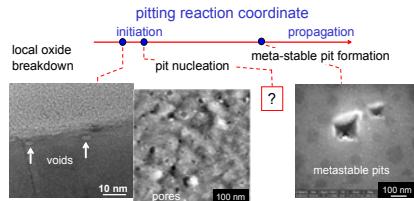


## Mapping a Pitting Reaction Coordinate



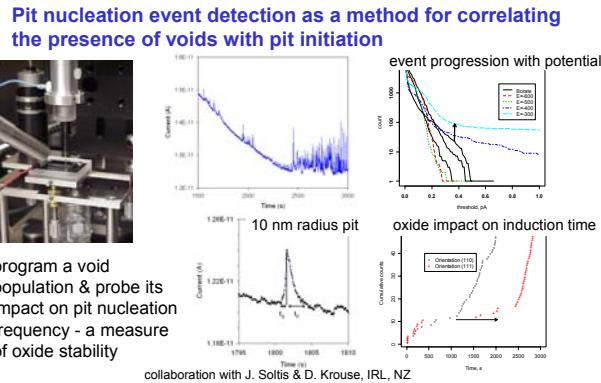
Zavadil et al. JES 153 (8), B296 (2006)

Nanostructure has historically been invoked to explain why passivity loss is localized and leads to pit initiation in passive metals

Materials reliability models require:

- sufficient chemical and physical descriptions of nanostructural entities
- establishment of these entities as causal agents for pit initiation

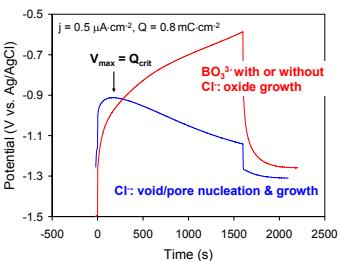
## Establishing Causality – Voids as Pit Precursors



## Mechanism of Nanostructure Formation

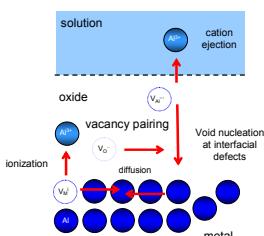
Applied anodic current (Al oxidation) produces two processes:

- oxide growth – vacancy filling
- interfacial void nucleation and growth – vacancy pairing



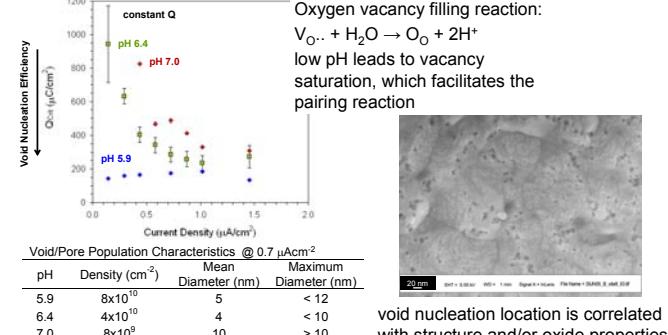
- Shape of the curve is a signature for dominant void nucleation & growth
- $Q_{crit}$  is a measure of the void nucleation efficiency

### vacancy filling vs. pairing reactions

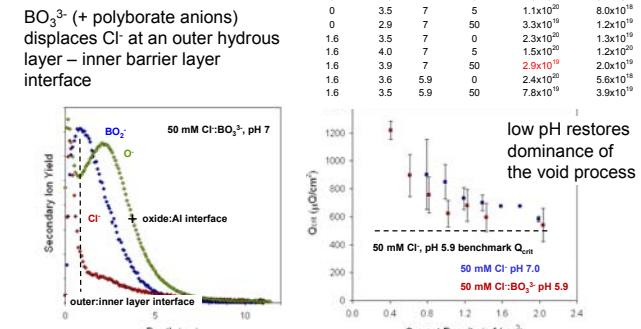


Knowledge of the void formation mechanism can be exploited to control the location, size & density of voids and resulting pores

### Void nucleation efficiency increases with increased $[H^+]$



### Competitive anion adsorption



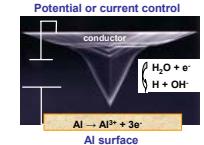
Sufficient Cl⁻ is required for efficient Al vacancy generation:  
 $Al_{Al} \rightarrow Al^{3+}(aq) + V_{Al^{3+}}$

## Inducing & Imaging Localized Passivity Breakdown

Localize electrochemical stress to define event location

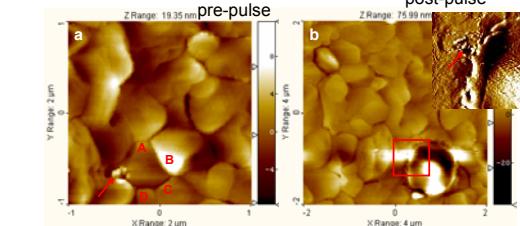
Combine AFM with electrochemical machining (Schuster & Ertl, Science 2000)  
 point-and-polarize – short times localize field and constrain location

$t = C_1 \cdot \rho_{soil} \cdot d$   
 μm resolution at  $10^1$  ns pulses widths



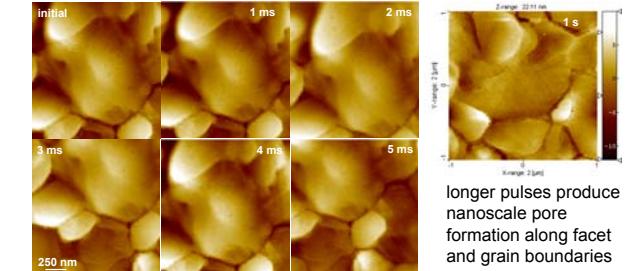
Pitting can be driven in proximity to a conductive tip

-300 mV (vs. SCE) 1 ms pulse



A degree of reproducibility is demonstrated for pit proximity to tip location  
 Potential method for pit susceptibility mapping

### In situ tracking of oxide structural changes



longer pulses produce nanoscale pore formation along facet and grain boundaries

### Future Work:

- Develop and exploit fast pulse (10 nsec) capability in EM-AFM experiment to conduct breakdown susceptibility mapping
- Correlate void nucleation location with oxide:metal interface structural motifs as directed by first principles calculations
- Statistically correlate void population characteristics with pit nucleation frequency
- Develop and apply spectroscopic STM to explore the nanocrystalline oxides on passive transition metals

### \*Localized Corrosion Project Team: N.A. Missett, P.J.

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