SAND2013-9508C

Visualizing Oxide Breakdown and Pit Initiation in Aluminum using *ex situ* Electron Microscopy

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DOE Basic Energy Sciences Office of Materials & Engineering Sciences

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NNSA National Nuclear Security Administration

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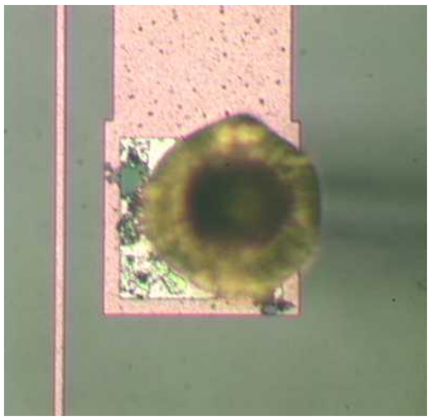
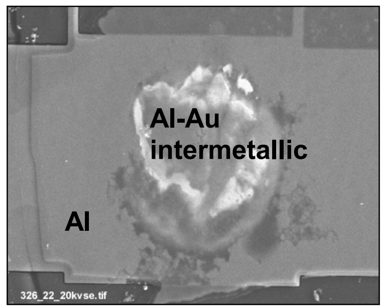
Why study pit initiation in aluminum?

High consequence systems: minimal separation between initiation and damage

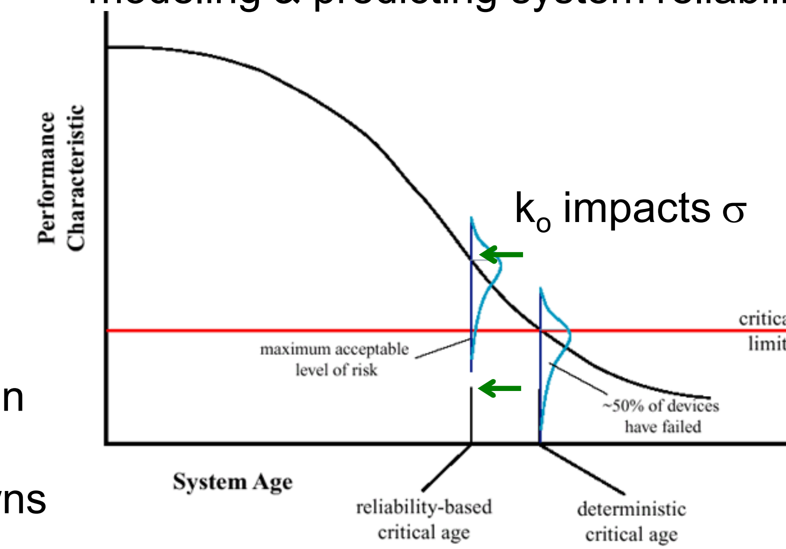
microelectronics – nanomaterials integration & devices





Al interconnects can undergo galvanic corrosion

modeling & predicting system reliability



rate constant (k_o) - lump sum term for unknowns

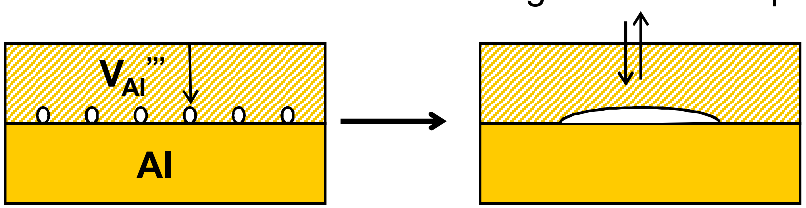
$$\frac{d(\Delta R/R_o)}{dt} = I(defects)k_o P_{Cl_2}(t)\left\{1-\exp\left[-\left(\frac{H(t)}{\eta}\right)^{\beta}\right]\right\}\exp\left[-\frac{E_a}{RT(t)}\right]$$

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

Proposed mechanisms for pit initiation

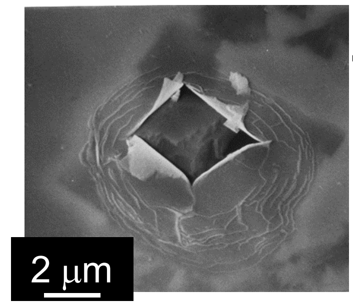
Vacancy condensation - Point Defect Model (Macdonald)

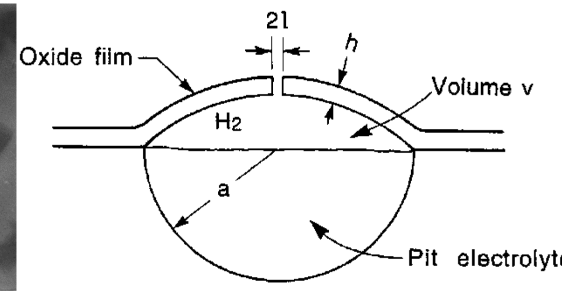
dissolution & growth rate disparity



2D void formation @ V_{crit}

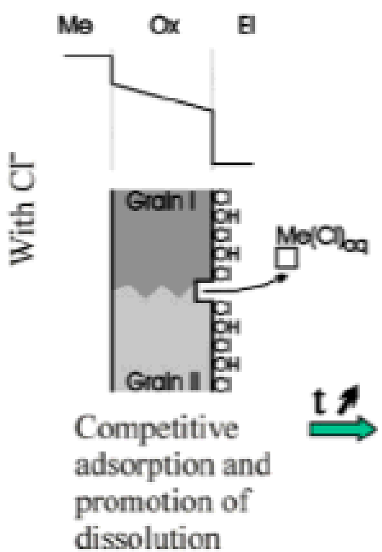
Nano-corrosion cells - Electrokinetic Model (McCafferty)



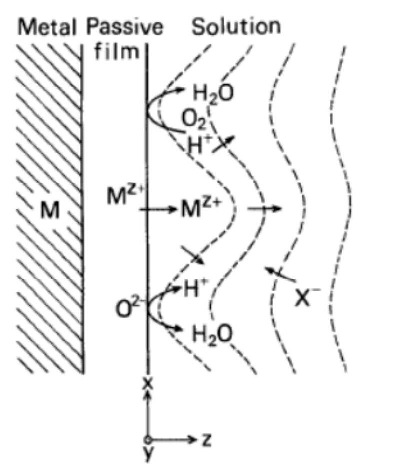


McCafferty & Natishan, 218th ECS #1322

Oxide grain boundaries - Marcus, Maurice & Strehblow



Aggressive anion and electric field perturbation - Okada



electrostriction

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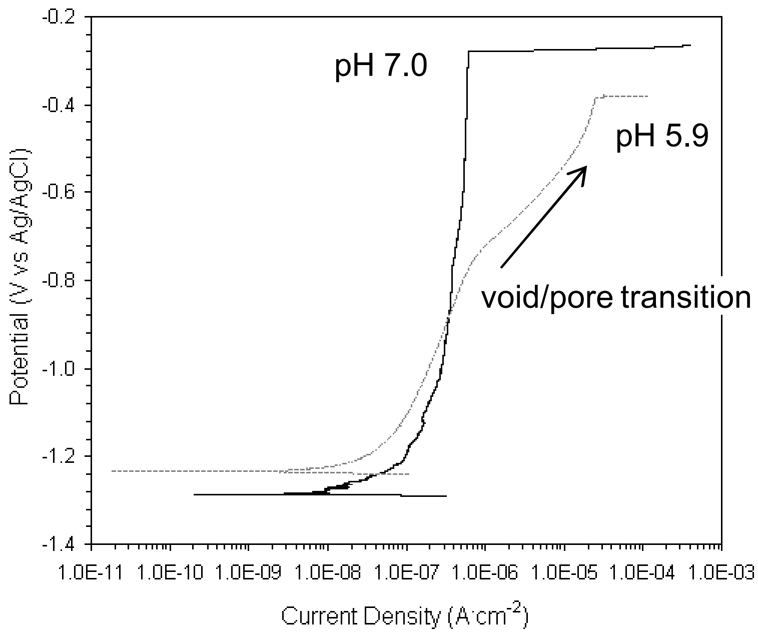
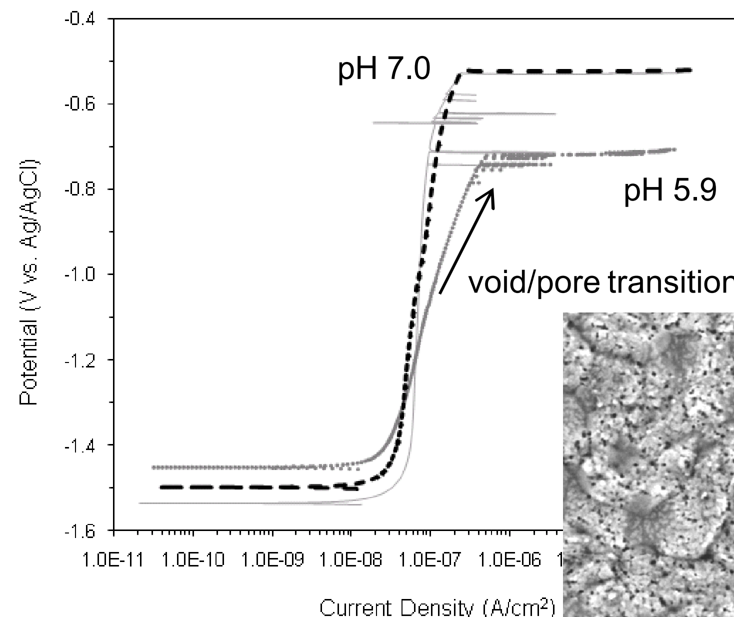
Pit initiation in an anhydrous oxide on Al coincides with oxide defect activity

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

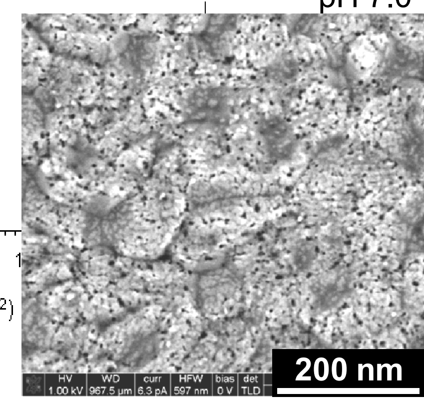
Macroscale measurements at 1 cm^2



Mesoscale capillary measurements at < 0.01 cm^2



pH 7.0



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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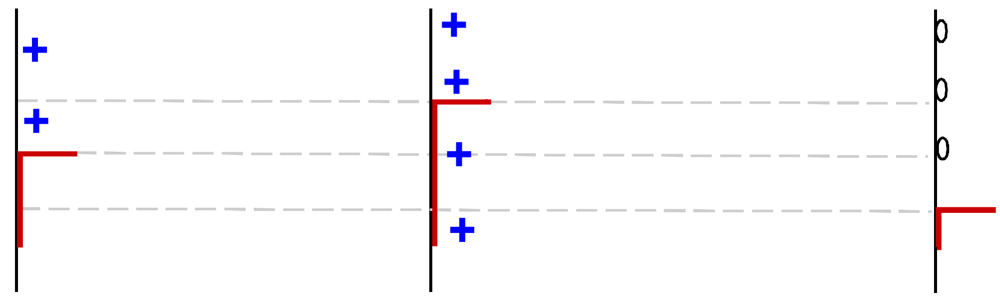
Void nucleation results from defect response to applied field

transport barrier | saturation | void nucleation



*interfacial $V_O^{i\cdot\cdot}$ | Al oxidation increases $V_O^{\cdot\cdot}$ | barrier relieved

$V_O^{\cdot\cdot}$ saturation through a simple equilibrium:

$V_O^{\cdot\cdot} + H_2O \rightarrow O_O + 2H^+$

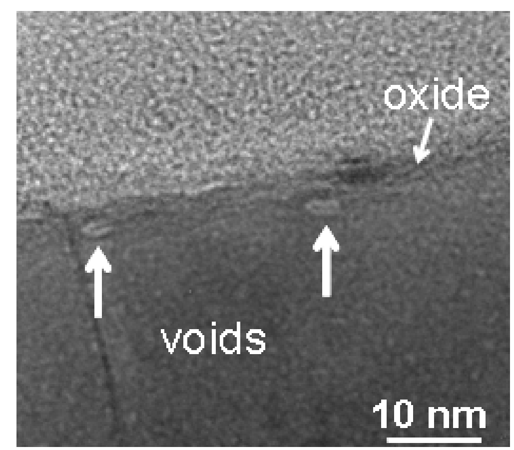
Alternate reaction to consider:

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

Ox:El interface barriers:

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

retarded by surface adsorbates or chelating species



Can voids contribute to pit initiation?

*Chang et al. *J.Phys Chem C* 2009

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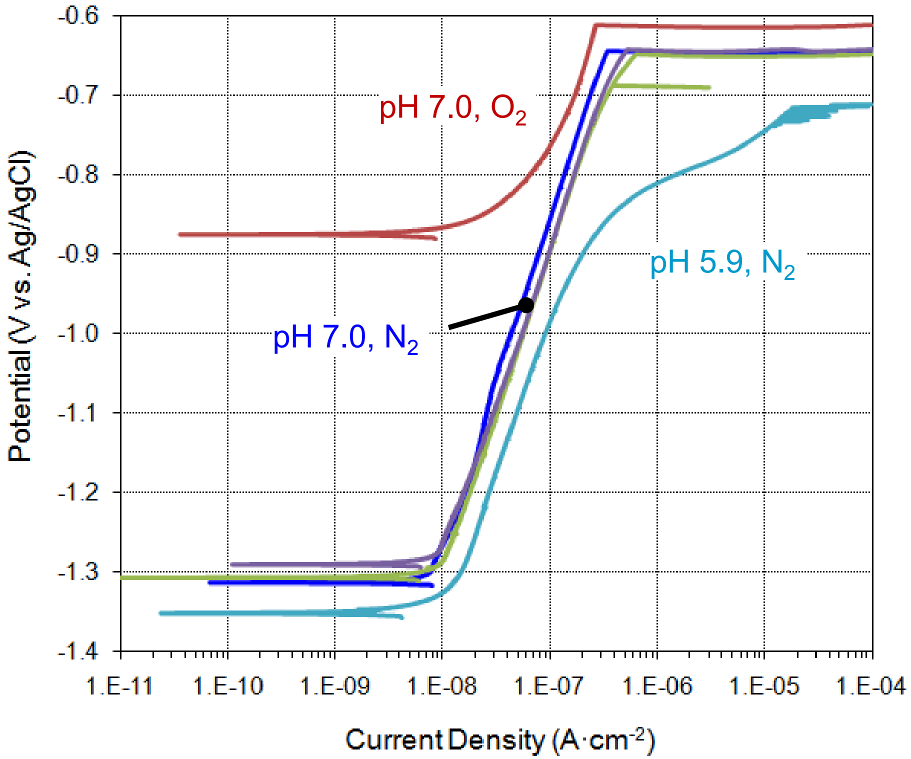
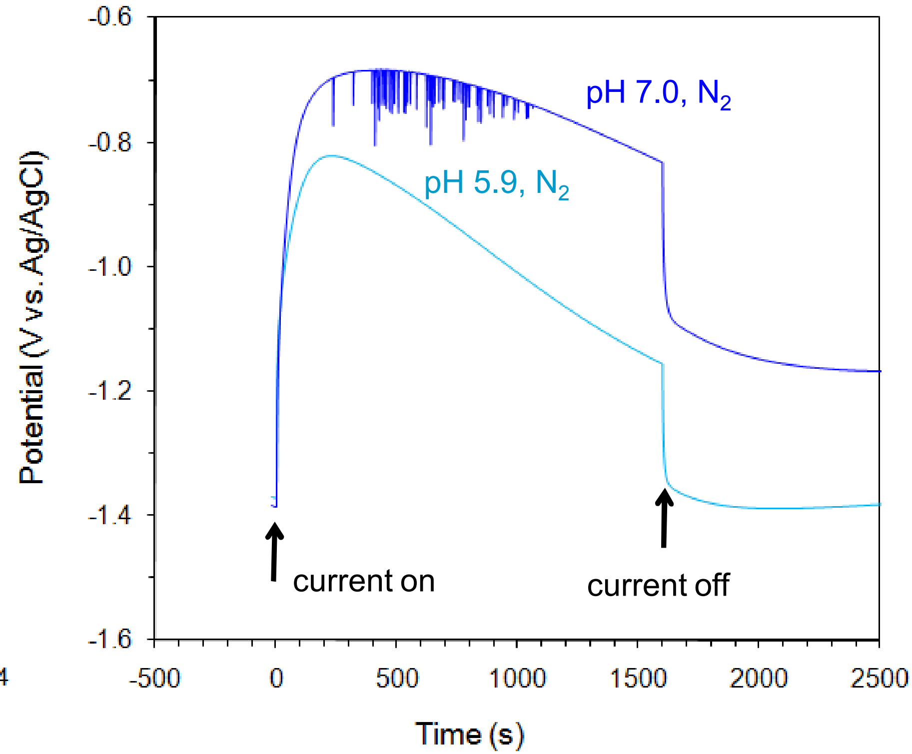
Chronopotentiometry highlights the co-incidence of pitting & defect activity

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





Pitting and accentuated dissolution compete

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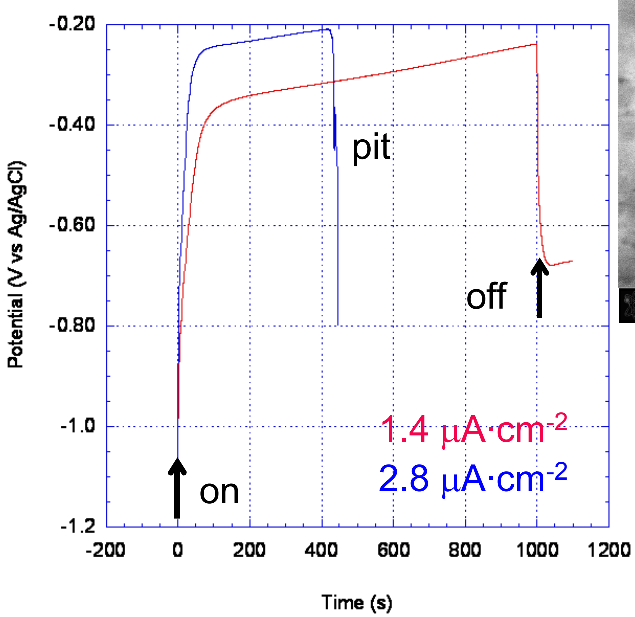
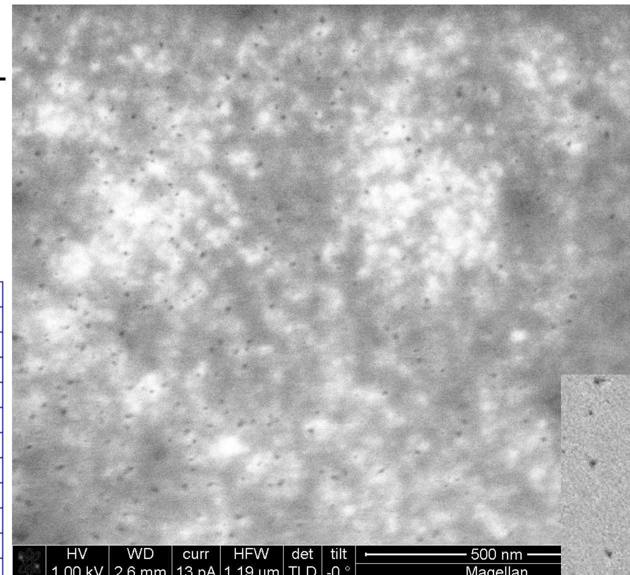
Similar defect processes operative in *not so model* oxides

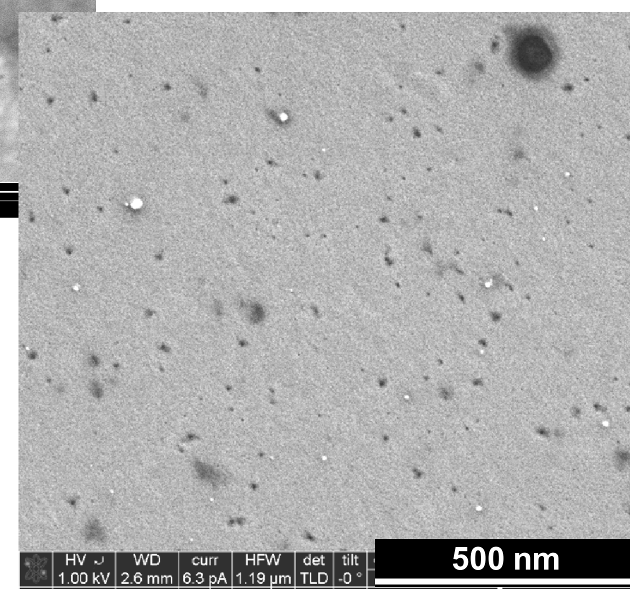
99.999% polycrystalline Al aqueous alumina (30 nm polish) – oxide allowed to dry

equilibrated 1 hour 50 mM Cl^-



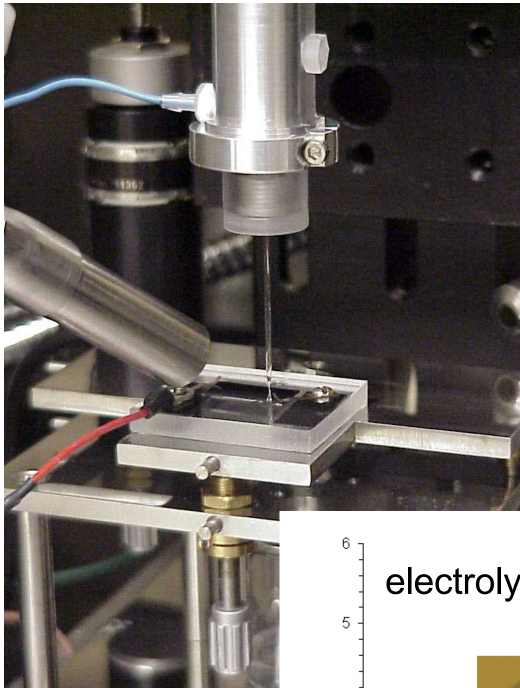


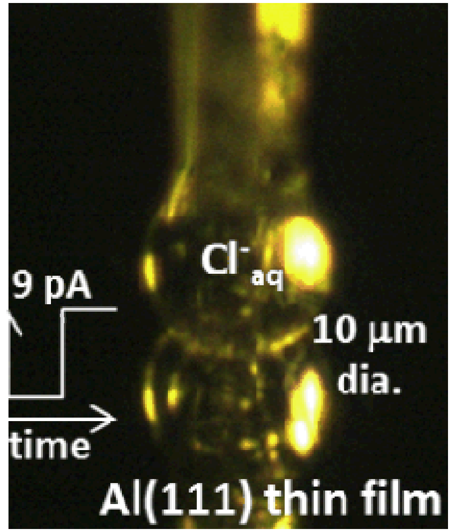
1.4 $\mu A \cdot cm^{-2}$, 1.4 mC



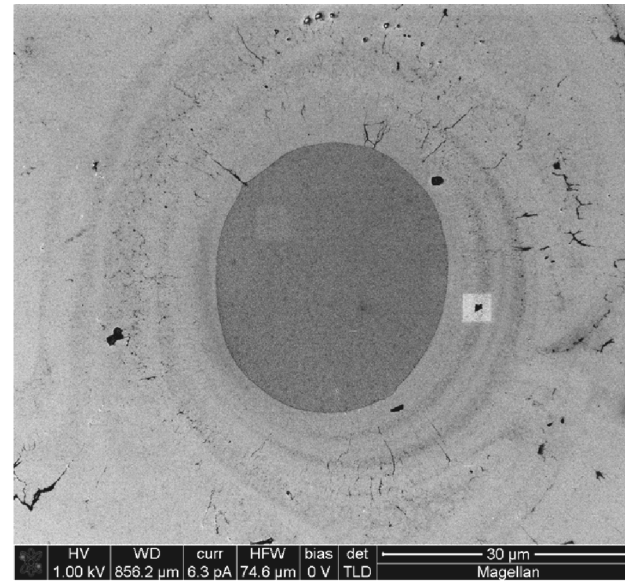
Model oxides may represent one way of probing the limiting cases of defect chemistry

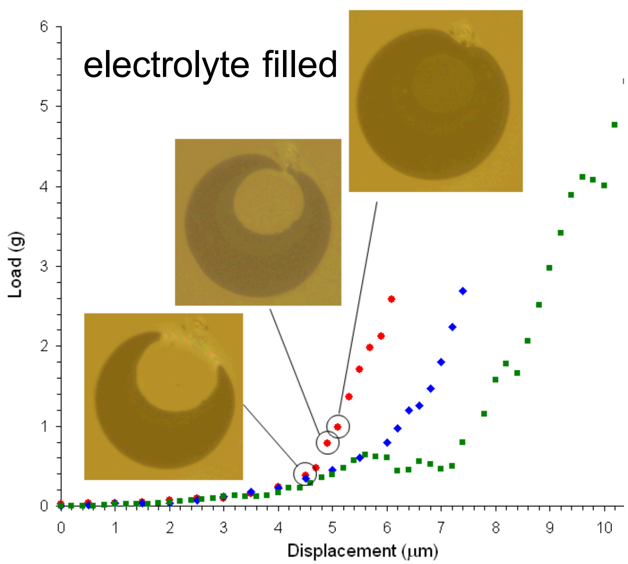
Can more detail be learned by restricting area to enable imaging?





Snapshot approach





Size limits – leak free seals with minimal under seal activity at 5 - 20 µm diameter, 1×10^{-7} - 1×10^{-6} cm^2

Current limits – galvanostatic polarization at relevant current densities

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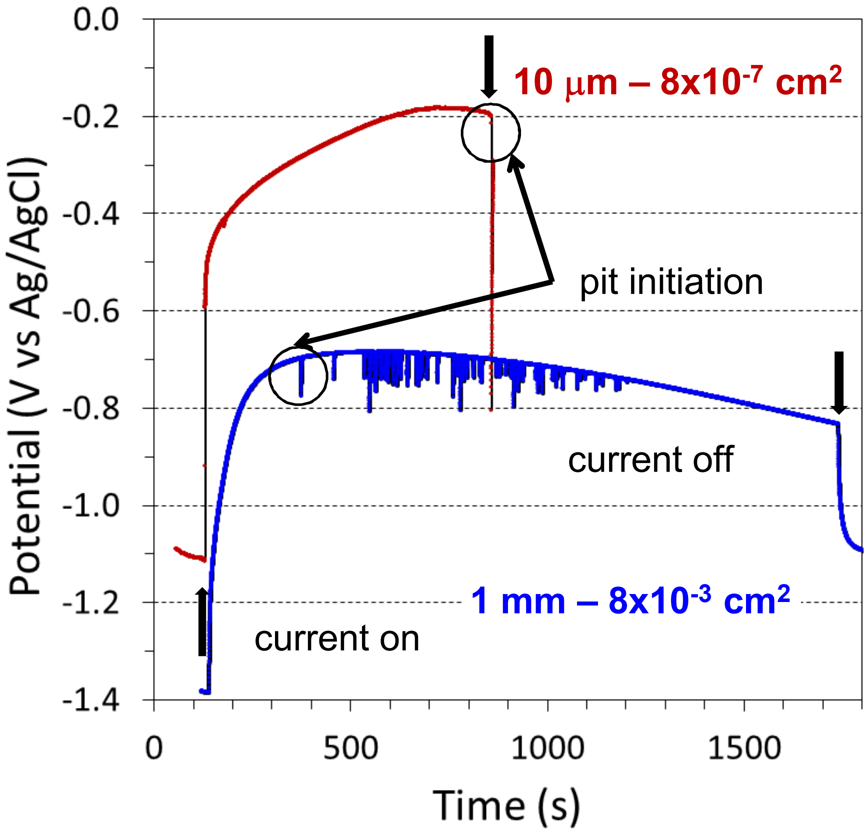
Microcell Measurements Yield Meaningful Data

Potential response to a current stimulus is consistent across 1 cm^2 to $2x10^{-7}$ cm^2



Single events are isolated with small areas

Reduced current – limited available to accelerate pit growth

Possible opportunity to characterize initiation sites

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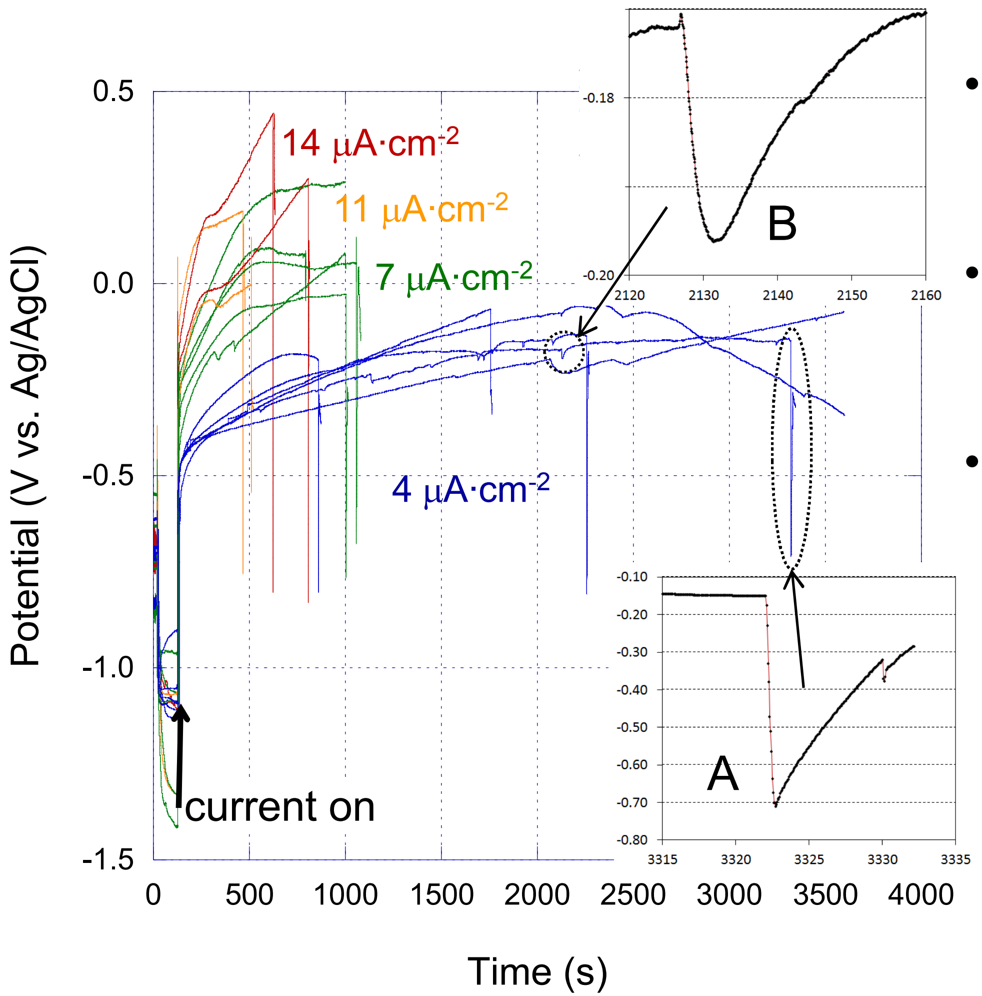
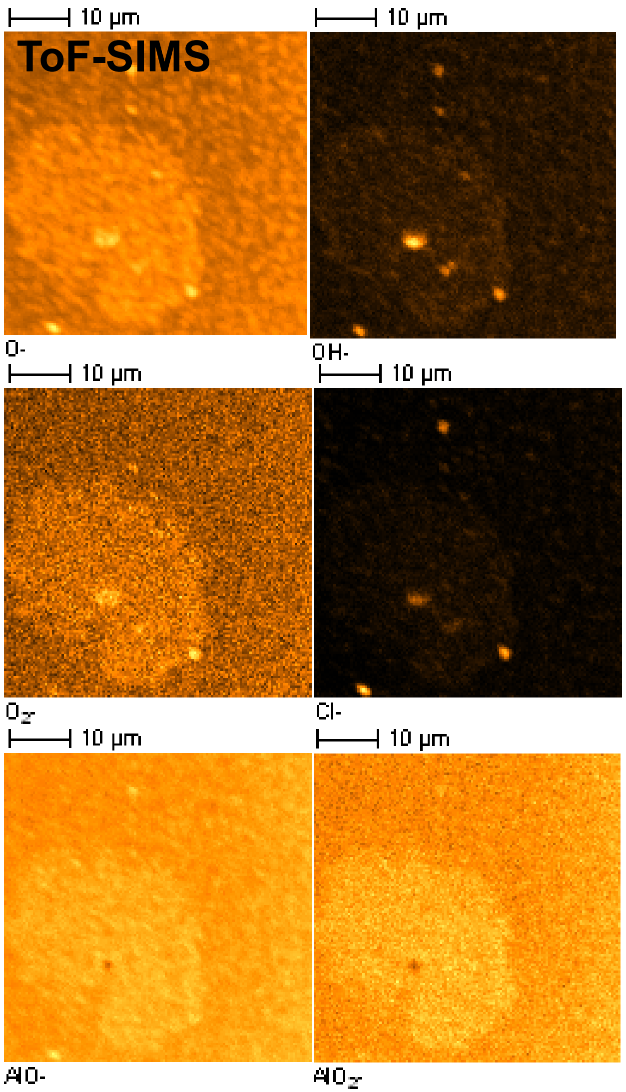
Attributes of Single Discharge Event Experiments

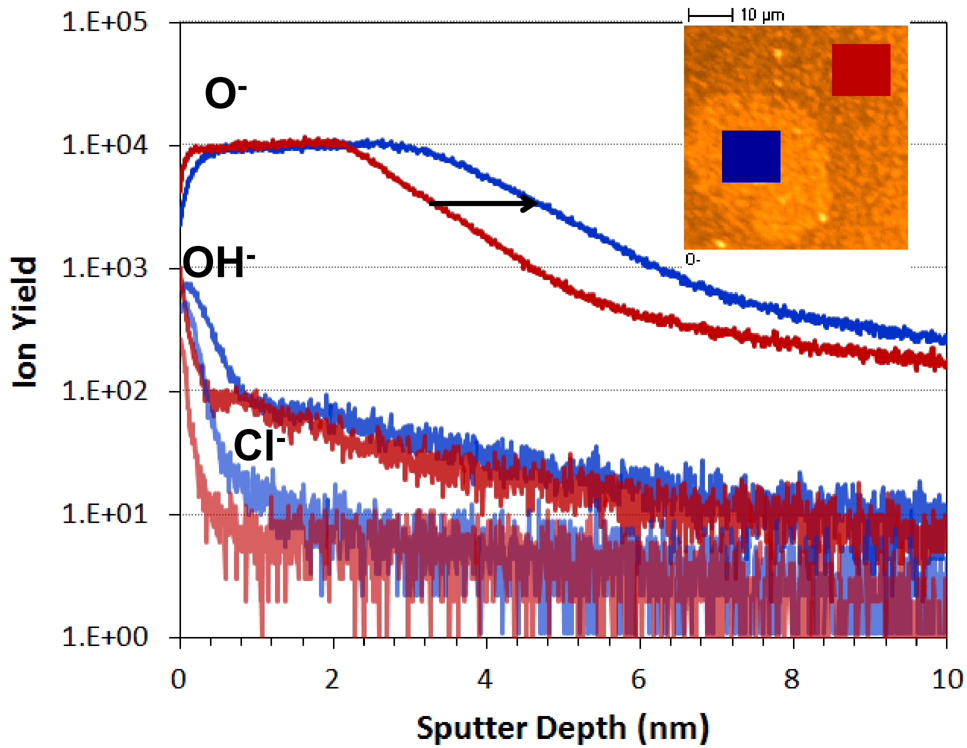


- Increased applied current density – higher probability of creating an event
- increased applied current density - shorter induction time for event occurrence
- Two types of depolarization signatures
  - large magnitude discharge events (A)
  - small magnitude or extended time perturbations (B)

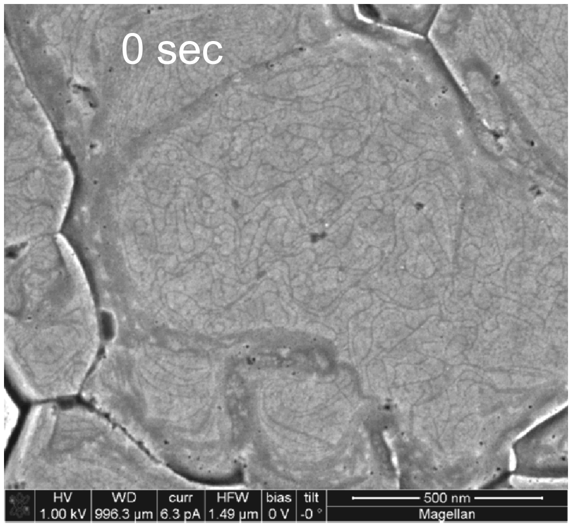
Polarization drives oxide growth with minimal compositional change to the film



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



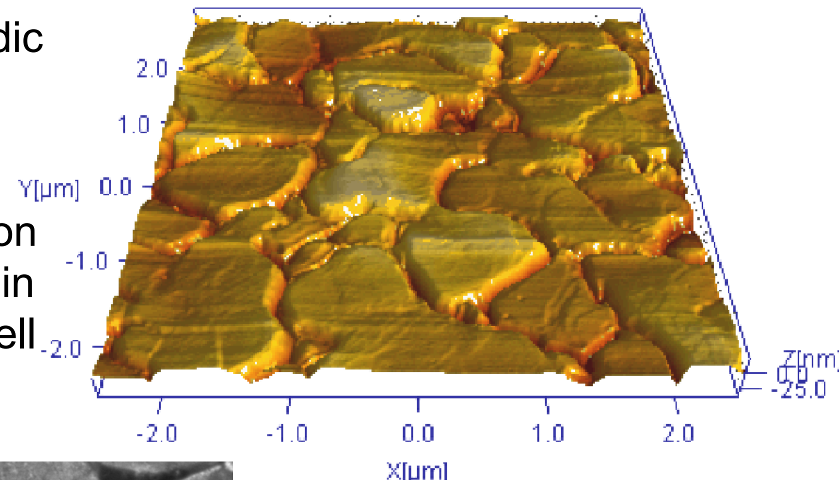
Structural impact of polarization is greatest at the high step density facets of the grains

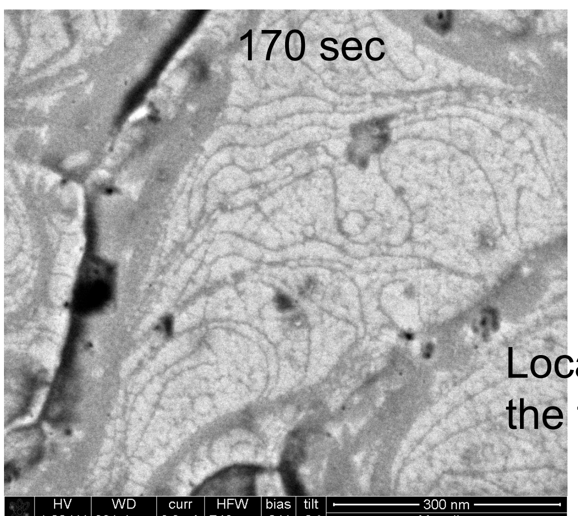


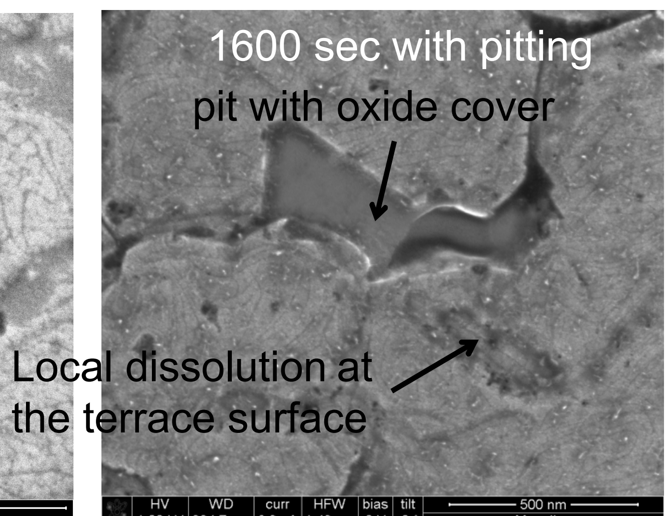
700 nm thick Al(111) film in de-aerated 50 mM NaCl pH 7
– larger grains for better spatial discrimination

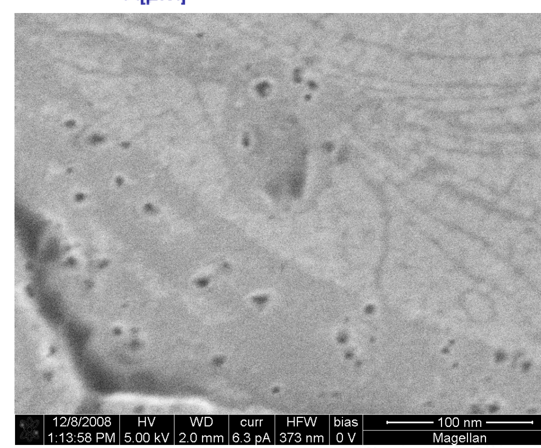
0.6 μA·cm^{-2} anodic polarization for variable time

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









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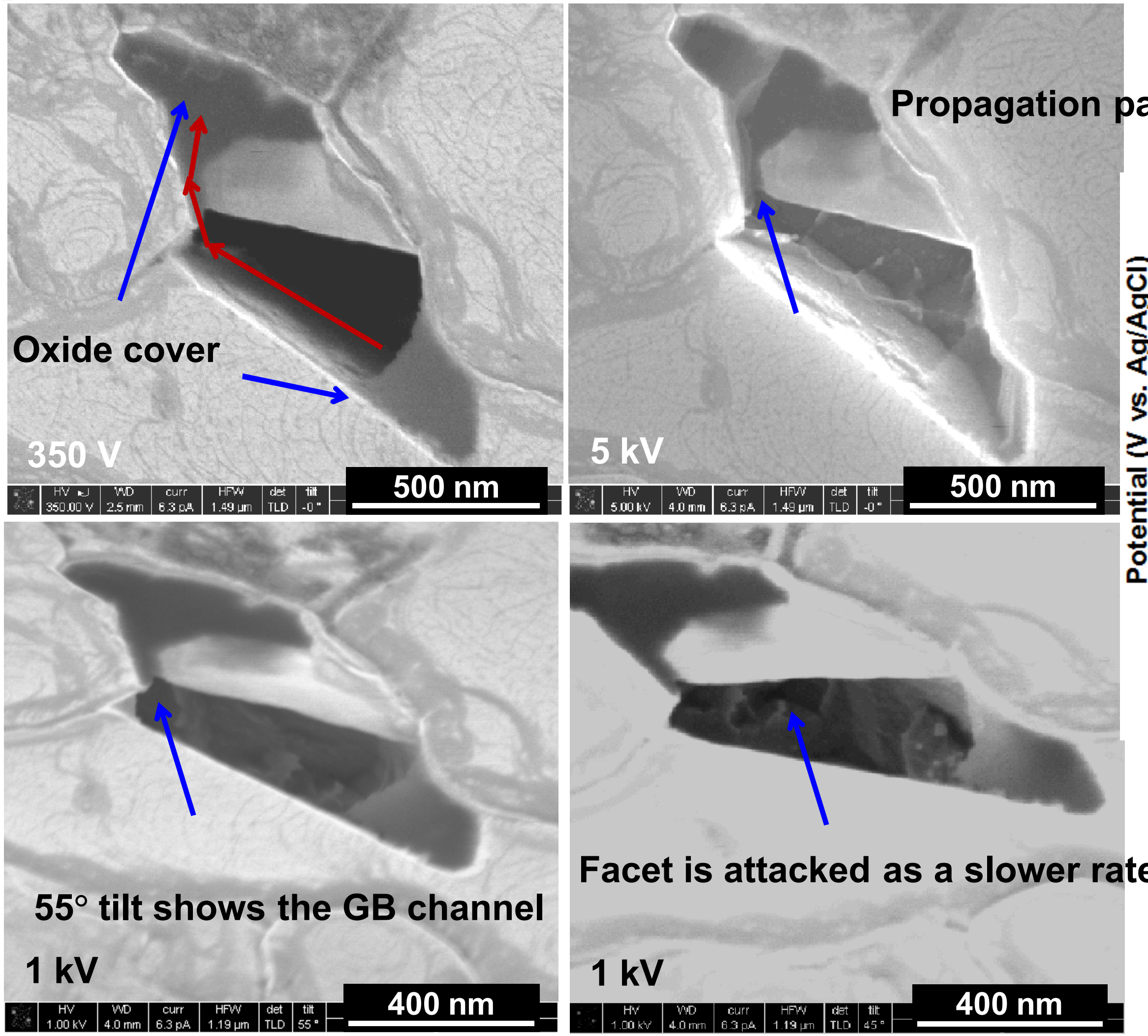
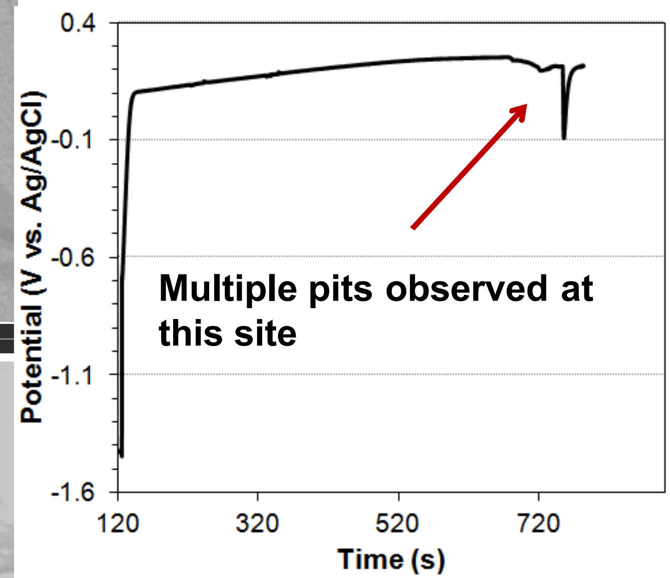
Evolved pits possess compliant oxide covers





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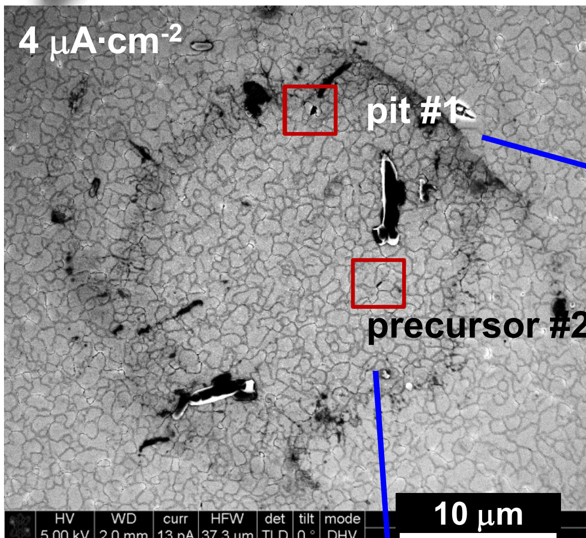
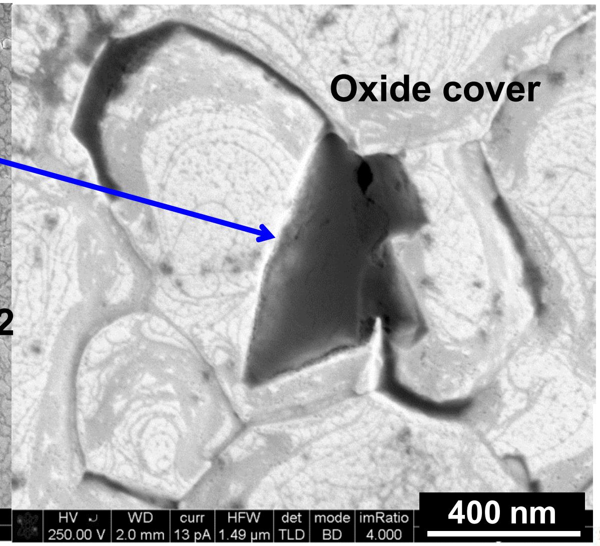
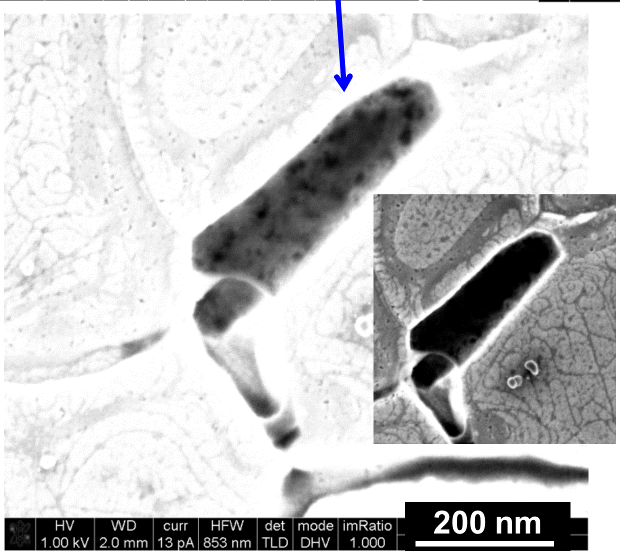
Sufficient current becomes localized to drive early stage pit formation

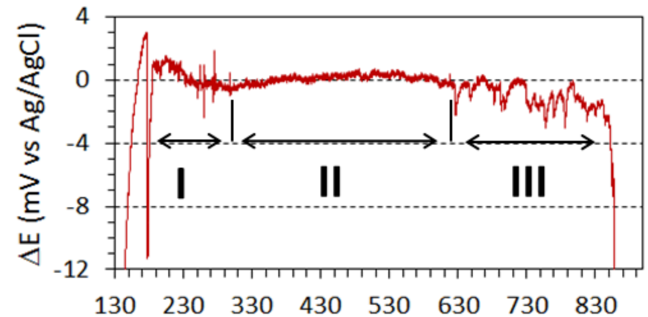


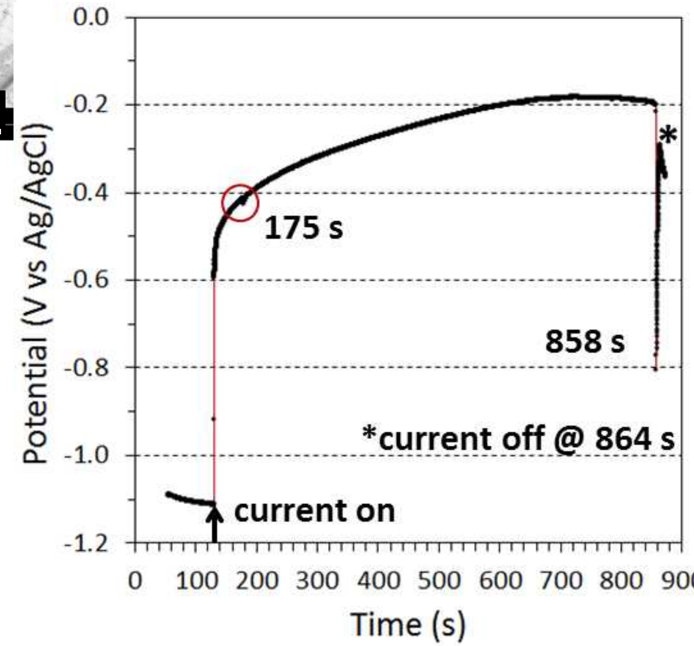




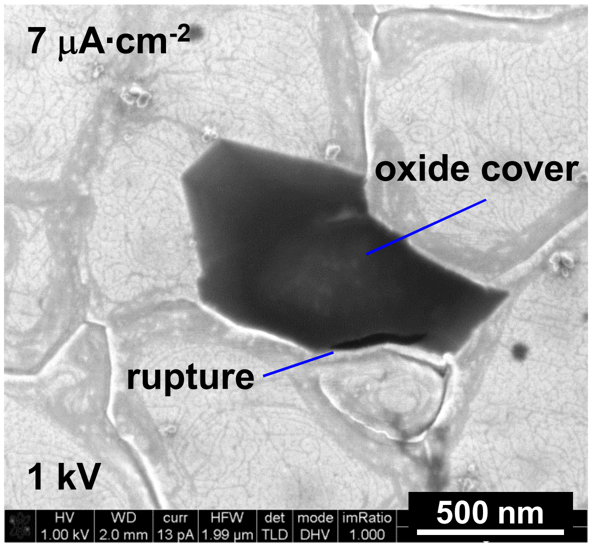
- Initiation sites – high topographic gradient (GBs)
- Void/pore formation is most prevalent in same regions
- Multiple initiation sites can be active concurrently

Initiation - δE/δt fluctuations



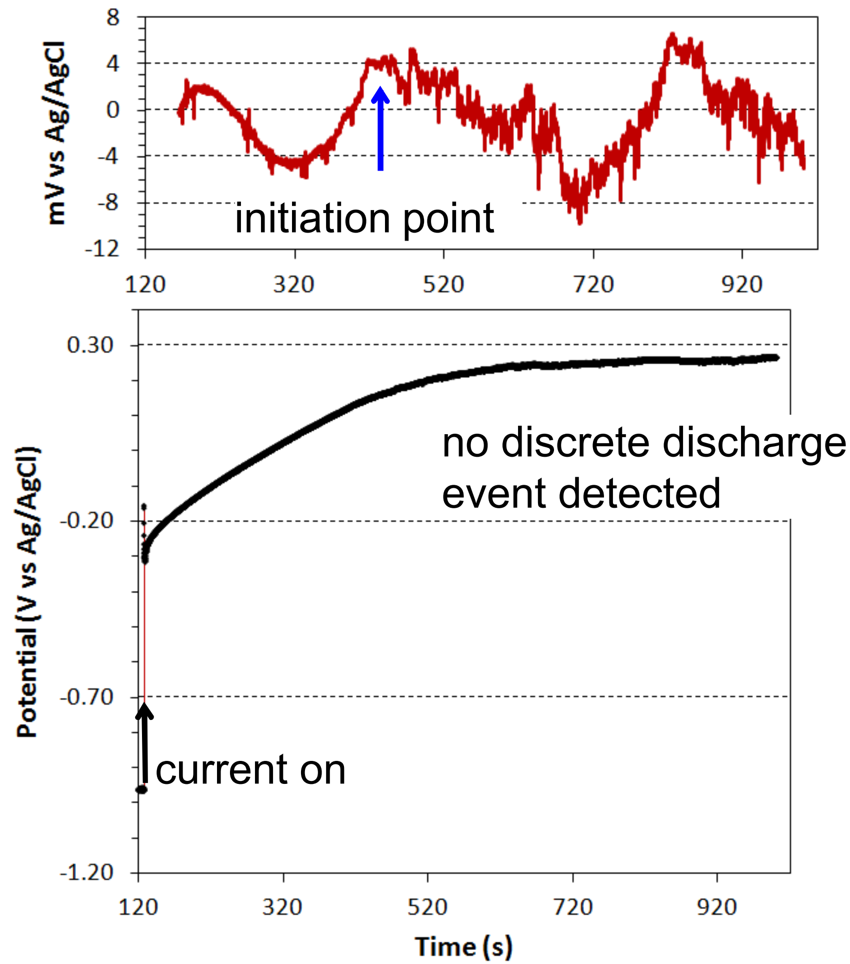


Electrochemical noise may also signal slow growth of an early stage pit

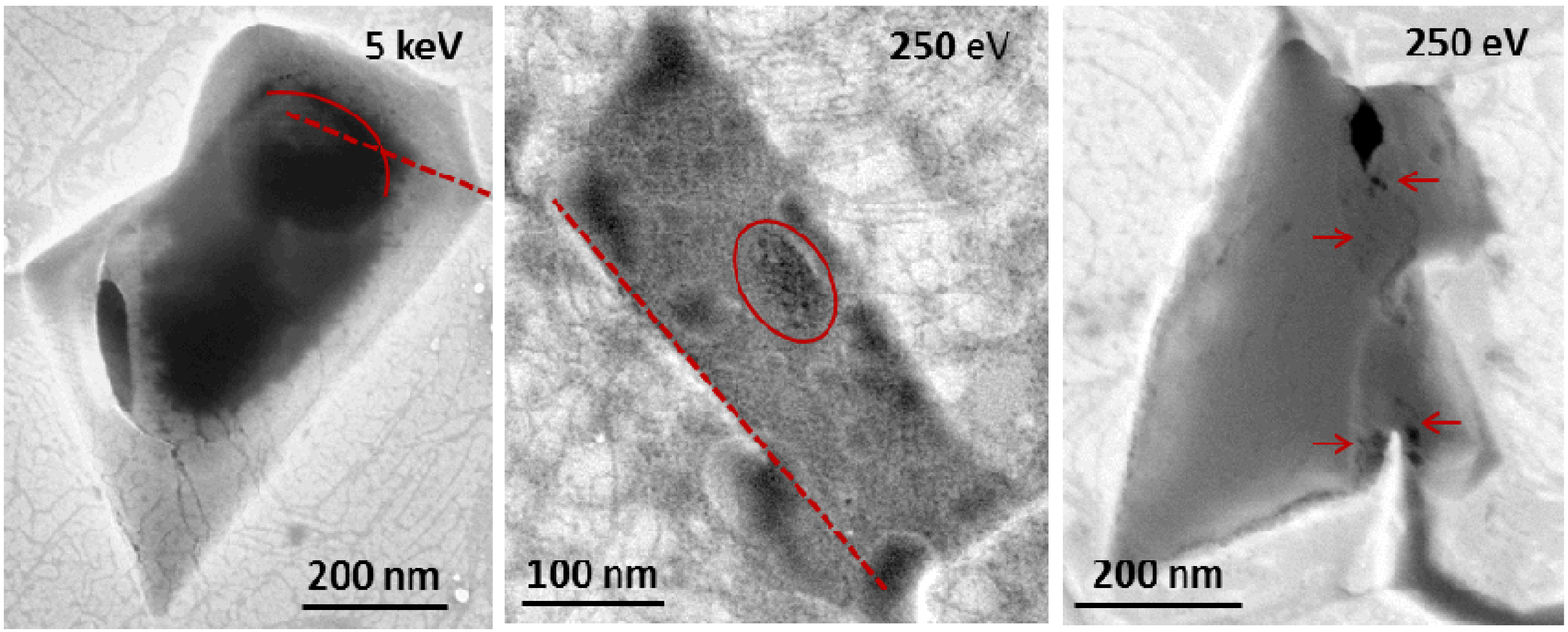


An occluded pit is observed despite the absence of a significant magnitude discharge event

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



Early stage pits: oxide membranes possess pore clusters



pore clusters appear near grain boundaries

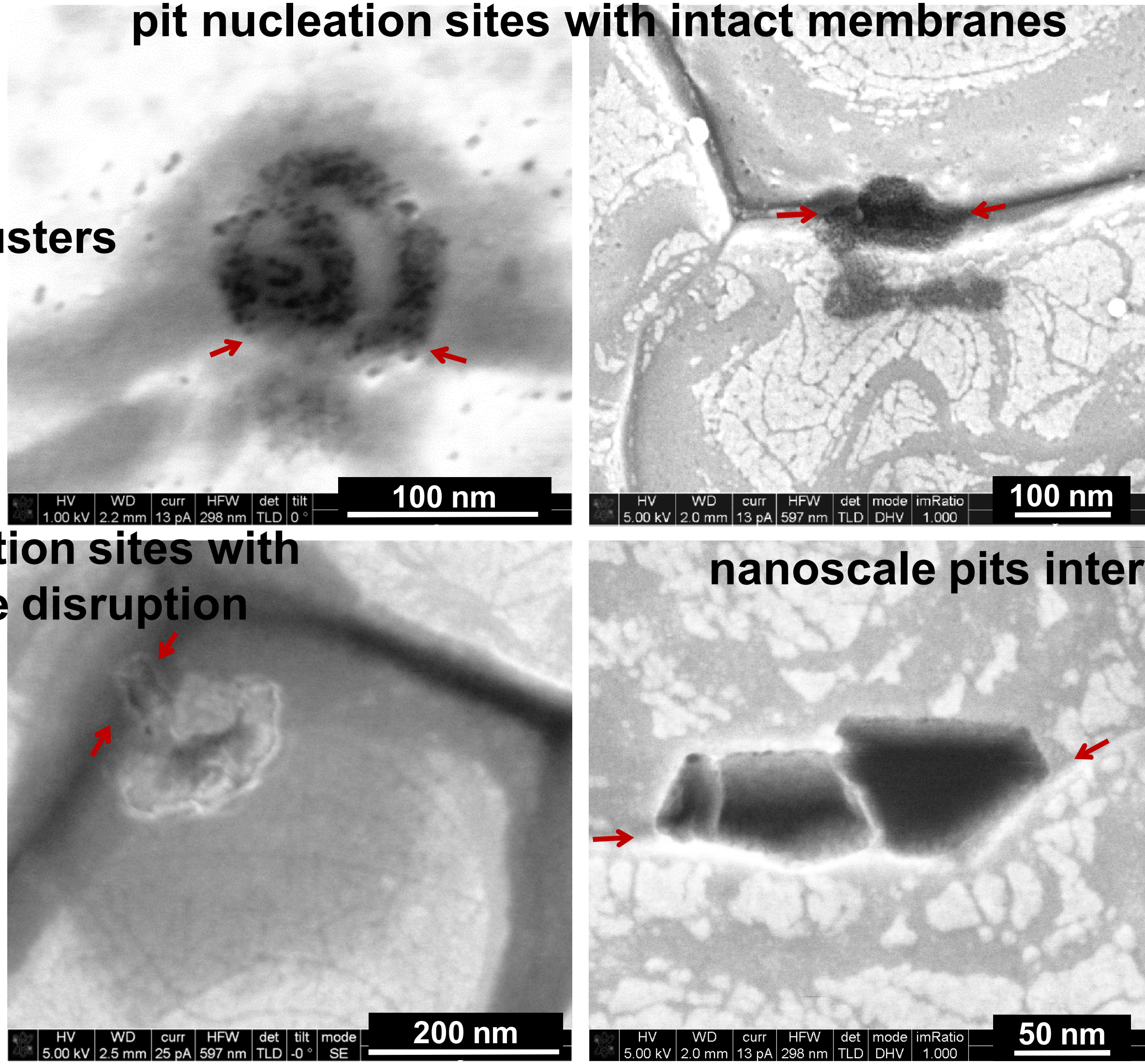
Pit precursors: concentrated pore clusters are common for high gradient regions

pit nucleation sites with intact membranes

pore clusters

pit nucleation sites with membrane disruption

nanoscale pits internal to a grain



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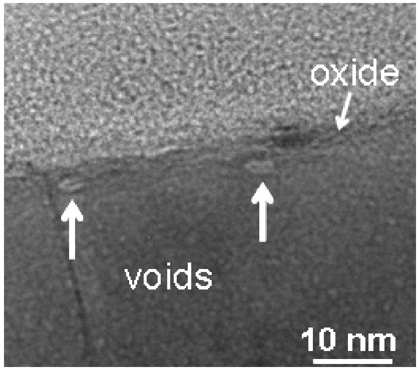
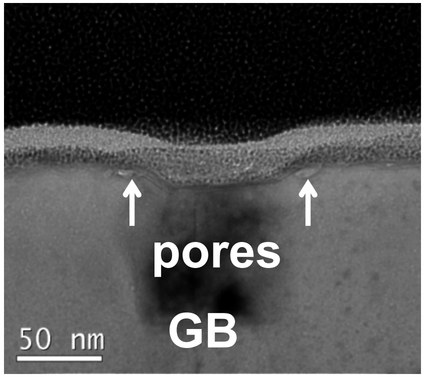
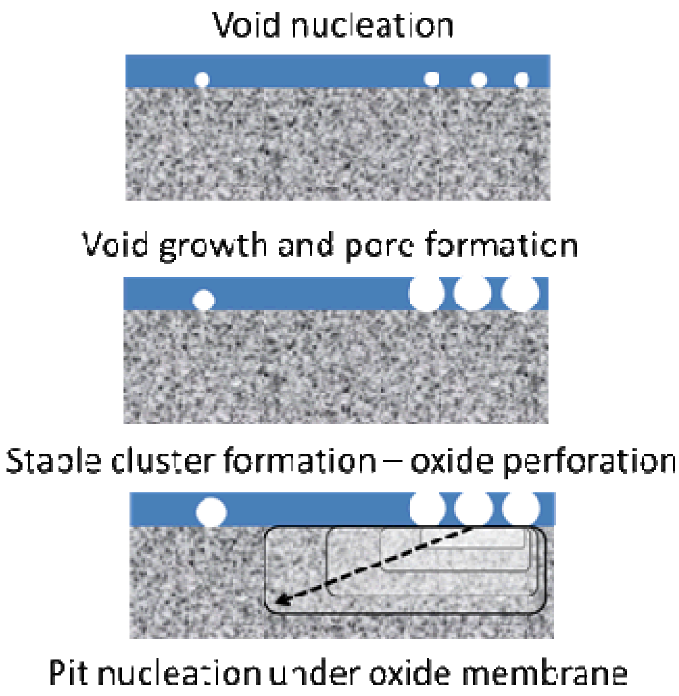
Interfacial Voids as Pit Precursors

Precursor sites preferentially at emergent facets







- O vacancy saturation and interfacial stress produces voids
- higher step densities – lower ionization barrier for Al ⇨ emergent facets more active
- steps serve to lower void nucleation barrier
- voids grow into pores
- initiation occurs – stress due to local topology – destabilizes the pore cluster toward passivation

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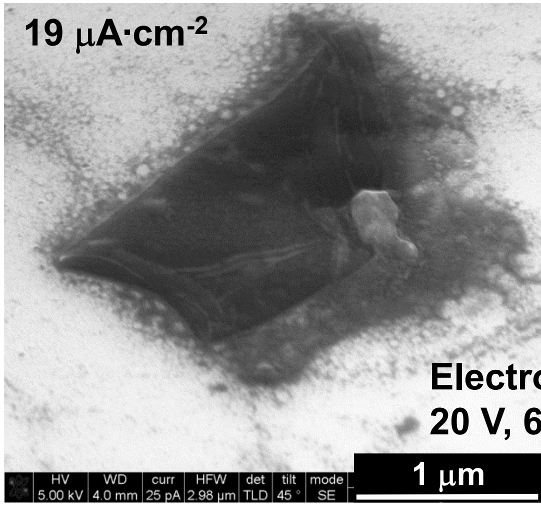
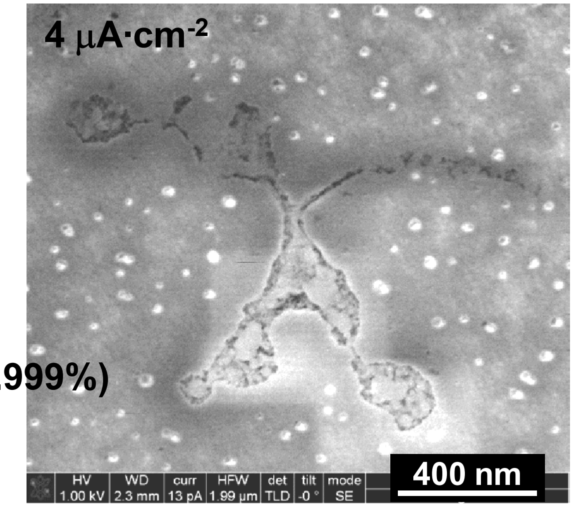
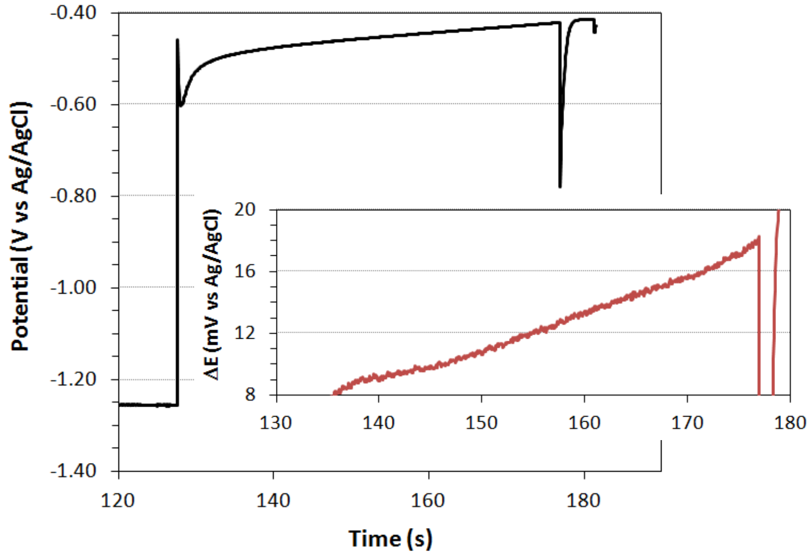
Hydrous oxides yield similar responses

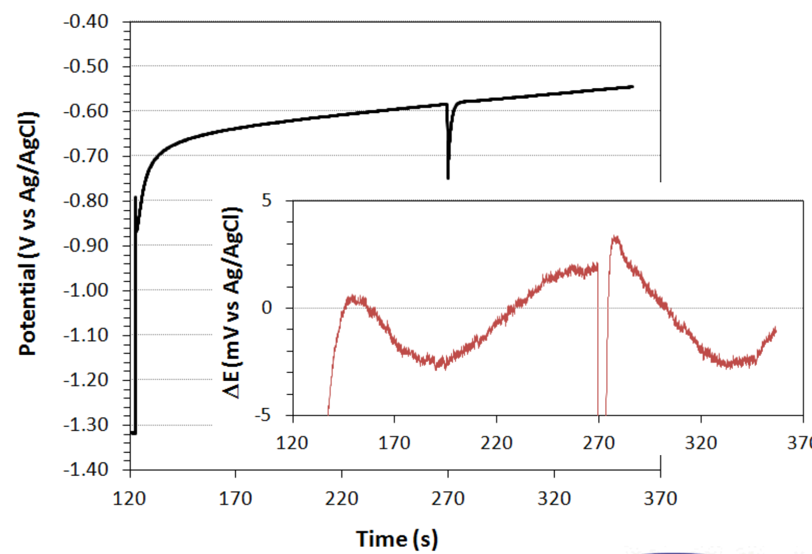


t_{ox}^{i} = 2.7 nm



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





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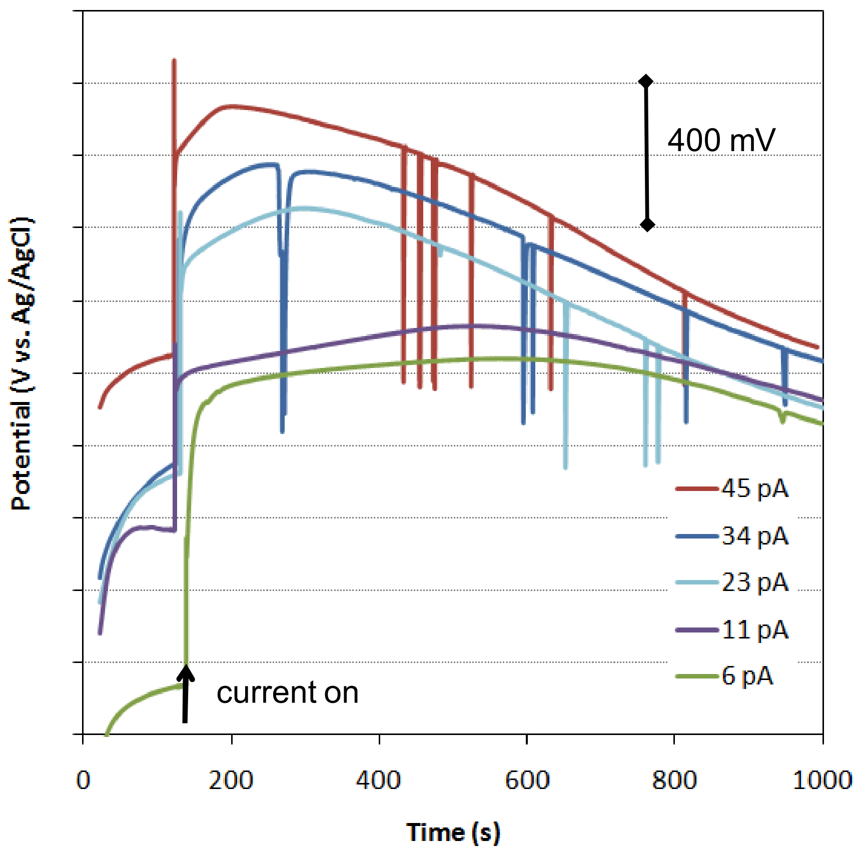
Back-up Slides

Defect and breakdown signatures are measureable in the micro-cell

Anodic polarization using a 20 μm diameter capillary



i (pA)	j ($\mu A \cdot cm^{-2}$)	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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