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Correlating Pit Initiation in Aluminum with Passive Oxide Defect Structure

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DOE Basic Energy Sciences Office of Materials & Engineering Sciences

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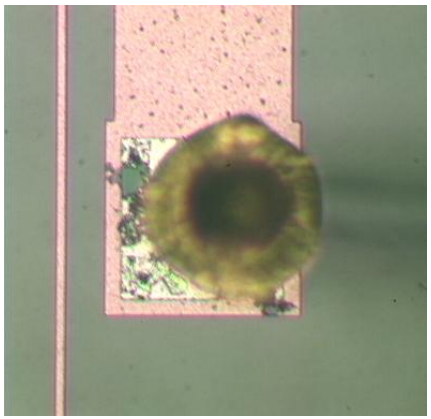
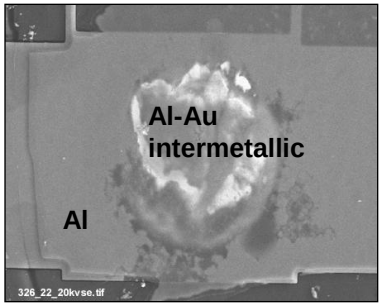
Why study pit initiation in Aluminum?

High consequence systems: minimal separation between initiation and damage

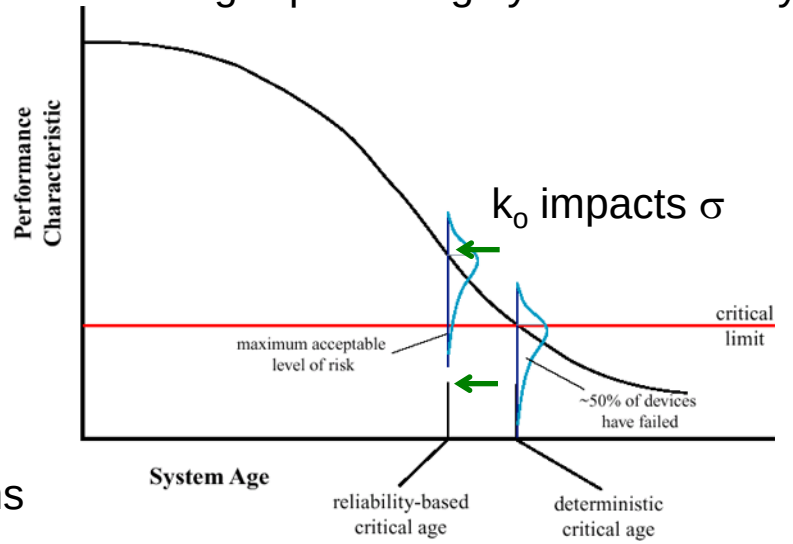
microelectronics – nanomaterials integration





Al interconnects can undergo galvanic corrosion

modeling & predicting system reliability



rate constant (k_o) - lump sum term for unknowns

$$\frac{d(\Delta R/R_o)}{dt} = I(defects)k_o P_{Cl_2}(t)\left\{1-\exp\left[-\left(\frac{H(t)}{\eta}\right)^{\beta}\right]\right\}\exp\left[-\frac{E_a}{RT(t)}\right]$$

Reliability prediction requires relevant physical & chemical inputs of localized corrosion mechanisms

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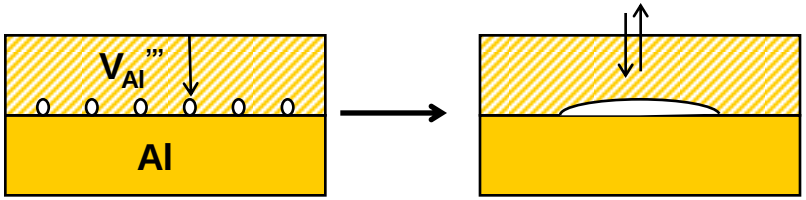
Proposed mechanisms for pit initiation

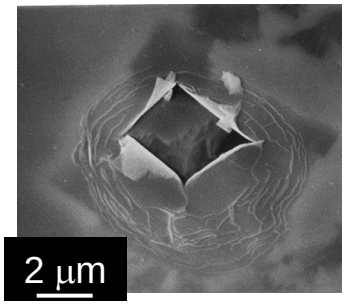
Vacancy condensation - Point Defect Model (Macdonald)

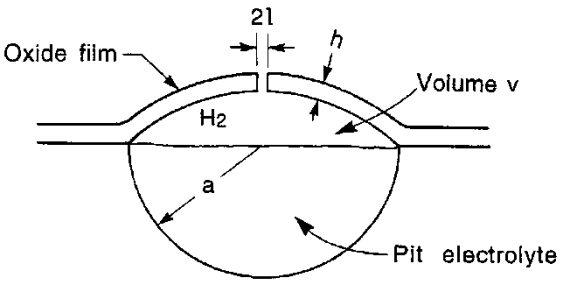
dissolution & growth rate disparity



2D void formation @ V_{crit}

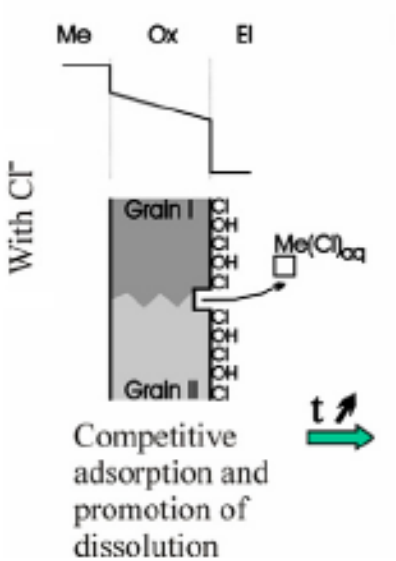
Nano-corrosion cells - Electrokinetic Model (McCafferty)



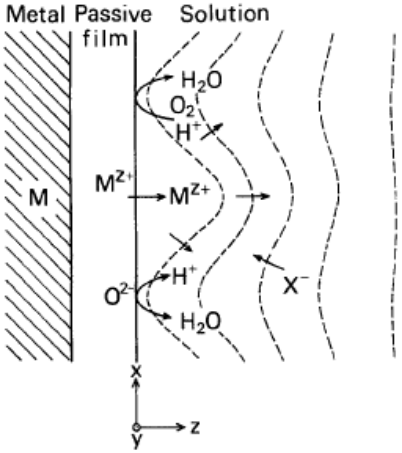


McCafferty & Natishan, 218th ECS #1322

Oxide grain boundaries - Marcus, Maurice & Strehblow



Aggressive anion and electric field perturbation - Okada



electrostriction

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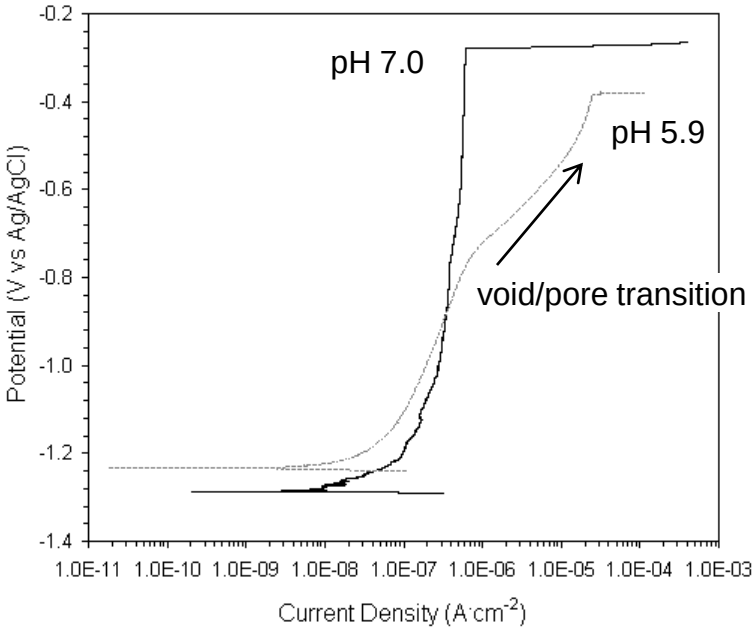
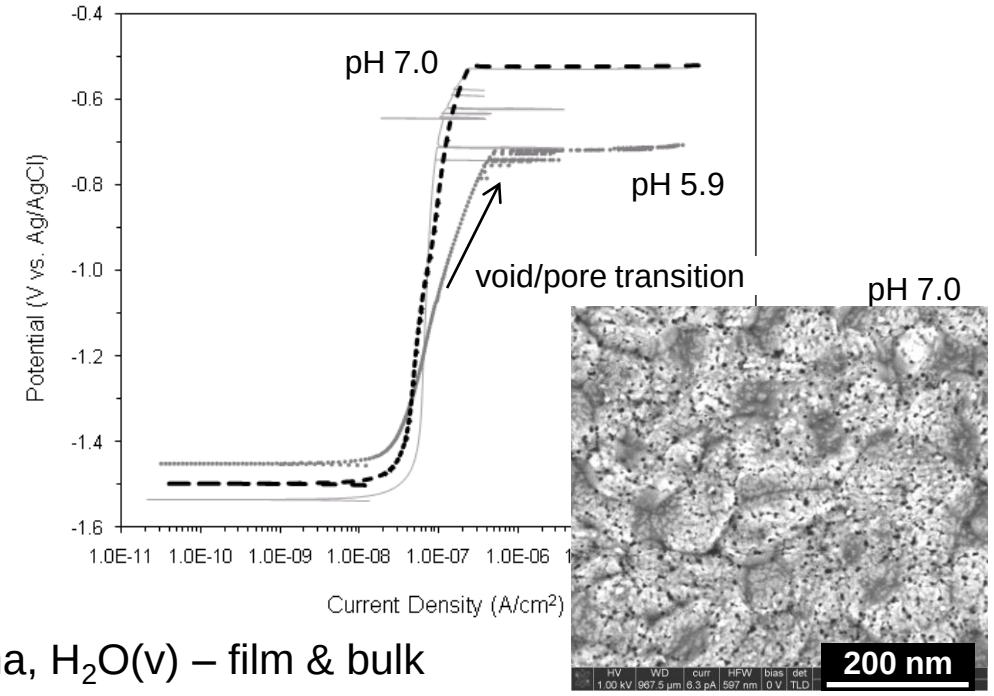
Pit initiation in model oxides on Al coincides with oxide defect activity

~150 nm diameter grain Al(111) film in de-aerated 50 mM NaCl

Macroscale measurements at 1 cm^2



Mesoscale capillary measurements at < 0.01 cm^2



Initially anhydrous oxides – O_2, O plasma, $H_2O(v)$ – film & bulk including single crystal

I/V response shows the presence of a proton-activated process that leads to accentuated current generation – anodic dissolution can compete with pit initiation

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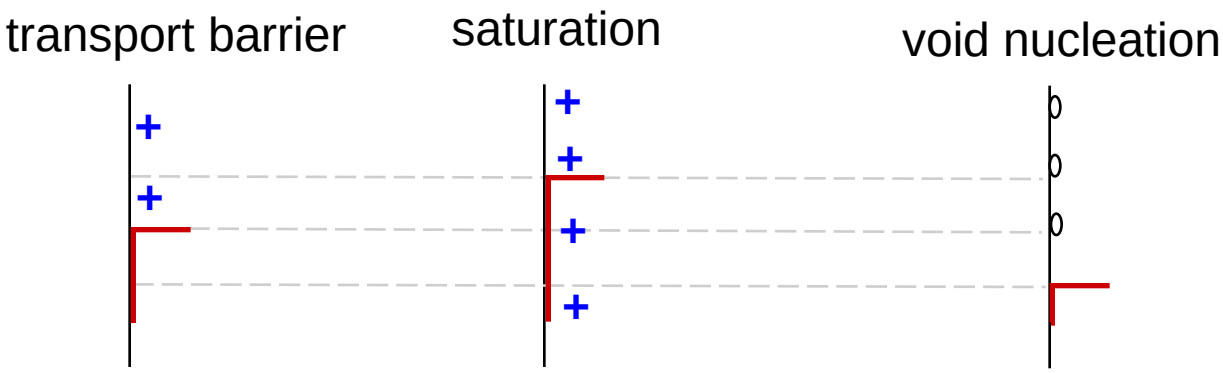
Void nucleation as a means for relieving charge transport impedance



*interfacial V_O^{i}.. Al oxidation increases V_O.. barrier relieved

V_O.. saturation through a simple equilibrium:

$V_O.. + H_2O \rightarrow O_O + 2H^+$

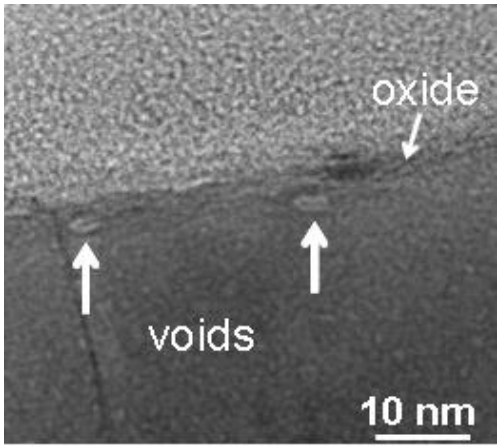
Alternate reaction to consider:

$V_O.. + H_2O + O_O^{2-} \rightarrow 2OH^{\cdot}$

Ox:El interface barriers:

$Al_{Al} \rightarrow Al^{3+}(aq) + V_{Al}'''$

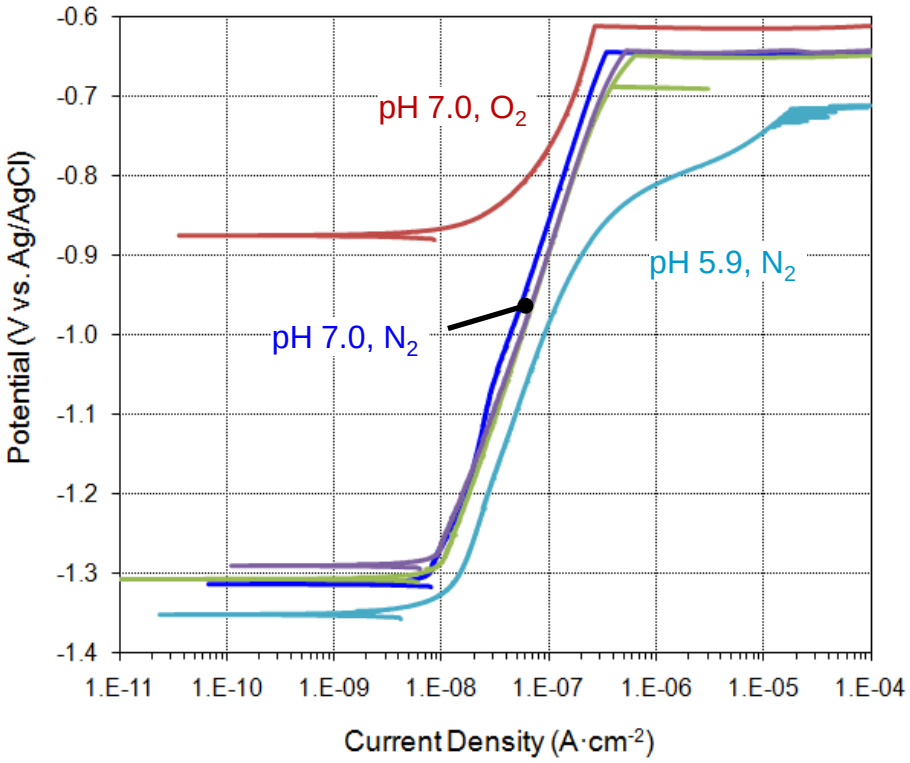
retarded by surface adsorbates or chelating species

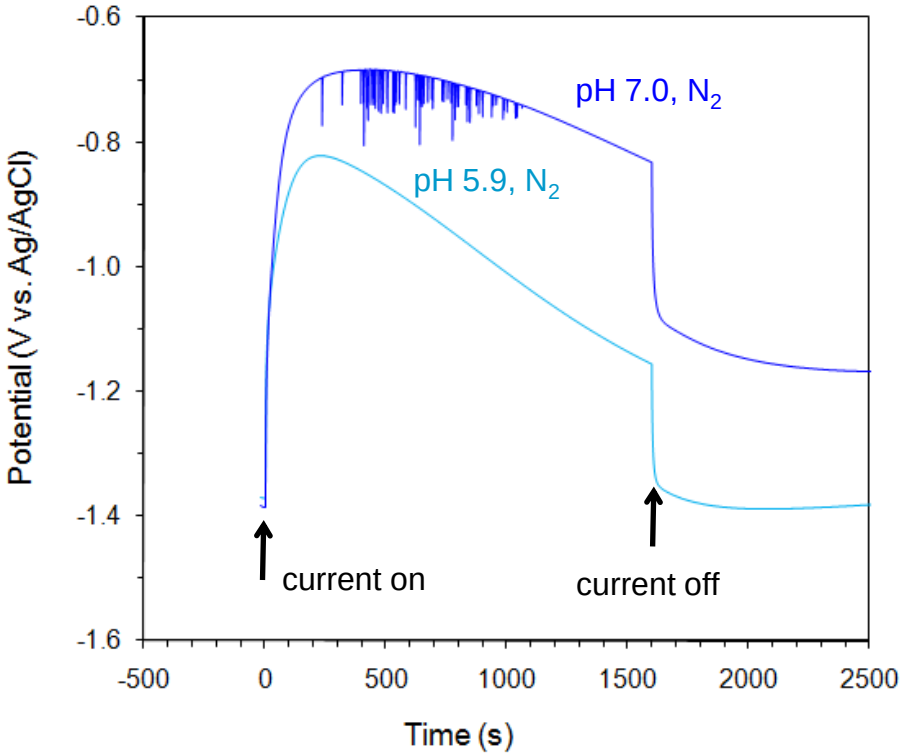


Can imaging help determine how voids contribute to pit initiation?

Chronopotentiometry highlights the co-incidence of pitting & defect activity

700 nm thick Al(111) film in de-aerated 50 mM NaCl





Pitting and accentuated dissolution compete

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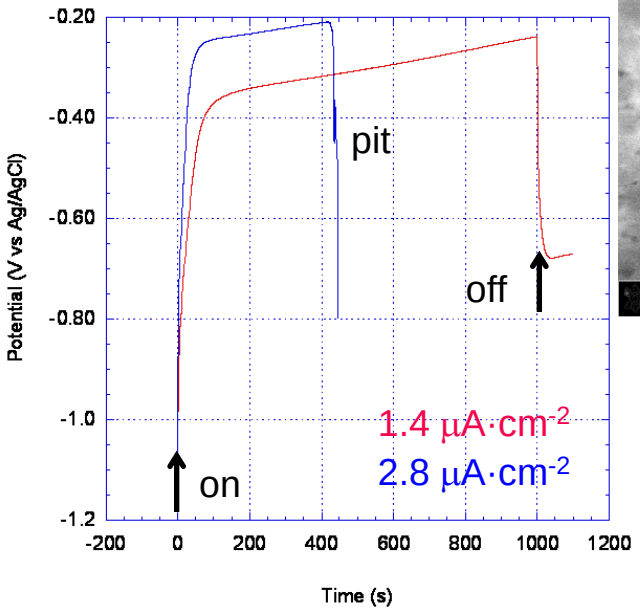
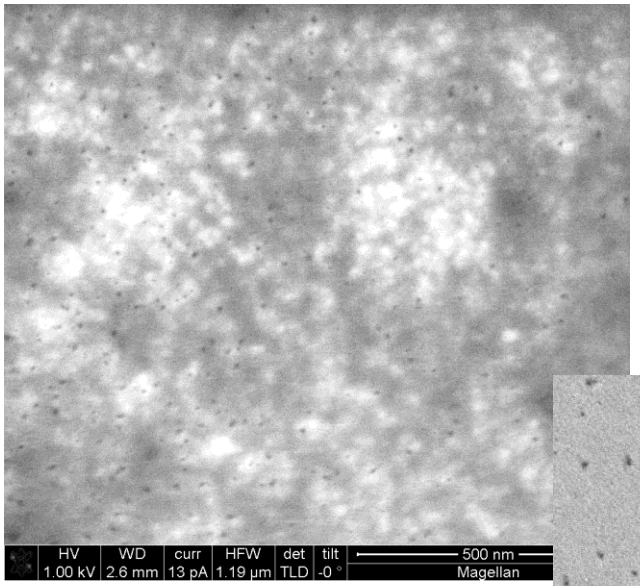
Similar defect processes operative in *not so model* oxides

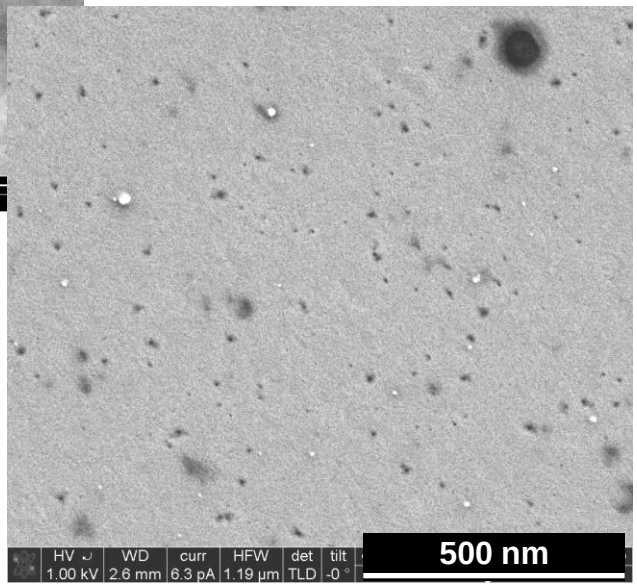
99.999% polycrystalline Al aqueous alumina (30 nm polish) – oxide allowed to dry

equilibrated 1 hour 50 mM Cl^-





1.4 $\mu A \cdot cm^{-2}$, 1.4 mC



Model oxides may represent one way of probing the limiting cases of defect chemistry

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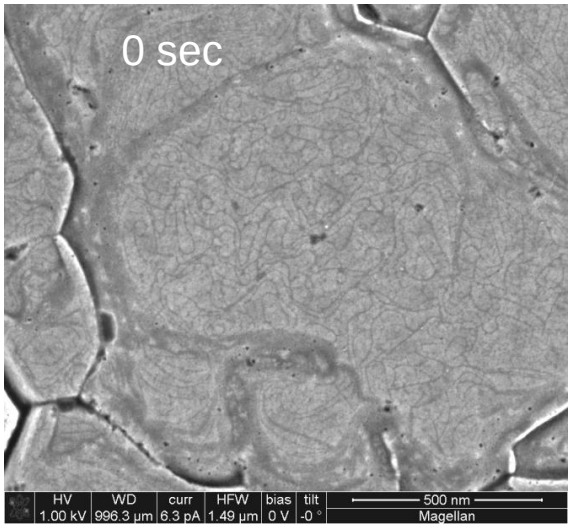
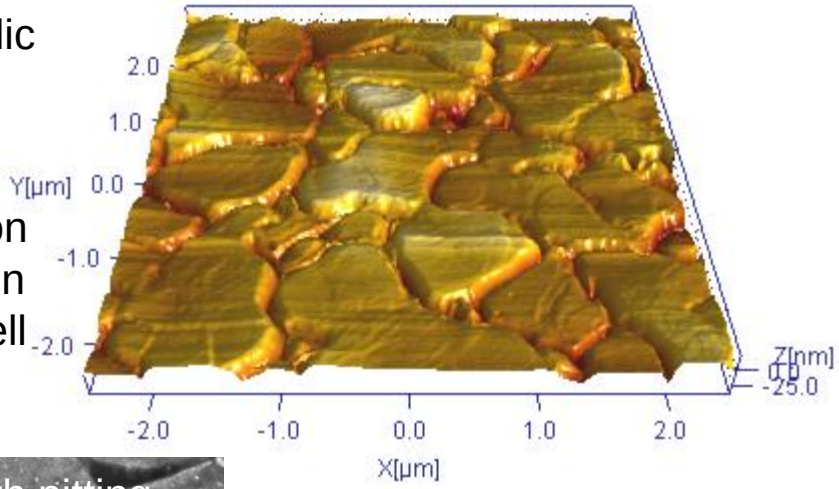
Structural impact of polarization is greatest at the high step density facets of the grains

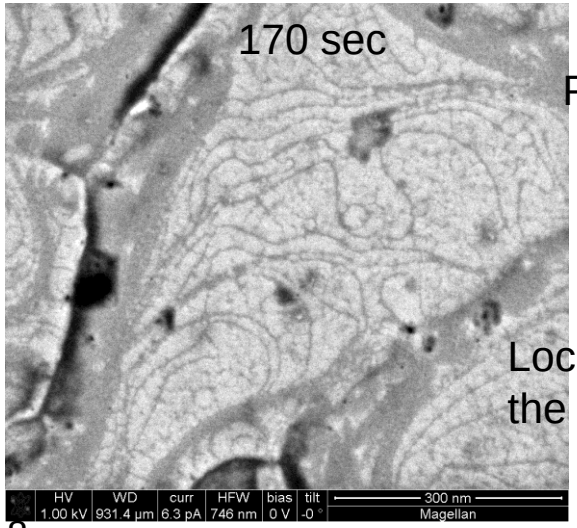
700 nm thick Al(111) film in de-aerated 50 mM NaCl pH 7
– larger grains for better spatial discrimination

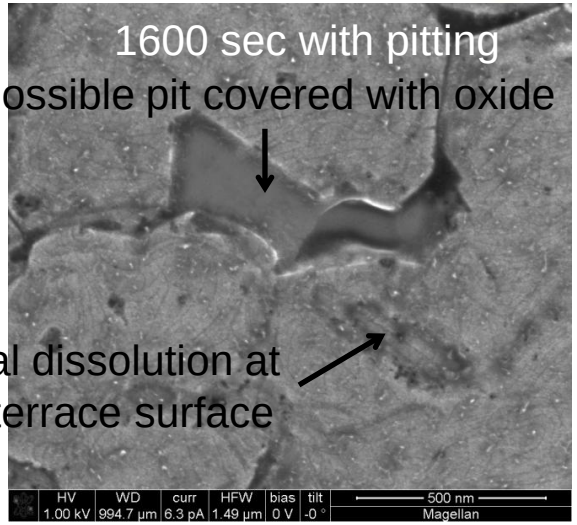


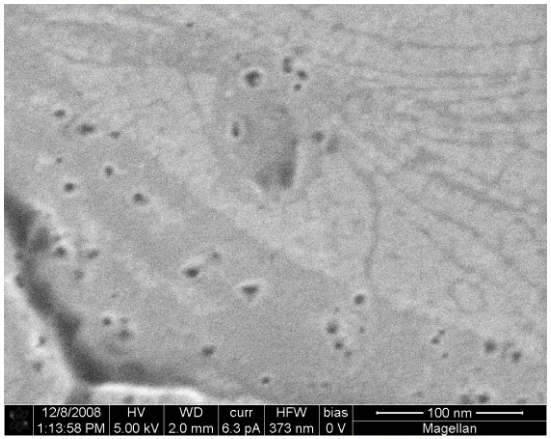
0.6 µA·cm^{-2} anodic polarization for variable time

void/pores form on contours into grain boundaries as well as terraces









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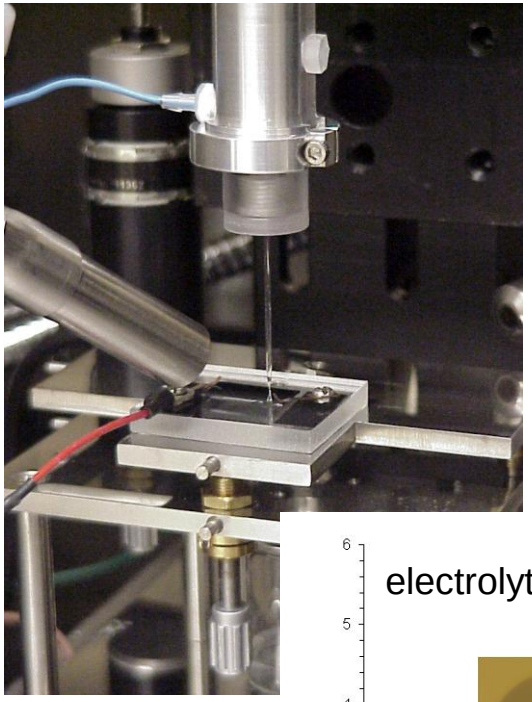
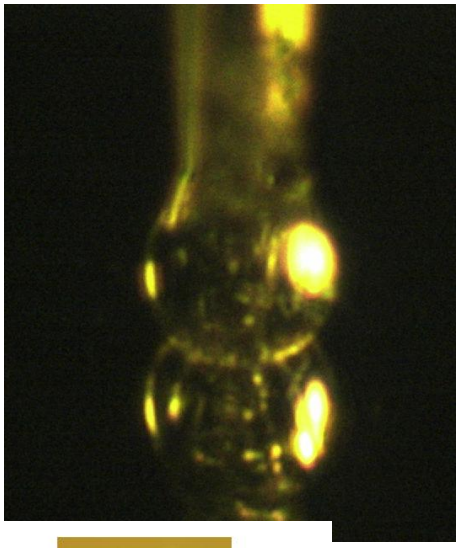
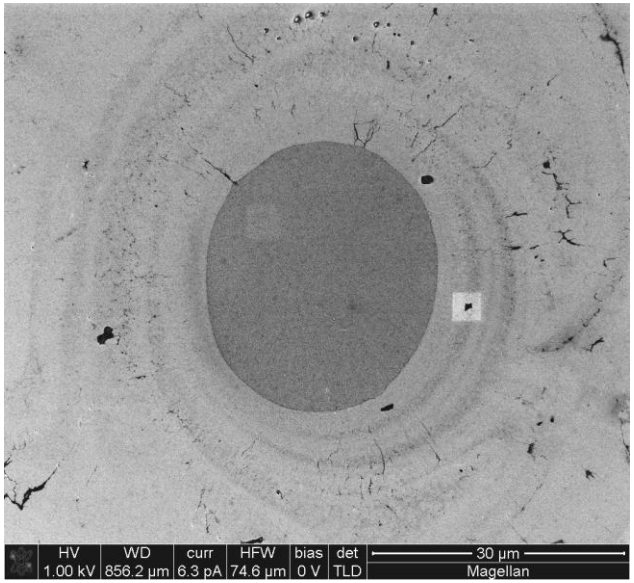
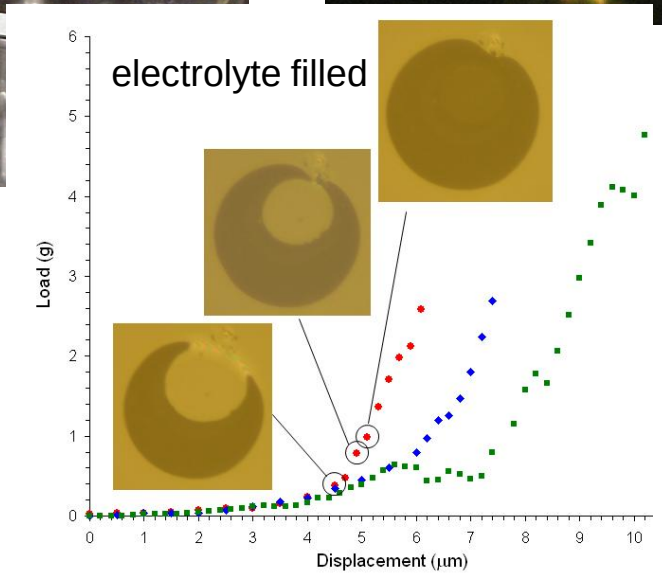
Can more detail be learned by restricting area to enable imaging?





Snapshot approach





Size limits – leak free seals with minimal under seal activity at 20 µm diameter, $1x10^{-6}$ cm^2

Current limits – galvanostatic polarization at relevant current densities

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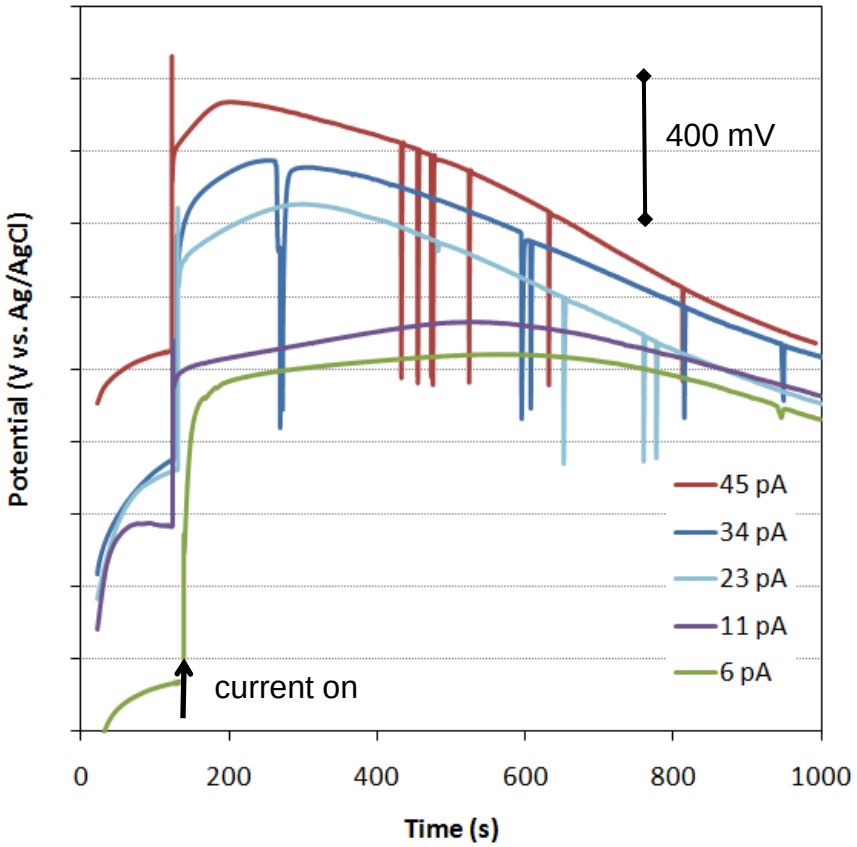
Defect and breakdown signatures are measureable in the micro-cell

Anodic polarization using a 20 μm diameter capillary



i (pA)	j (μA·cm^{-2})	t_{max} (s)	E^{*}_{max} (mV)	events
45	15	73	45	multiple, frequent
34	11	125	-38	multiple, frequent
23	7	320	-82	multiple, infrequent
11	4	480	-172	multiple, infrequent
6	2	450	-159	single, rarely
3	1	1930	-252	none detected

*vs. Ag/AgCl

Defect response is observed with anodic polarization

Breakdown events are observed at potentials > -550 mV vs. Ag/AgCl

Likelihood of a breakdown event scales with current magnitude

Drive single breakdown events – characterize the event signature – correlate events with evolved surface structure

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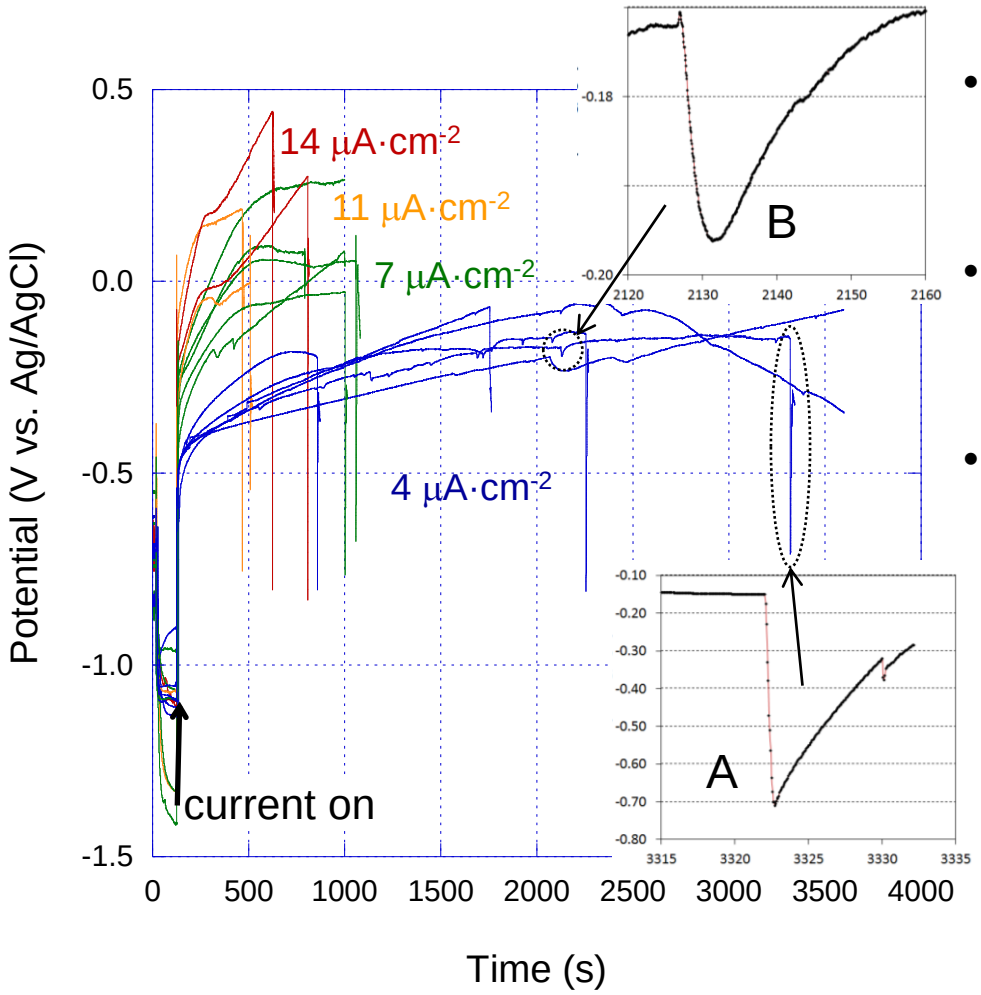
Attributes of Single Discharge Event Experiments



- Increased applied current density – higher probability of creating an event
- increased applied current density - shorter induction time for event occurrence
- Two types of depolarization signatures
  - large magnitude discharge events (A)
  - small magnitude or extended time perturbations (B)

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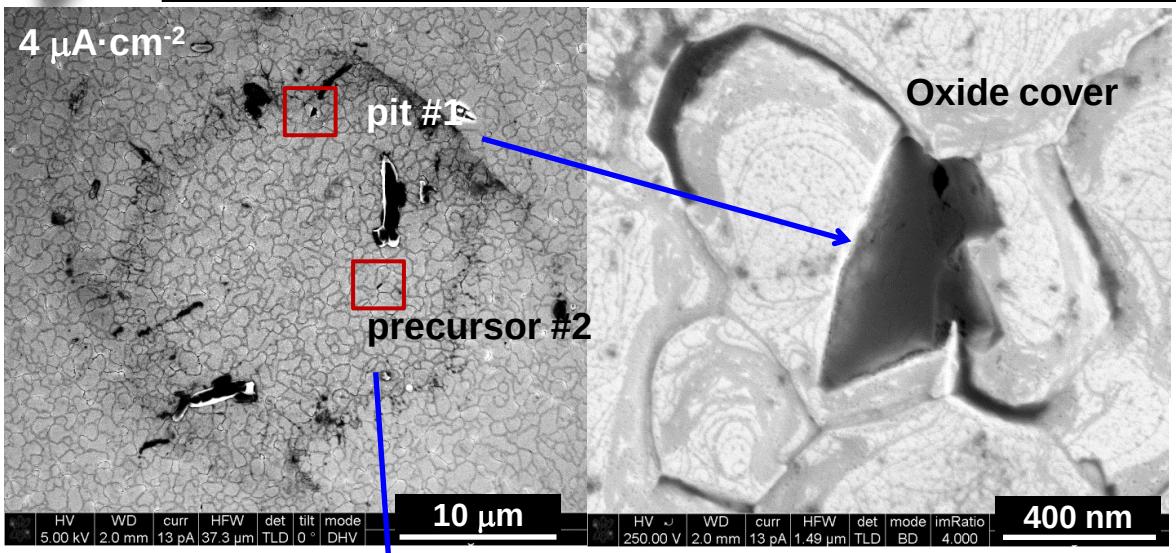
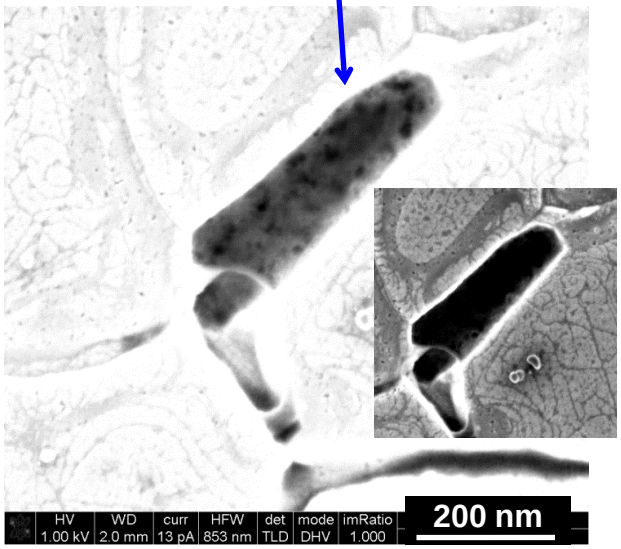
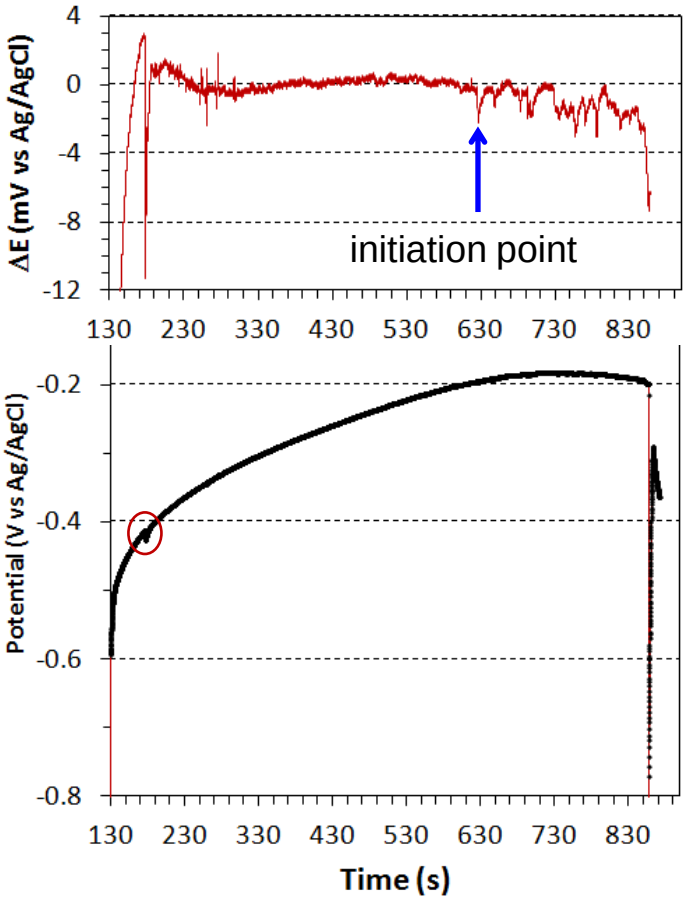
Sufficient current becomes localized to drive early stage pit formation





- Initiation sites – high topographic gradient (GBs)
- Void/pore formation is most prevalent in same regions
- Multiple initiation sites can be active concurrently

- Initiation signature appears to be the small $\delta E/\delta t$ fluctuations



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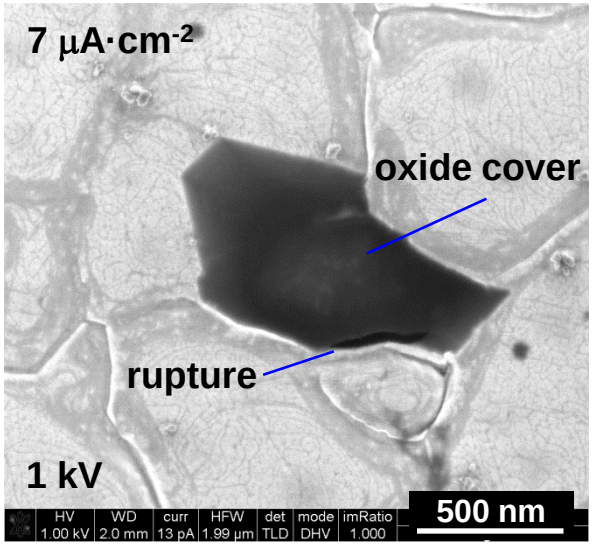
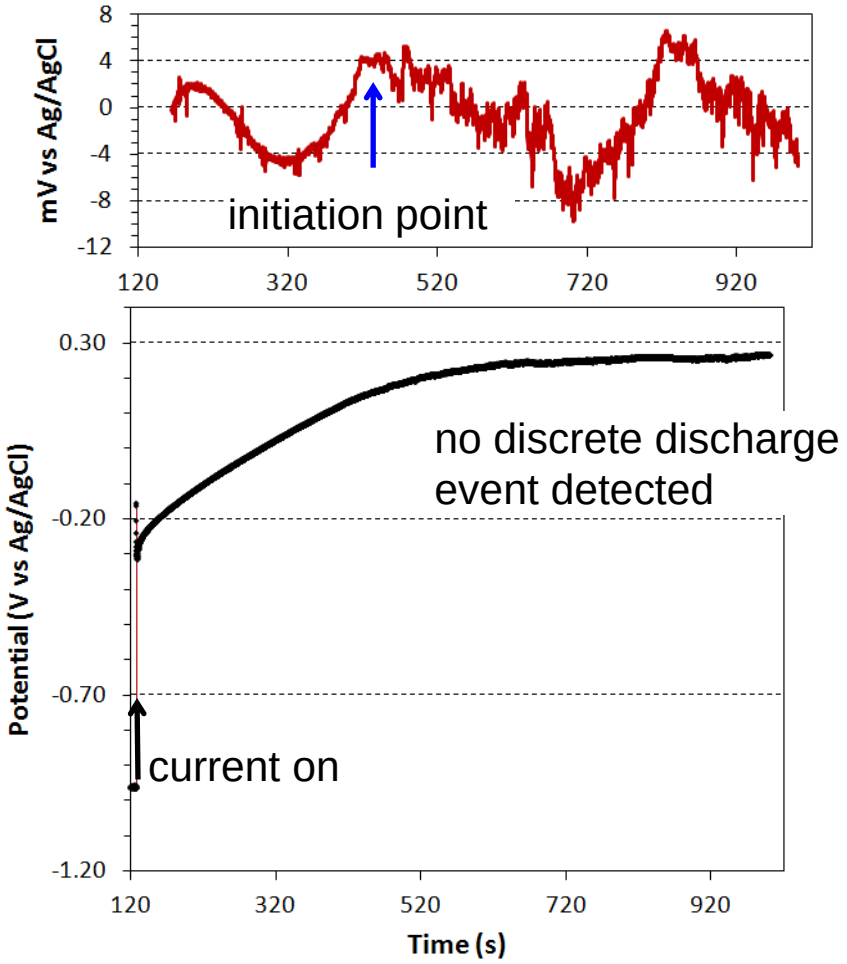
Electrochemical noise may also signal slow growth of an early stage pit



An occluded pit is observed despite the absence of a significant magnitude discharge event

- EC noise is a better indicator of micro-cell activity



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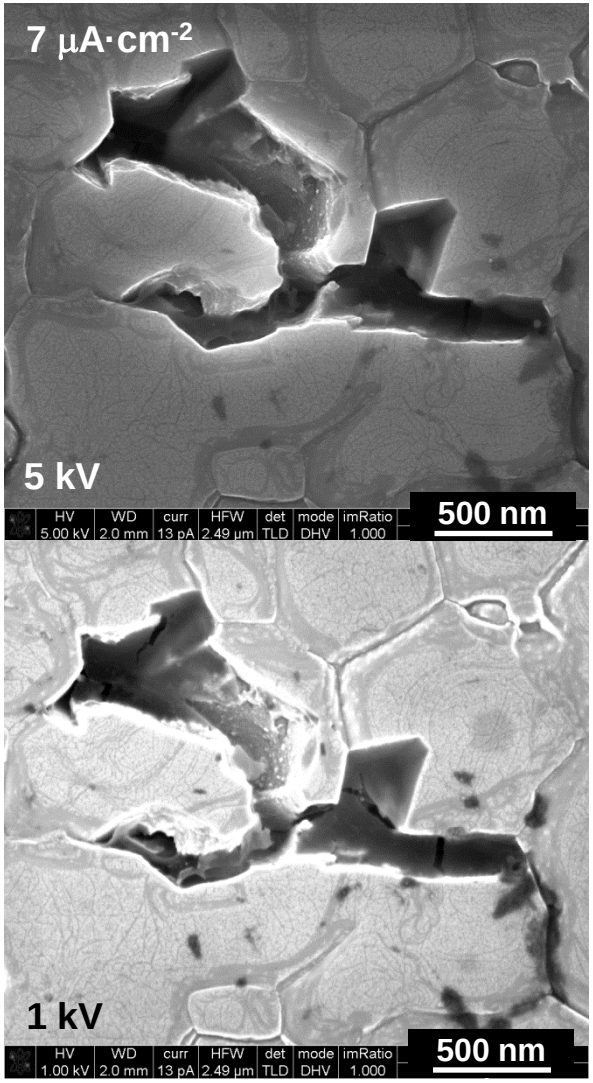
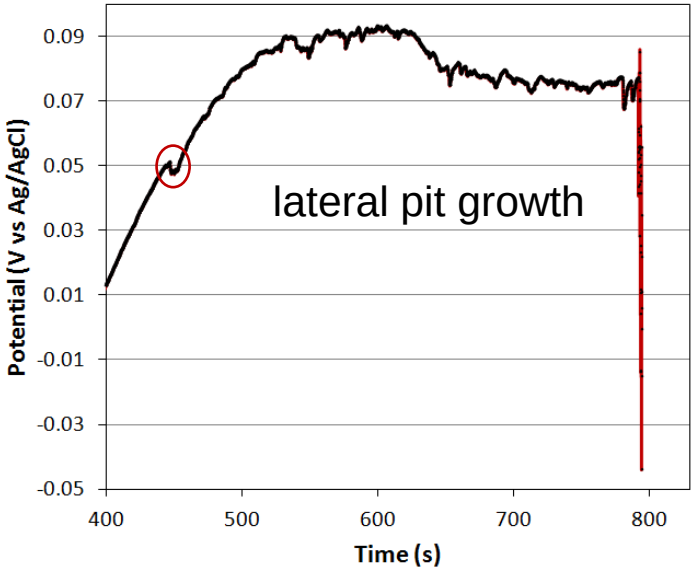
Extended lateral growth of a pit complex can exhibit a similar low amplitude signature



Single active area detected for this experiment



Lateral propagation favored by several factors

- (111) texture – favored dissolution planes are in-plane
- Grain boundary as a short circuit

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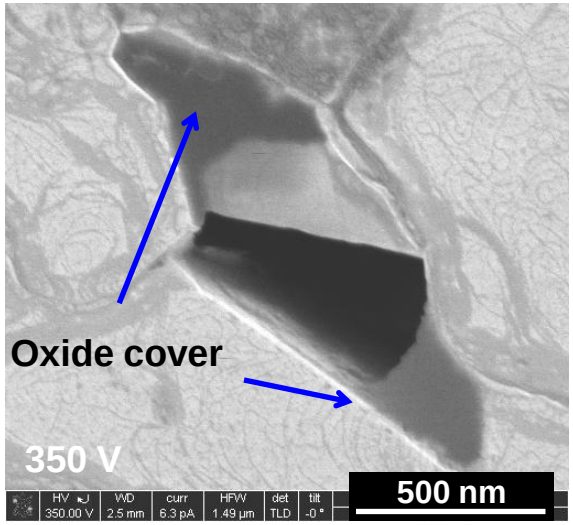
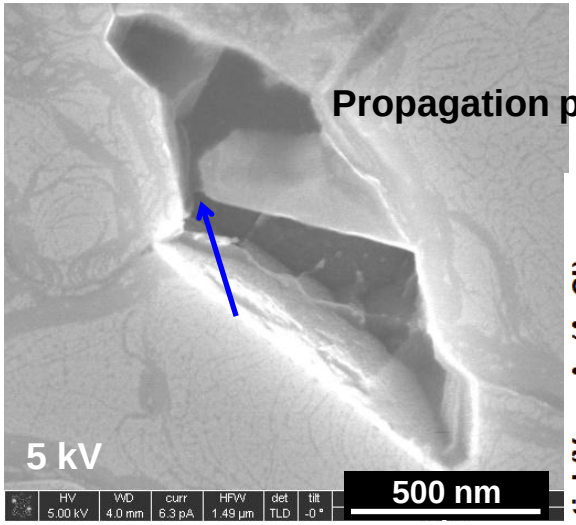
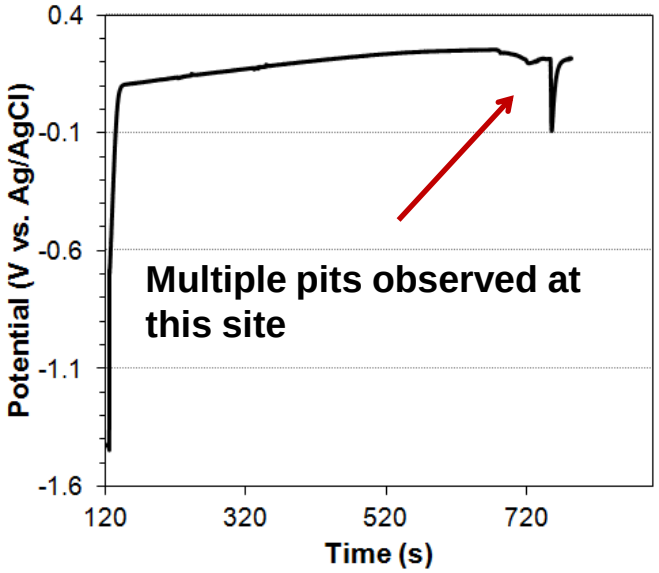
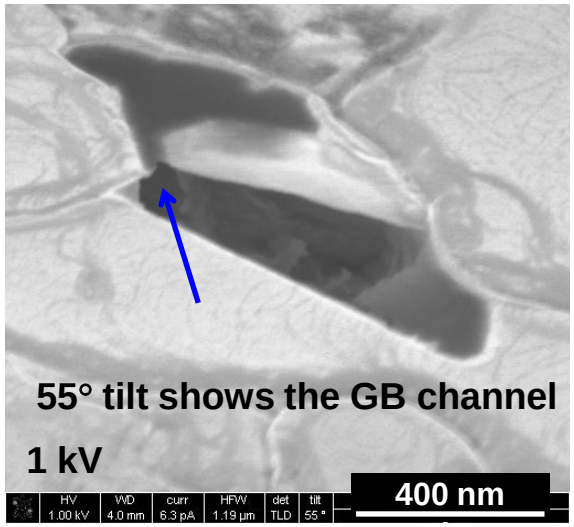
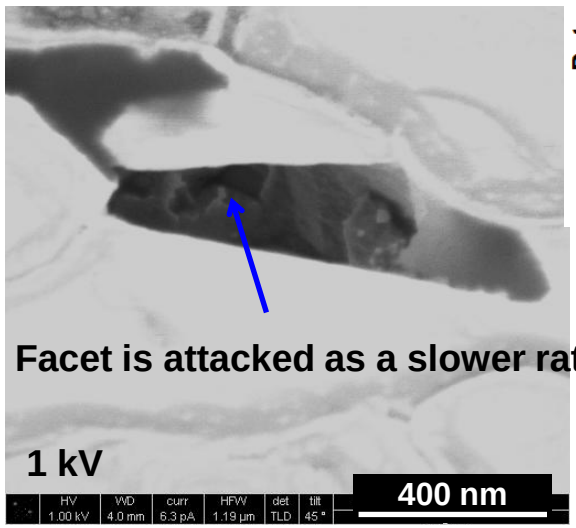
Staged pit growth aided by a grain boundary and compliant oxide cover











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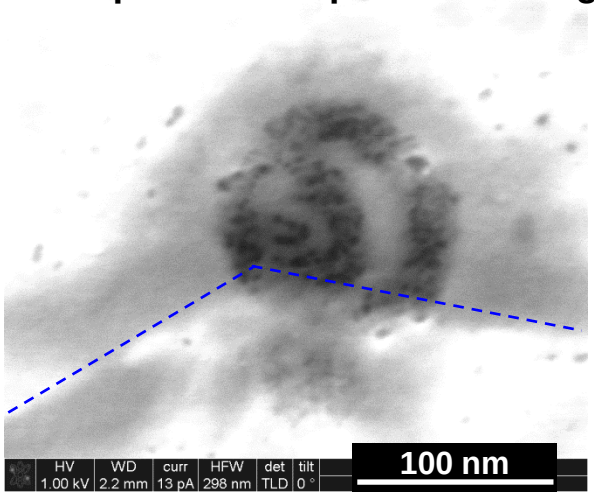
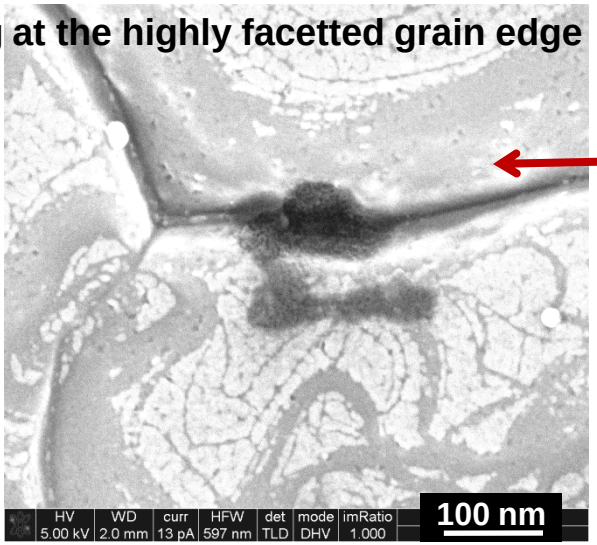
Evidence exists for interfacial voids acting as initiation sites

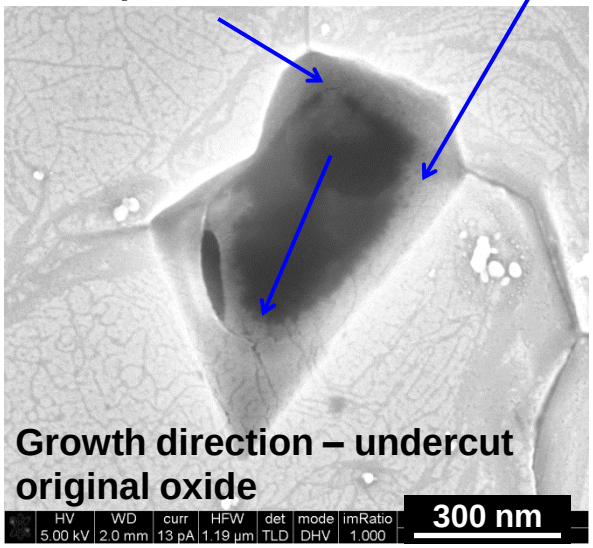
Examples of void/pore clustering at the highly facetted grain edge

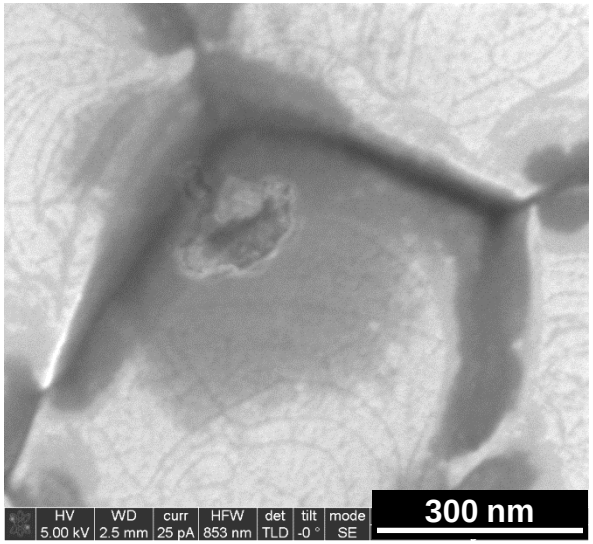


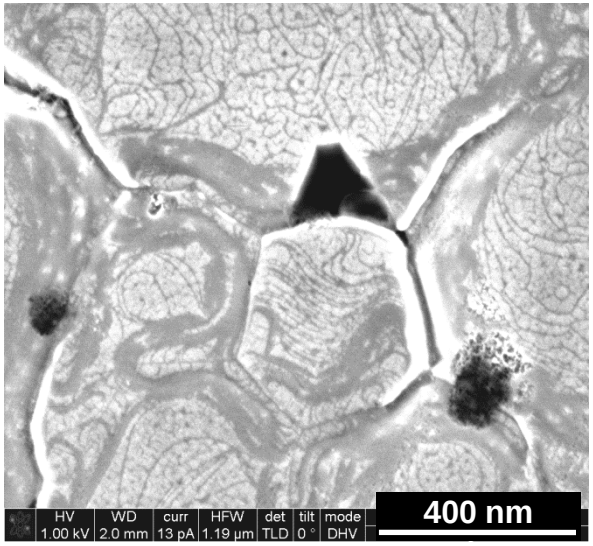


These initiation structures are seen in evolving pit structures

Pore perforated initiation site







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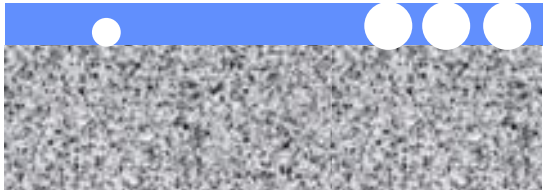
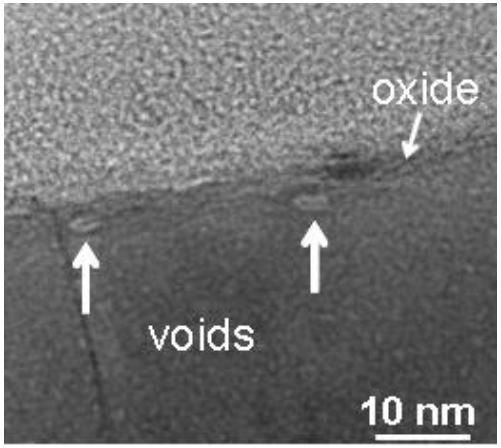
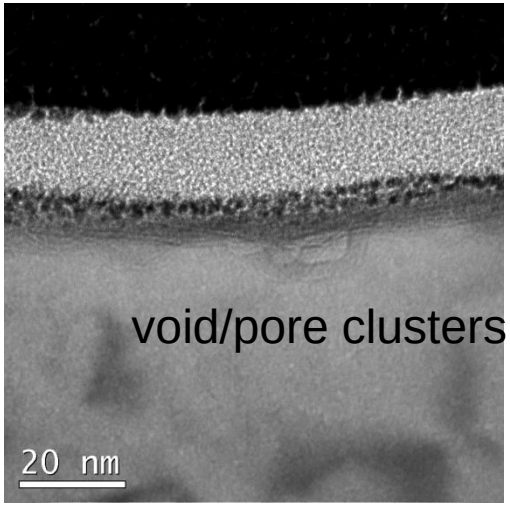
Interfacial voids as pit precursors

Void nucleation

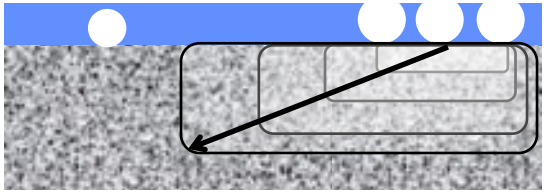
Growth and pore formation







Stable cluster formation – oxide perforation



Pit nucleation under oxide membrane

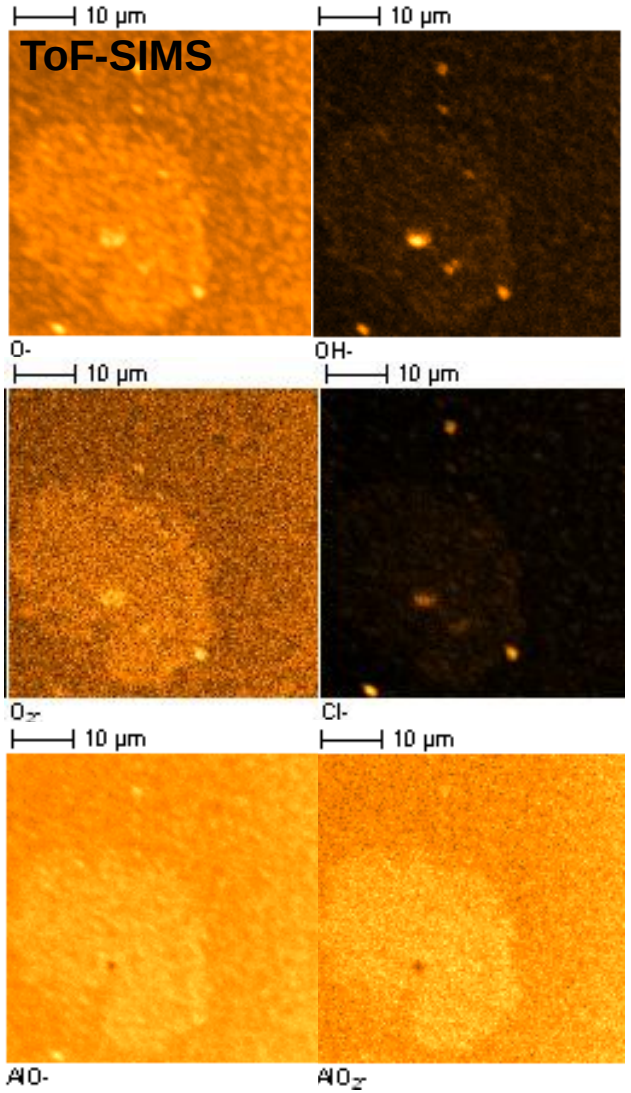
High gradient topology as the nucleation region:

Greatest local flux of Al cations

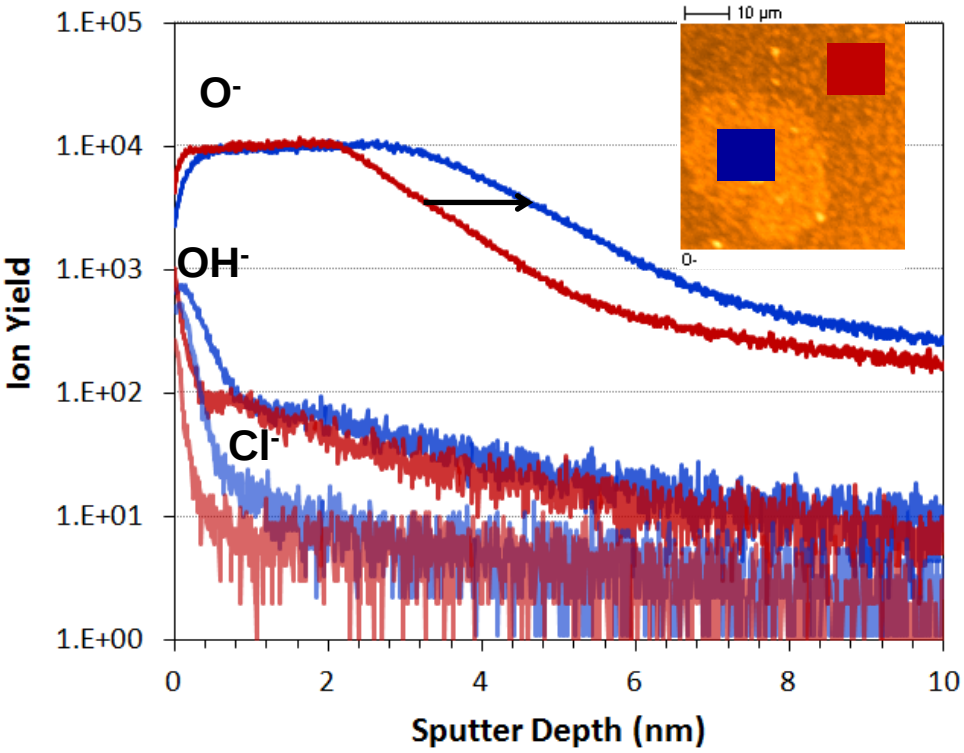
Structurally strained oxide

Steps stabilize void nucleation

Polarization drives oxide growth with minimal compositional change to the film



- Oxide growth: 10% from electrolyte immersion, 20 to 40% with polarization
- Cl^- primarily restricted to the hydrated outer layer



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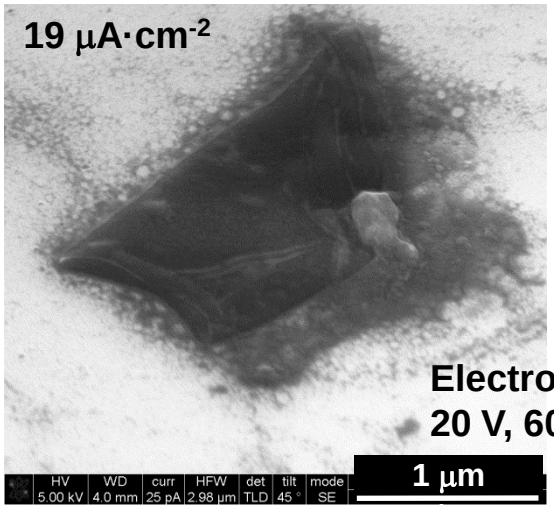
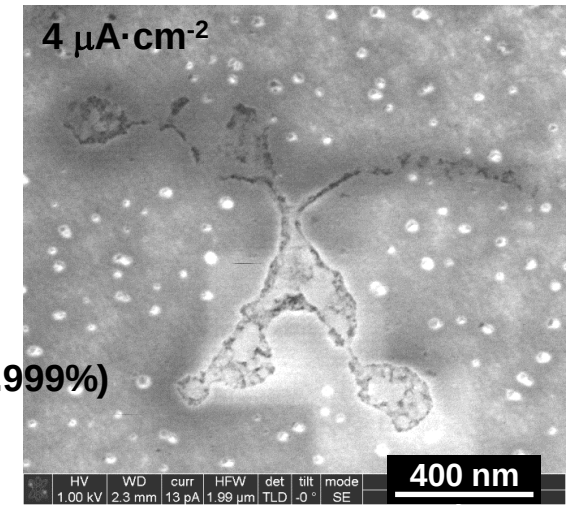
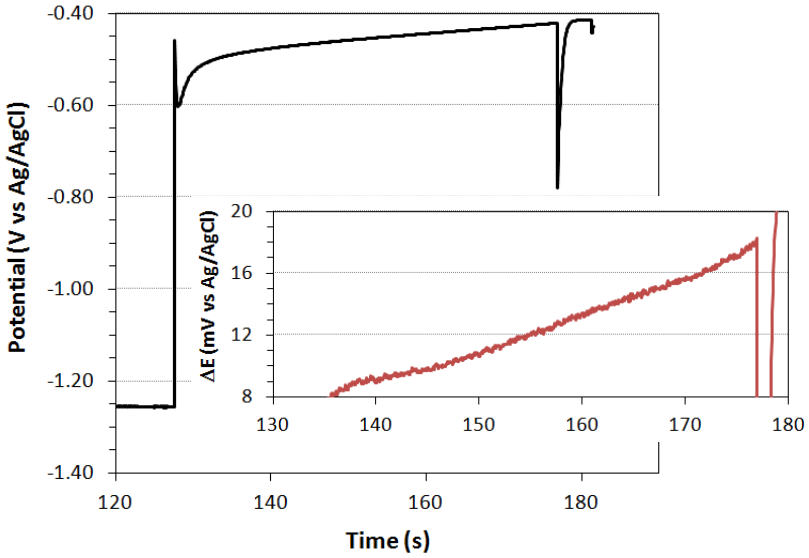
The lower impedance of a hydrous oxide requires higher currents to yield pits

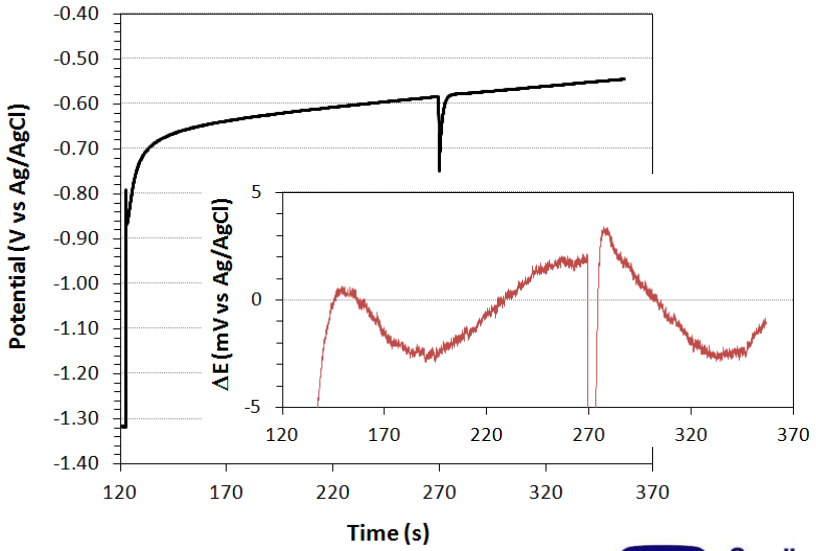


t_{ox}^{i} = 2.7 nm



Electropolished Al (99.999%)
20 V, 60 sec, -35°C





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Conclusions

- Restriction of electrode size and controlled galvanostatic polarization can be used to drive and characterize single breakdown events
- Breakdown produces structures ranging from undercut membranes to oxide capped early stage pits
- Pits initiate predominantly at the highly stepped perimeters of the grain boundaries – regions demonstrated to be active void and pore nucleation sites
- Void/pore structure is observed in evolved pits arguing that void nucleation serves as the precursor event for pit initiation in aluminum
- Currently working to apply this demonstrated level of control in *in situ* observation of pit initiation