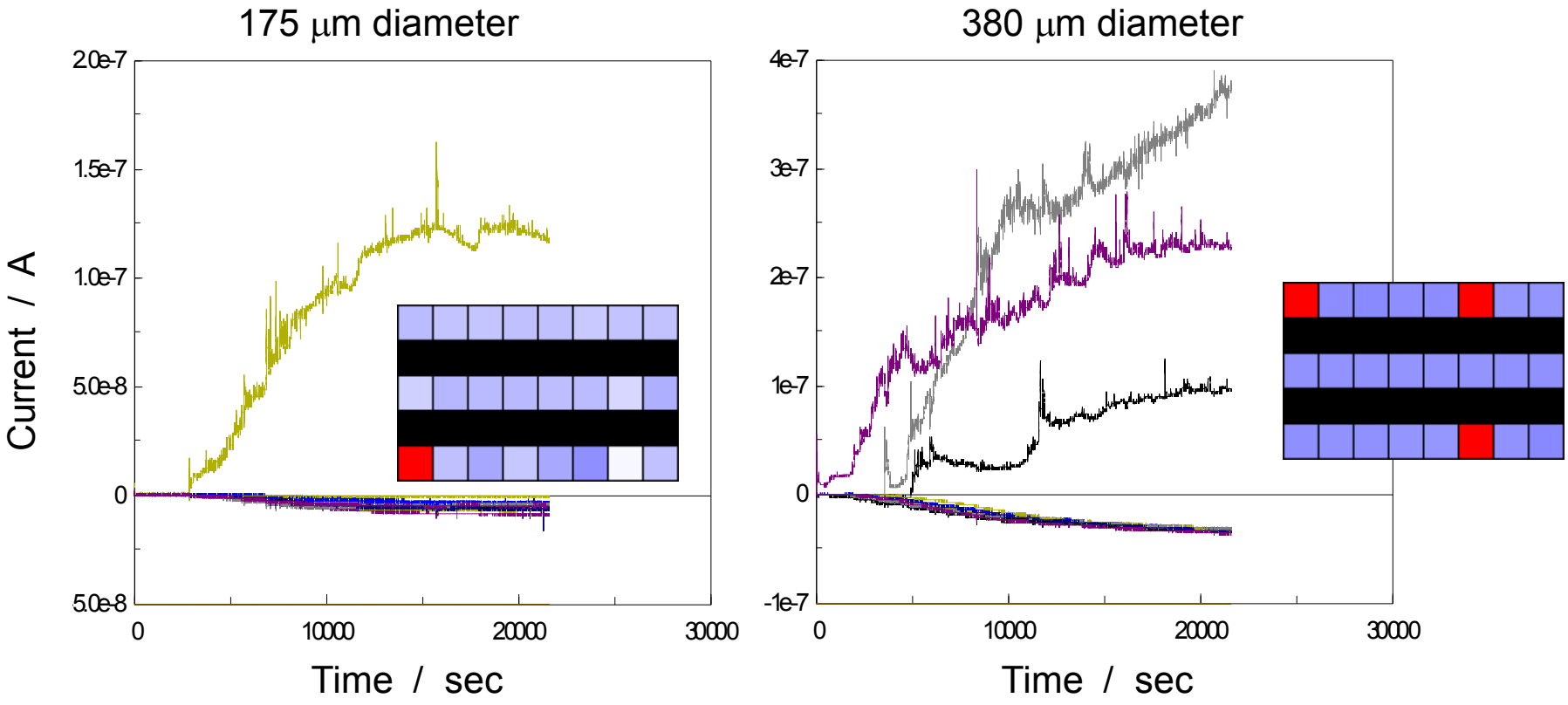


- 3x8 array
- Individually addressable
- 175 μm diameter wires
- 380 μm diameter wires

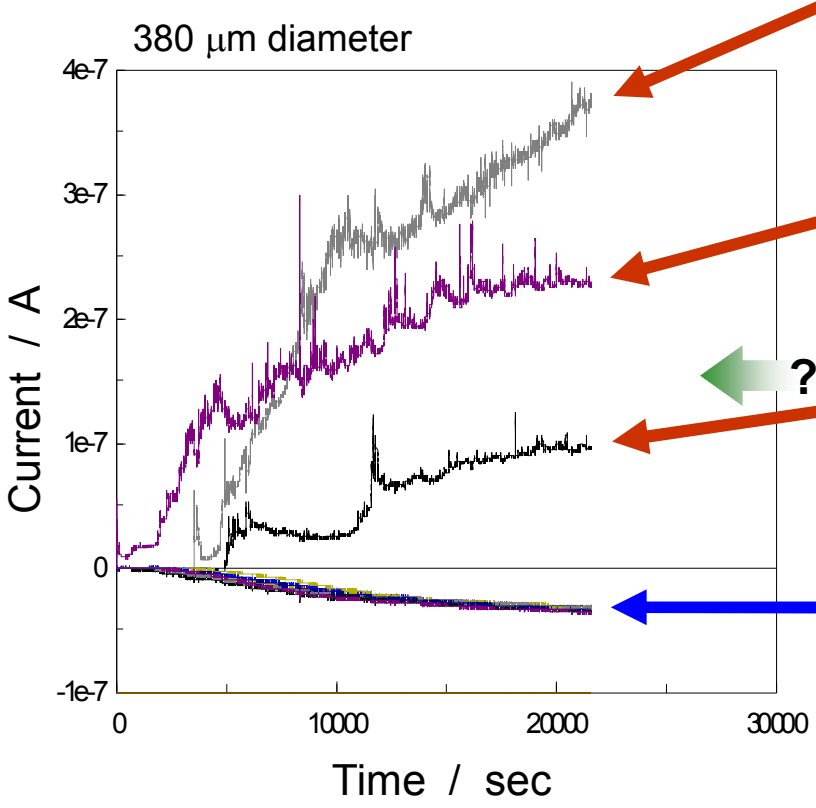


Average potential response for Al−4Cu electrodes in 50mM NaCl

Local measurements show where and when pitting nucleates on the electrode arrays.



Direct correlation of signal and image helps to overcome biases in interpretation of visual data.



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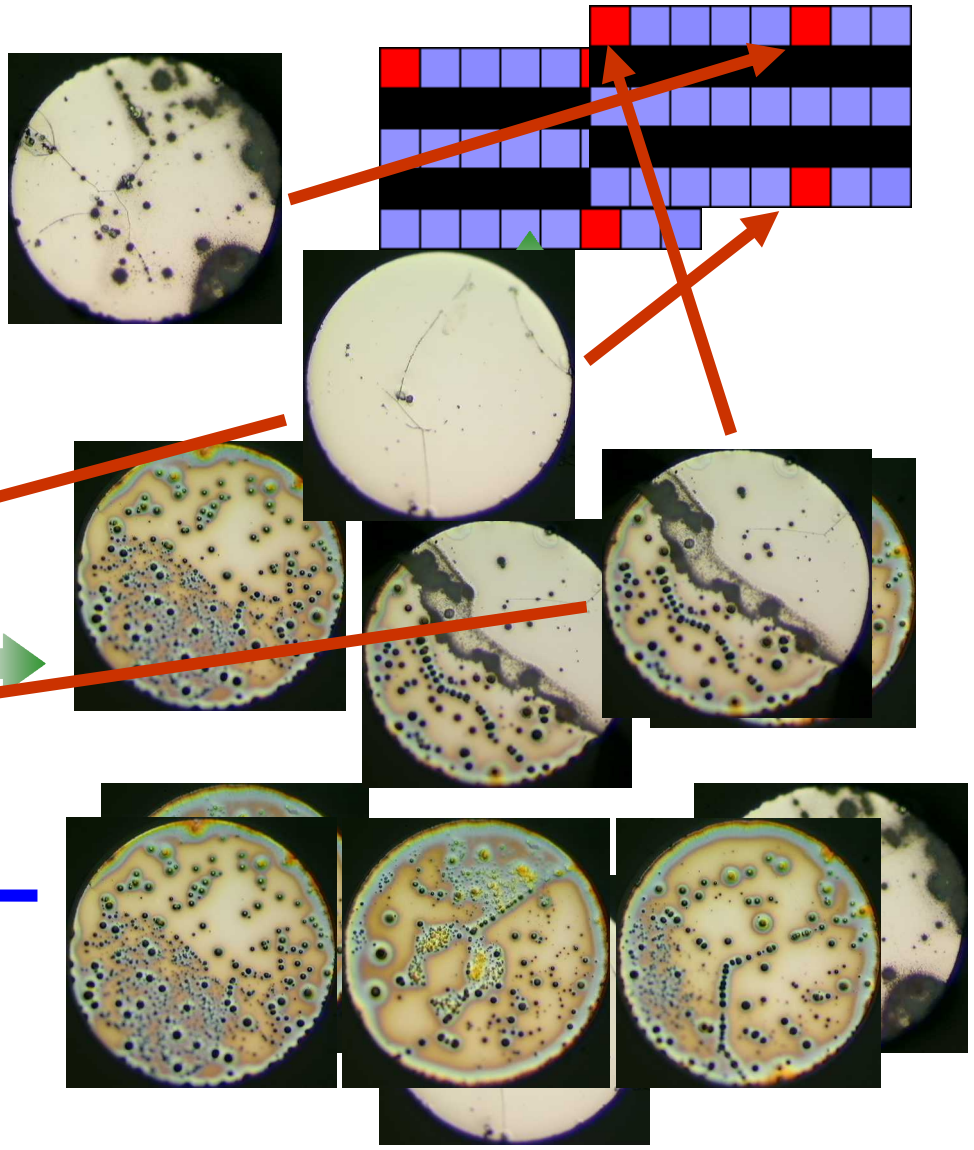
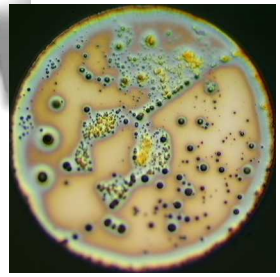
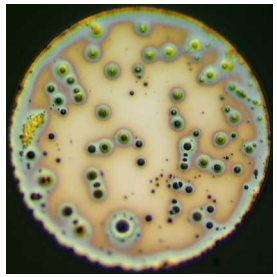


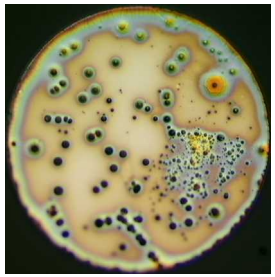
Linking damage to charge

MMA# / Photo#, charge density (nano-coul/cm^2)

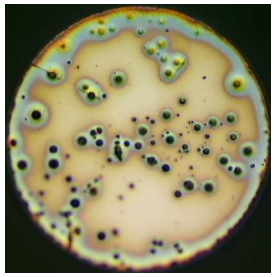
380 μm diameter electrodes


3/3: -4.224

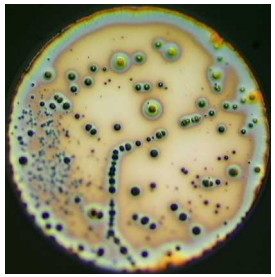

24/17: -4.056

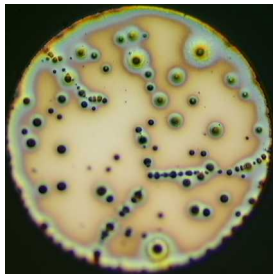

5/5: -4.030

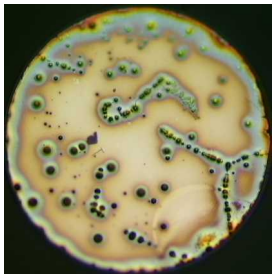

18/23: -3.941


4/4: -3.941

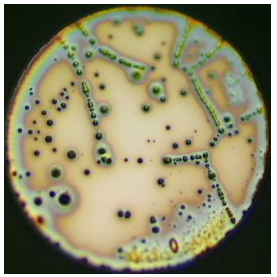

7/7: -3.897


2/2: -3.871

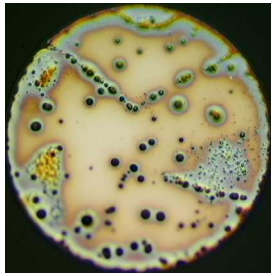

9/9: -3.747


13/13: -3.747


14/14: -3.730


11/11: -3.730


12/12: -3.686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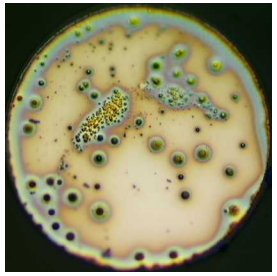
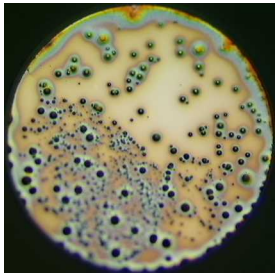
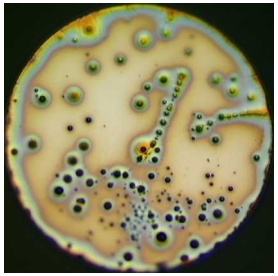
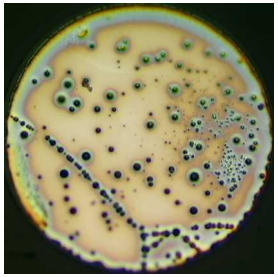

8/8: -3.668


10/10: -3.659


19/22: -3.624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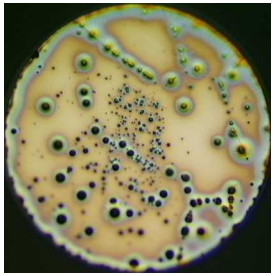
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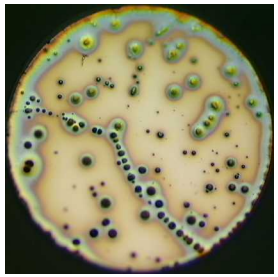
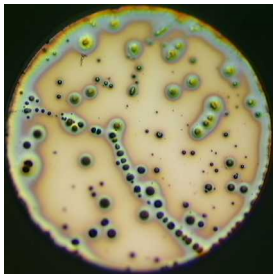
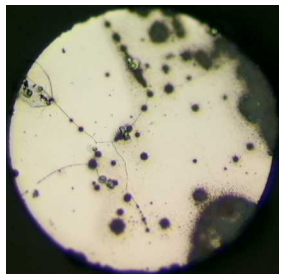

21/20: -3.465


15/15: -3.377


23/18: -3.227

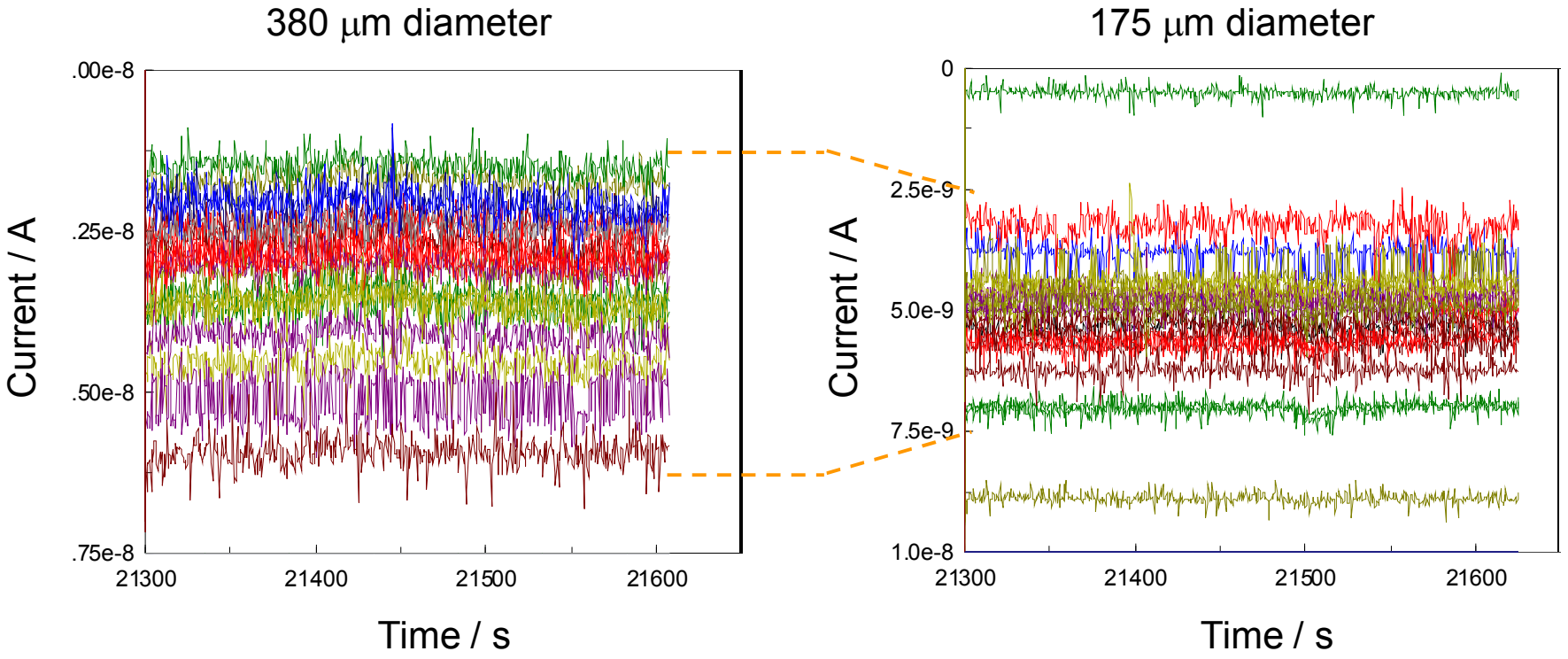

1/1: 9.082


22/19: 30.773


6/6: 38.180

F. D.

Local measurements give insight into the size scale that gives rise to heterogeneous cathodic behavior.



Defines how small of element is needed to accurately describe distribution in cathodic behavior; i.e., for modeling corrosion under open circuit conditions.

Care must be taken when using microelectrode arrays to characterize open-circuit behavior.

If the total area considered is too small …

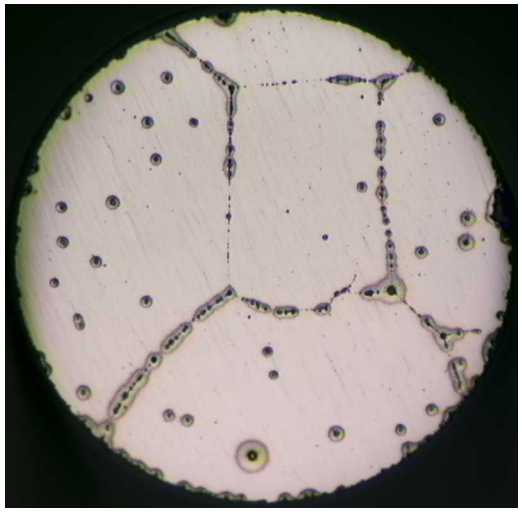
- The probability of pit nucleation may be reduced to the point where critical events are not observed during the experiment.

$$\lambda = A\,\beta\,\exp\left(E\,\gamma\right)$$

- There may be insufficient cathodic area to support the corrosion processes. A larger electrode would enable a greater rate of corrosion damage to be supported.

If the diameter of the electrodes is too small ….

- Edge effects may dominate the response.
- May act as an artificial pit.
- Diffusion of reactants / products may not represent case for macroelectrode.



Case 5: electrode arrays are required to enable combinatorial studies on electrochemical systems.

Problem: Identify a good catalyst and electrolyte for continuous oxidation of glucose as an energy source.

Motivation:

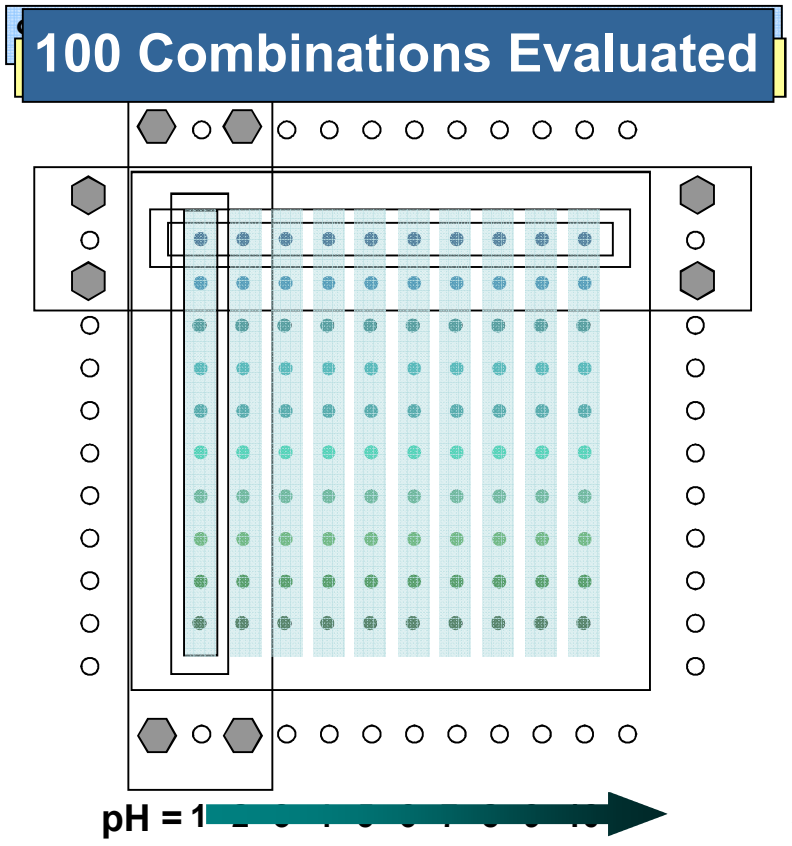
- In order to prevent poisoning from glucose oxidation products, binary, ternary or higher order compositions may be necessary.
- Effects of alloying cannot be predicted.
- Sequential approaches can be time-consuming and costly.

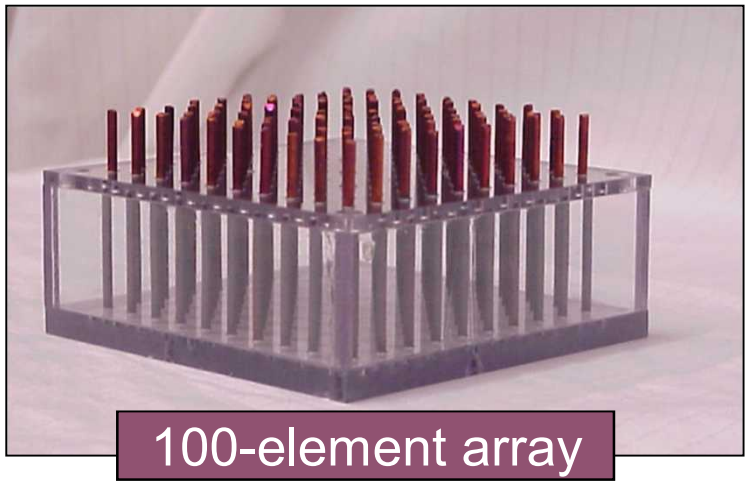
Some Limitations:

- May limit or add complications to available fabrication routes.
- Less precise compositional control.
- Cannot rely on complex data analysis; less information content compared to traditional CV analysis.
- Link from experiment to application is not guaranteed.

Philosophy: Use high-throughput techniques to define direction for traditional development activities.

Combinatorial approaches are being developed to screen large numbers of candidate systems





Evaluation of 100 catalyst / environment combinations

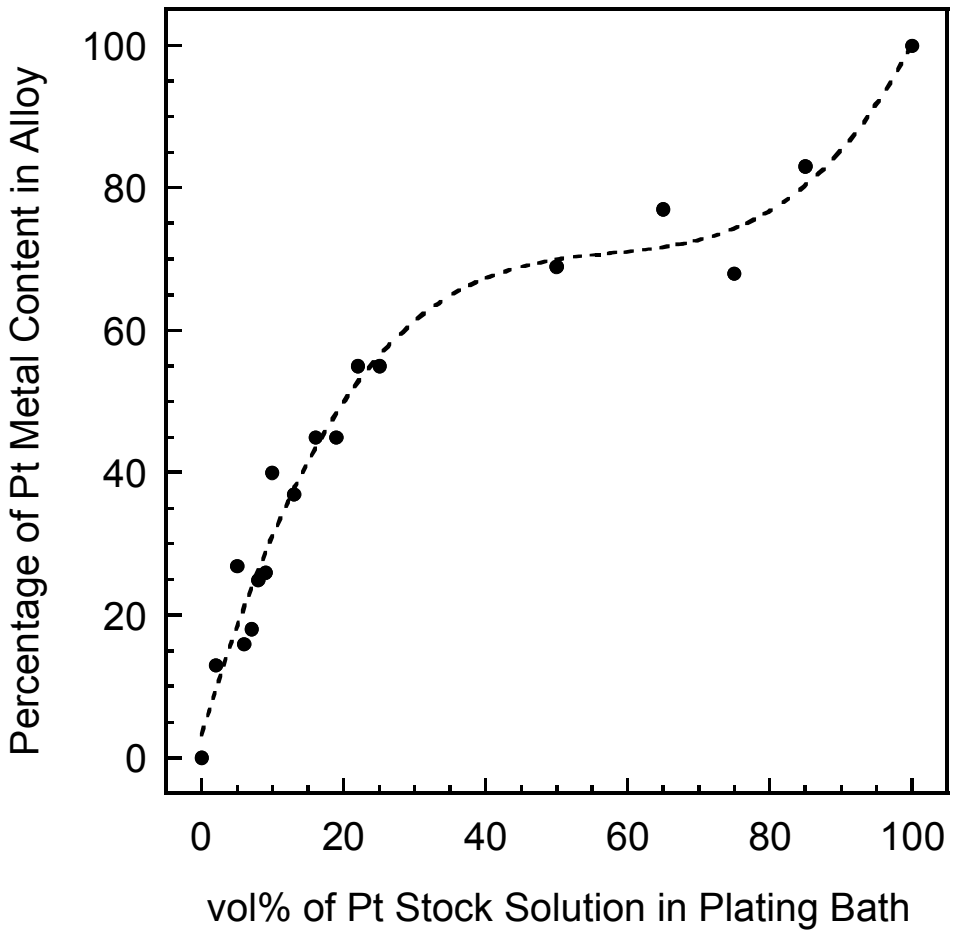
	Sequential	Combinatorial
depositions	100	10
voltammagrams	100	10
total steps	**200**	**20**

10X increase in throughput

An empirical relationship was established between electroplating conditions and catalyst composition.

Pt stock solution:
10 mM $PtCl_6$ + 50 mM K_2SO_4
Ru stock solution:
10 mM $RuCl_3$ + 50 mM K_2SO_4

- Mix stock solutions for desired composition
- Apply -0.350 V_{SCE} for 30 s
- Ramp to -0.65 V_{SCE} at 1 $mV\text{-}s^{-1}$
- Hold at -0.65 V_{SCE} for 600 s

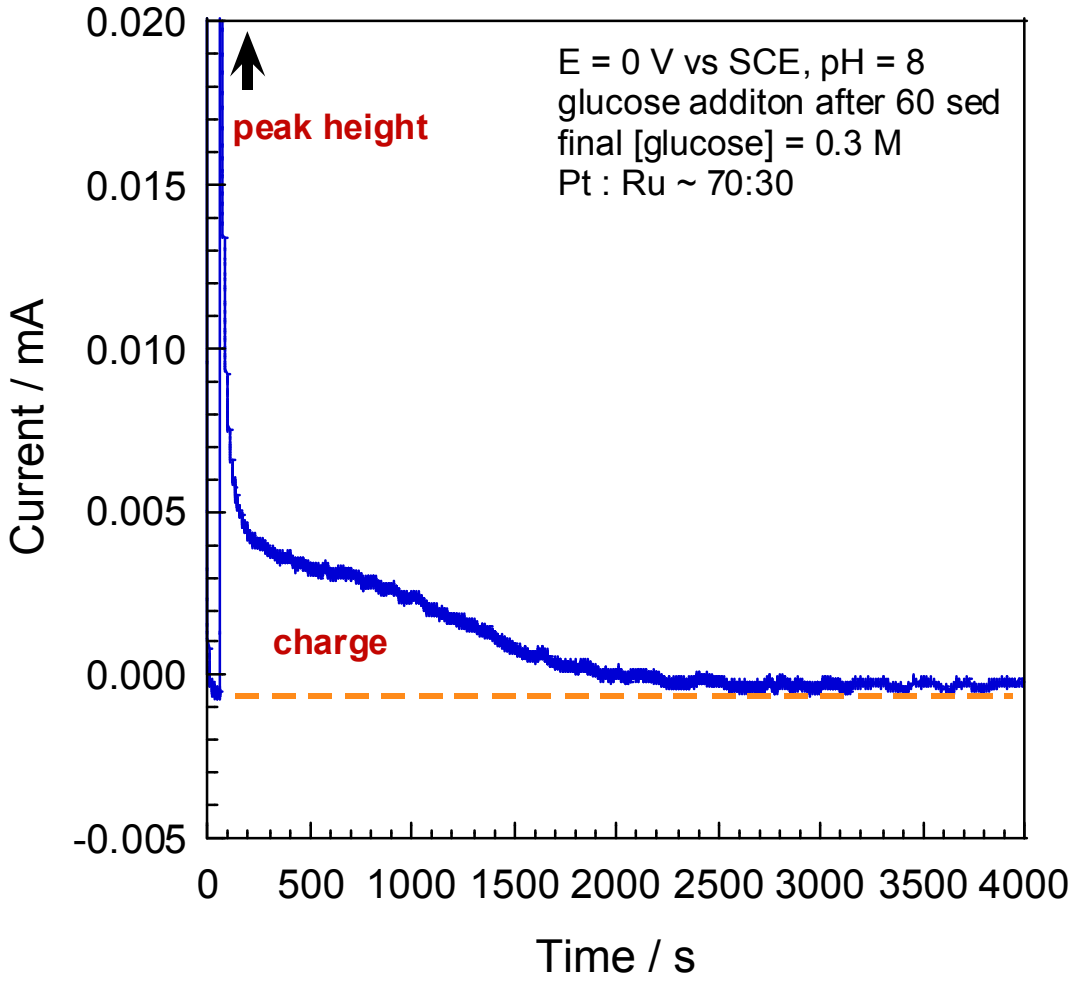


$$\%Pt\ in\ electrodeposit = 4.85 + 3.17X - 0.0528X^2 + 0.000306X^3$$

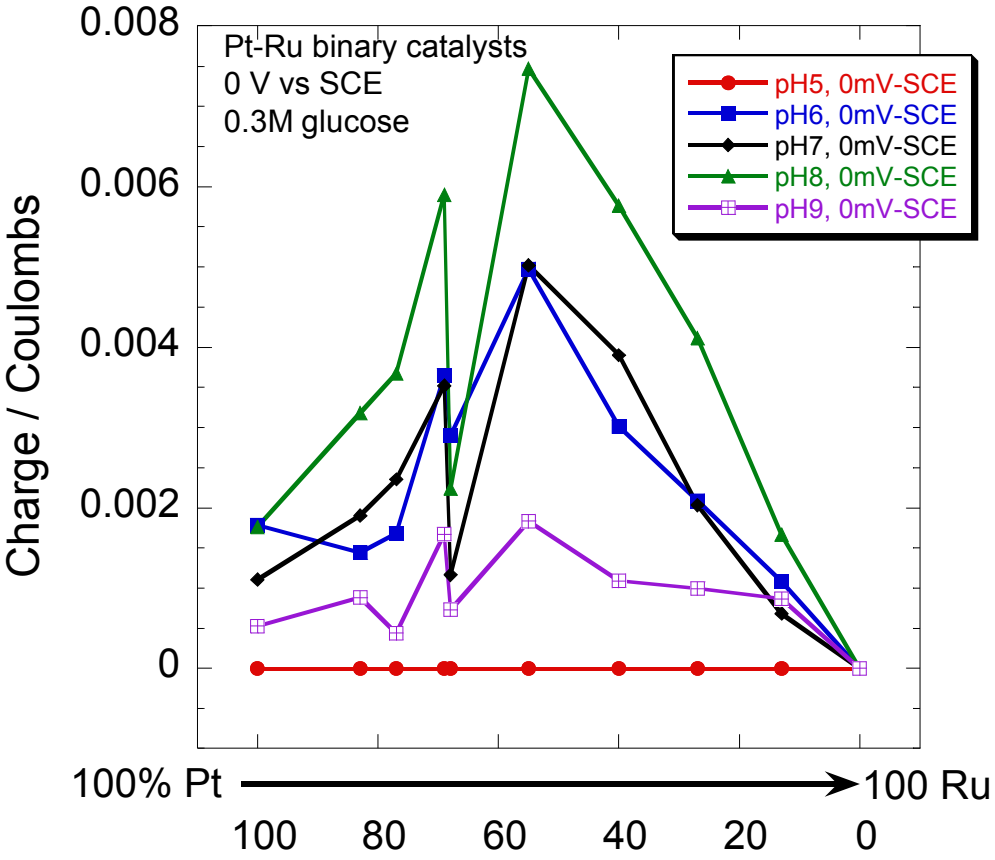
where X = vol% Pt in the electroplating solution

Potentiostatic experiments were used to evaluate catalyst performance.

- Apply fixed potential in glucose-free buffer solution
- Allow current to stabilize
- Add concentrated glucose solution
- Monitor current decay until steady state is reached
- Integrate charge following glucose addition



A combinatorial study was used to identify the optimal pH and electrode composition for Pt-Ru electroplated catalysts.



Conditions for maximum charge { 55:45 Pt:Ru
pH = 8

Summary:

We have successfully applied multielectrode techniques to a number of corrosion and electrochemical research projects:

- **Pitting of Al**
- **Al corrosion under atmospheric conditions**
- **Degradation of microelectronics under atmospheric conditions**
- **Pitting of Al-Cu**
- **Combinatorial screening of glucose catalysts**