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Electrolyte Ion Effects on the Formation of Nanoscale Structure in Aluminum's Passive Oxide Prior to Pit Initiation

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Our goal is to identify relevant nanostructure and establish causal links with pit initiation

pitting reaction coordinate

initiation

propagation

local oxide
breakdown

pit nucleation

meta-stable pit formation

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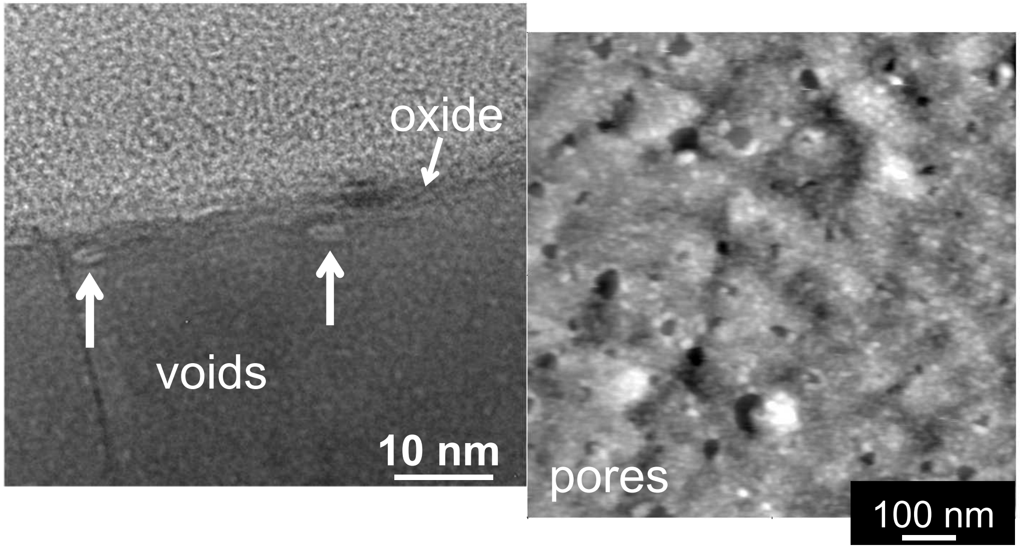

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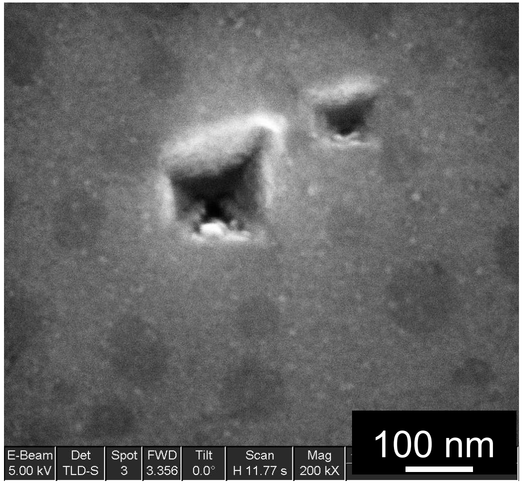


possible metastable pits

sufficient chemical and physical descriptions do not exist for these entities to support reliability models for high consequence applications of passive metals

Void nucleation and growth is viewed as a competing reaction with oxide growth

parallel paths for ion (vacancy) transport :

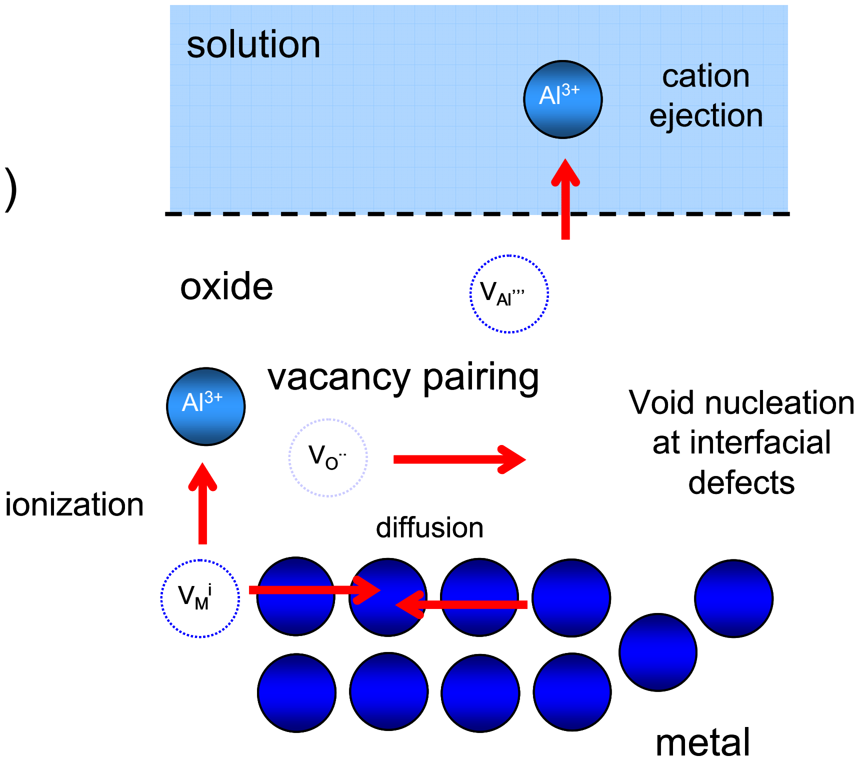
- oxide growth (vacancy filling)
- void nucleation (vacancy pairing)

Reactions & constituents of interest

Oxygen vacancy filling:
$V_O\cdot\cdot + H_2O \rightarrow O_O + 2H^+$

Cl^- competition for surface $V_O\cdot\cdot$ (Point Defect Model)

Al vacancy generation:
$Al_{Al} \rightarrow Al^{3+}(aq) + V_{Al}'''$ surface adsorbates or chelating species that interfere with ejection



Anhydrous oxides on Al thin films are the system of study

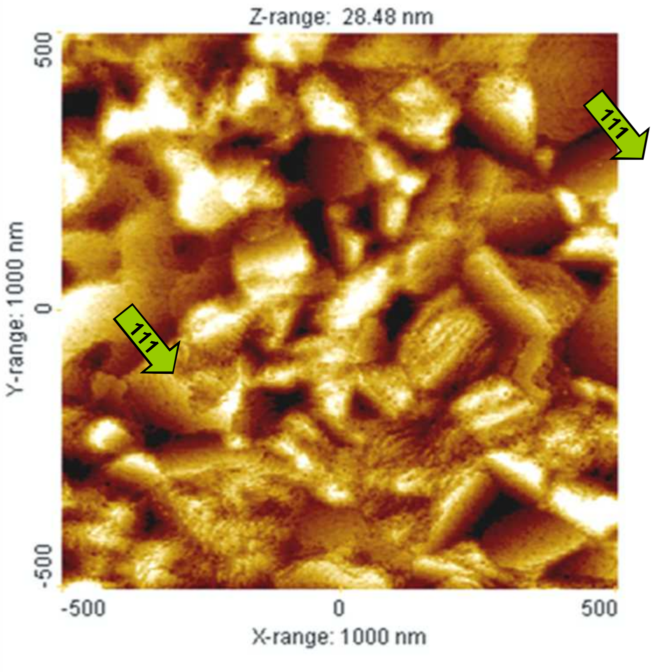
Al thin films electron beam deposited onto SiO_2:Si

Nanocrystalline Al(111) textured films are formed - grain dia. 100 to 150 nm)

Anhydrous oxides O_2 grown immediately after film deposition

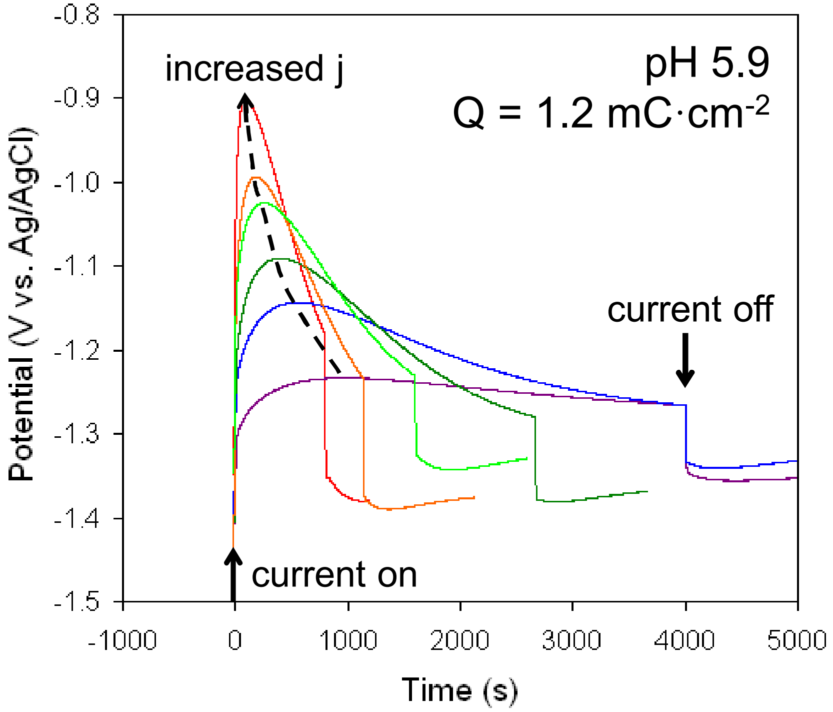
Electrochemistry conducted using meso-scale capillaries – 9×10^{-3} cm^2

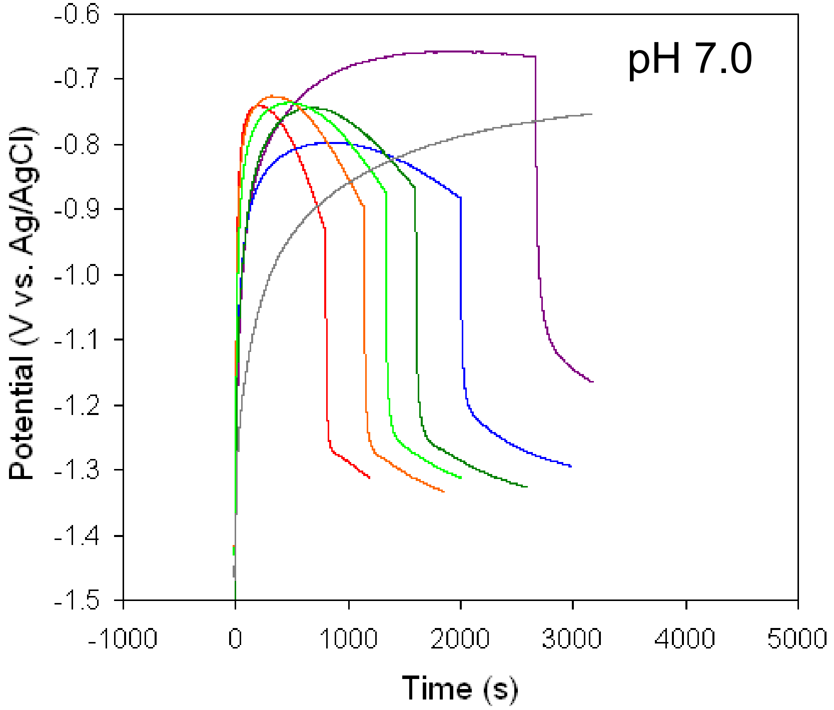
hydrated Al(111) in H_2O



Galvanostatic polarization is a means of probing the passive oxide's response to controlled ion fluxes

Current density (j) is varied from 0.15 to 1.5 $\mu A cm^{-2}$ – relevant passive values





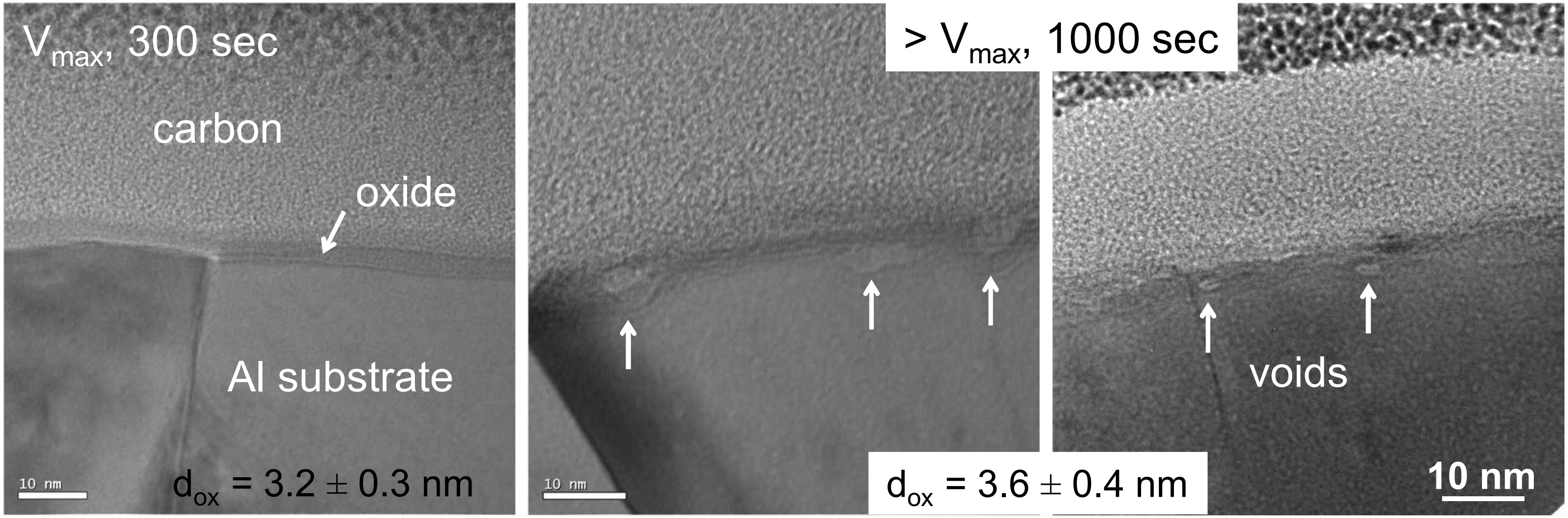
Non-classic curves – defect dominated resulting in lower barriers for ion transport

higher pH produce higher potentials & less rapid decay with time

Lower pH produces a more defective response

The detected potential maximum and void nucleation are correlated

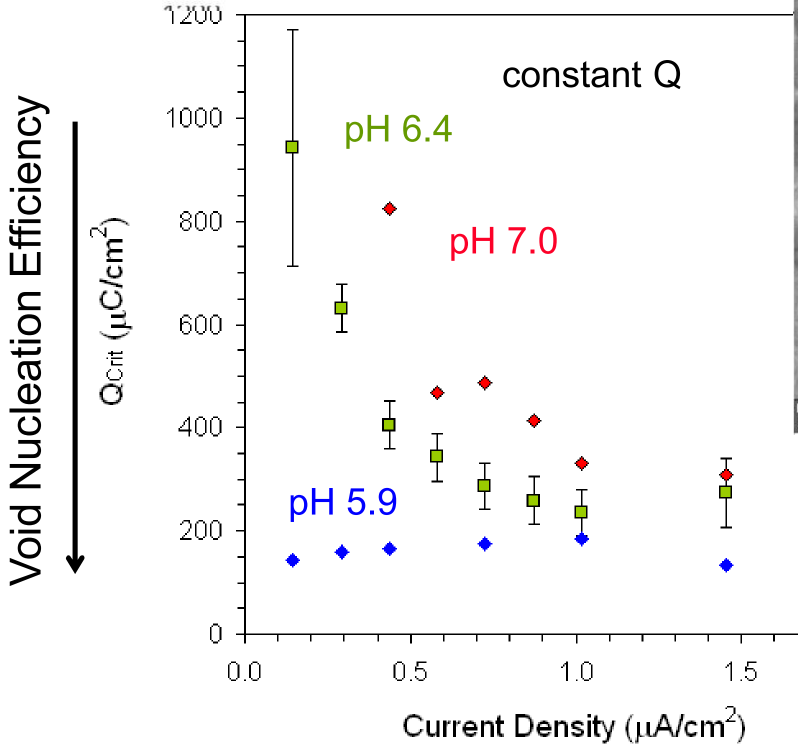
0.7 $\mu A \cdot cm^{-2}$, 50 mM Cl^-, pH 5.9

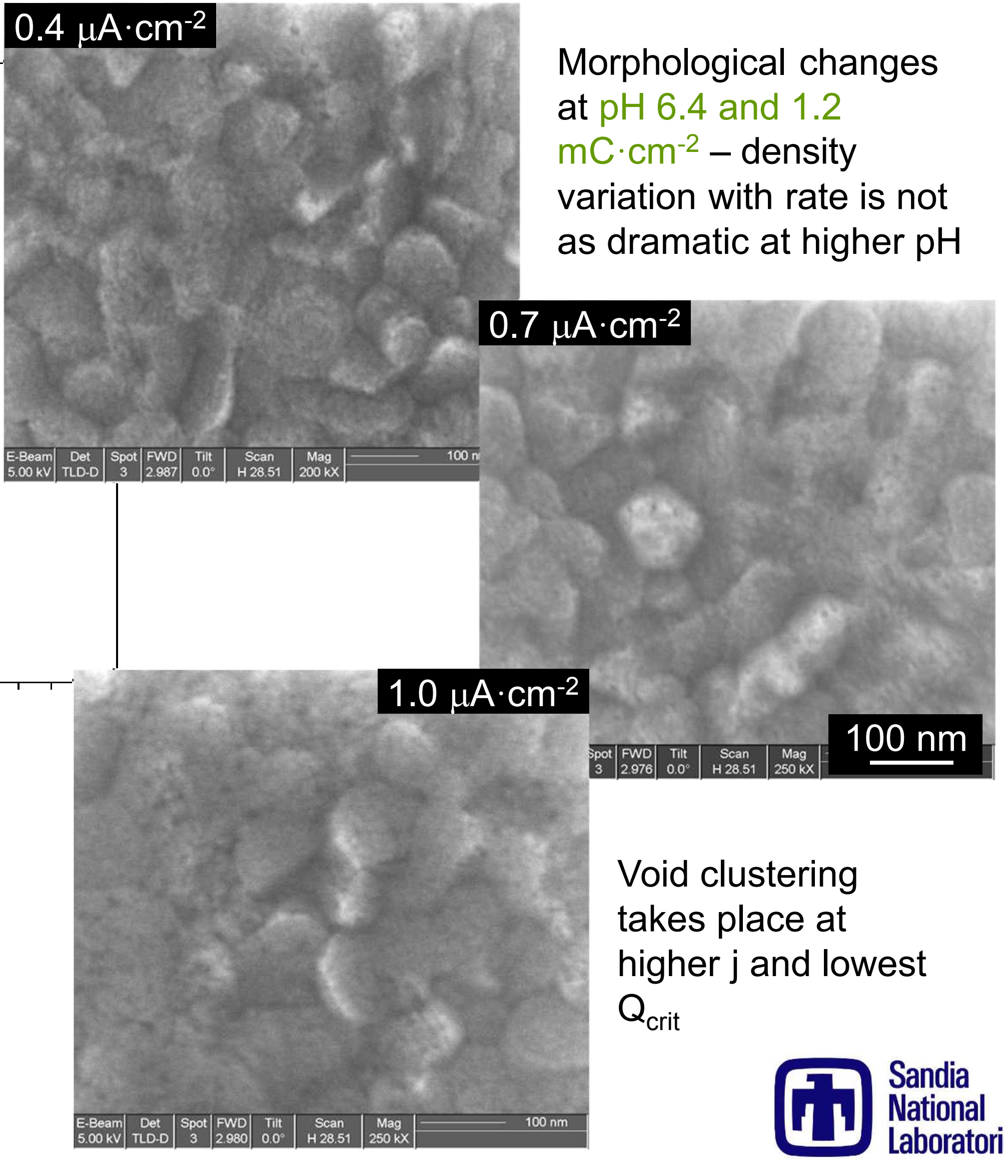


A variety of structure is observed: voids within the oxide, voids that penetrate the Al substrate and pores

Chronopotentiometric traces represent an electrochemical signature for void/pore formation at lower pH values

pH has a significant effect on the efficiency for nucleating voids





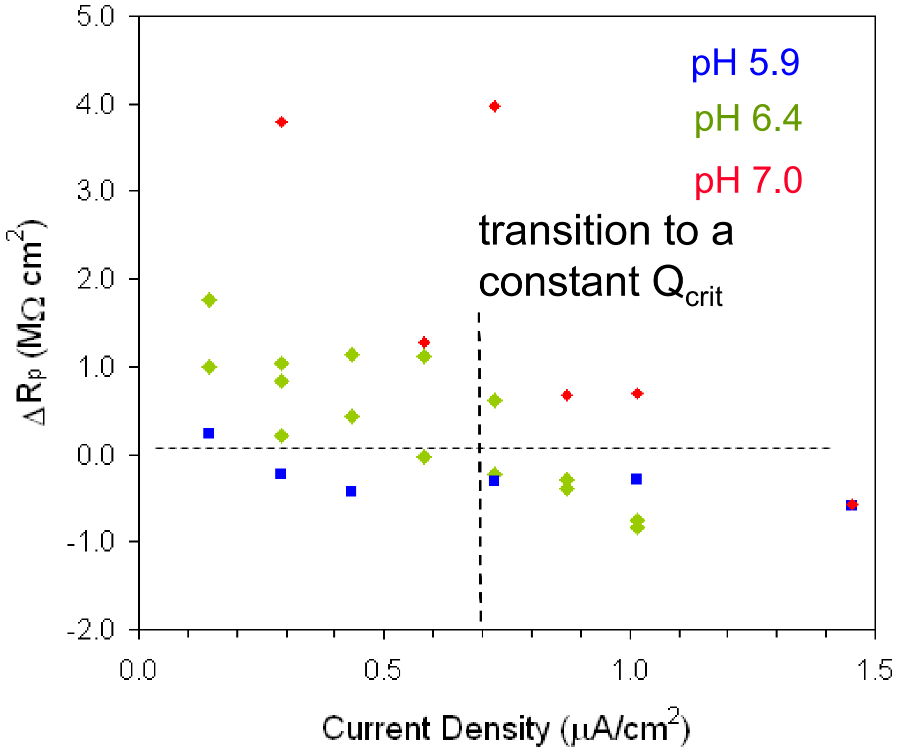
Morphological changes at pH 6.4 and 1.2 mC·cm^{-2} – density variation with rate is not as dramatic at higher pH

pH 5.9: Void density ranges from 4x10^{10} to >8x10^{10} cm^{-2} with clustering at high current density (j)

Void clustering takes place at higher j and lowest Q_{crit}

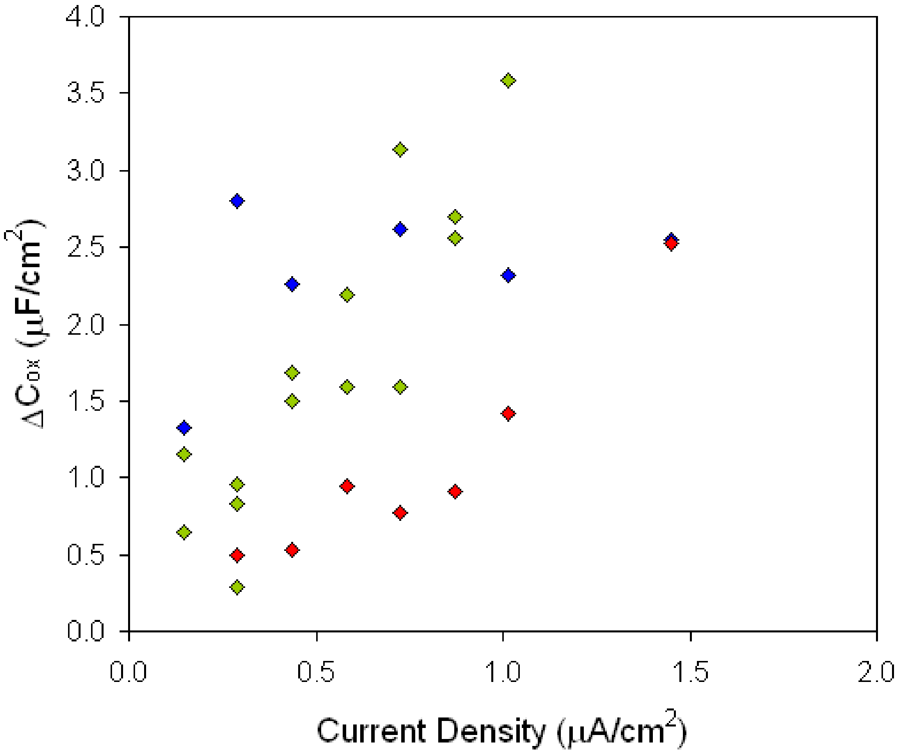
Impedance results do not reflect clearly a balance between oxide growth and void nucleation

Impedance response of the polarized oxide conforms to a Randles type description – parallel CPE and polarization resistance



transition to a constant Q_{crit}

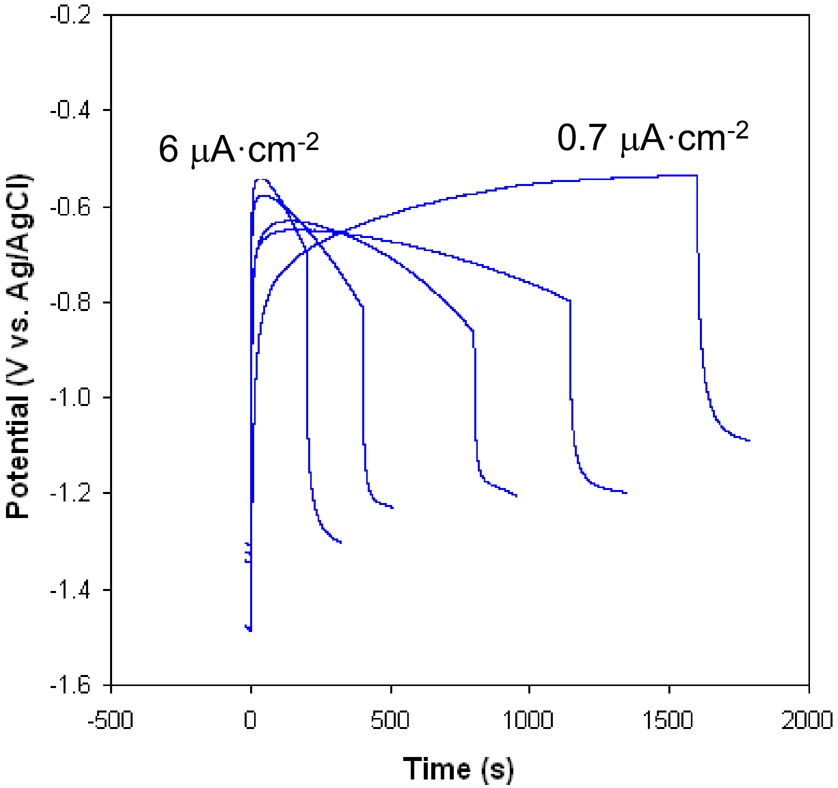
oxide thickening would argue for both R_p increases and C_{ox} decreases



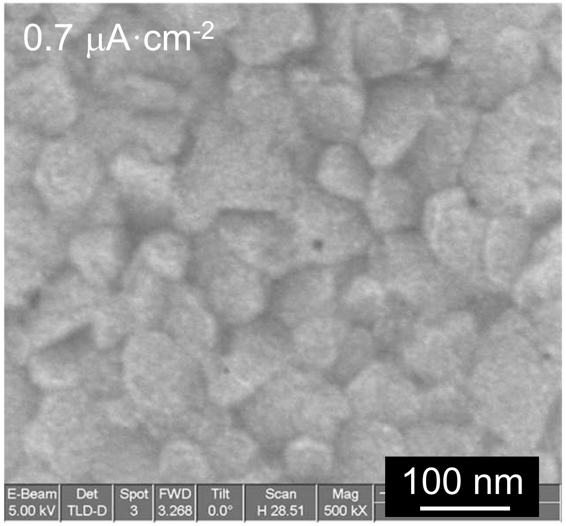
oxide capacitance always increases due to charged defect population

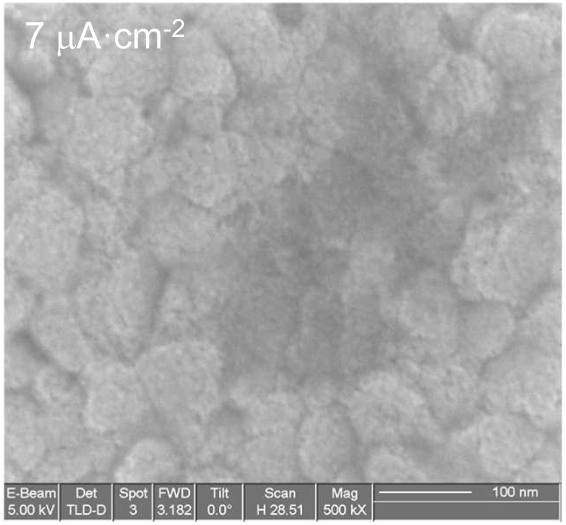
Polarization at net basic pH highlights the defect nature of the potential response

metastable pitting is dominant unless short (1000 s) open circuit equilibration times are used



higher current produces defect response without detectable void/pore growth

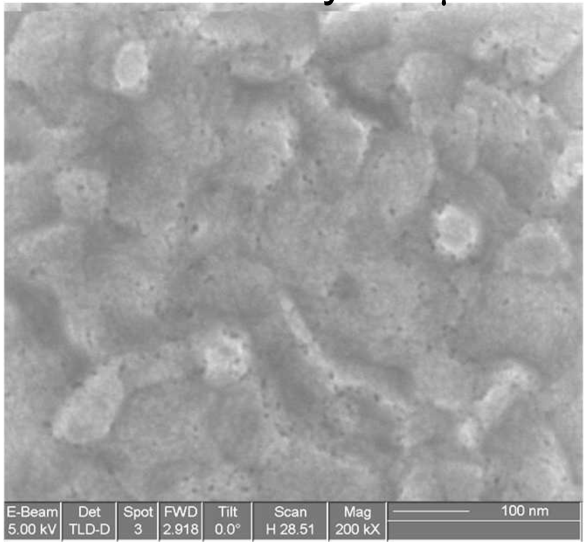




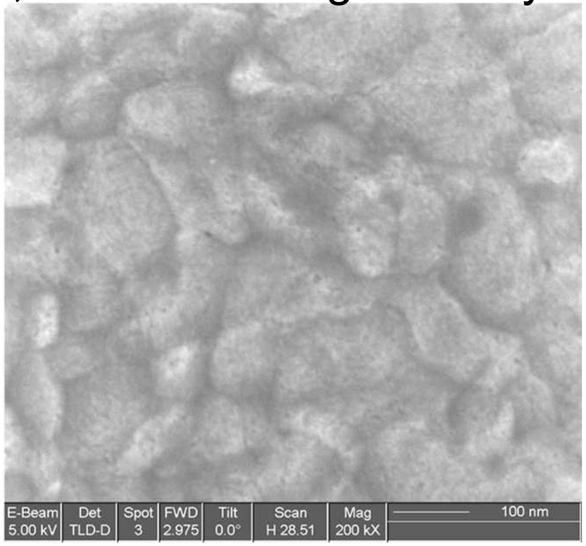
Increased pH results in decreased void/pore densities with increased average size

constant current density 0.7 $\mu A \cdot cm^{-2}$, constant charge density 1.2 $mC \cdot cm^{-2}$

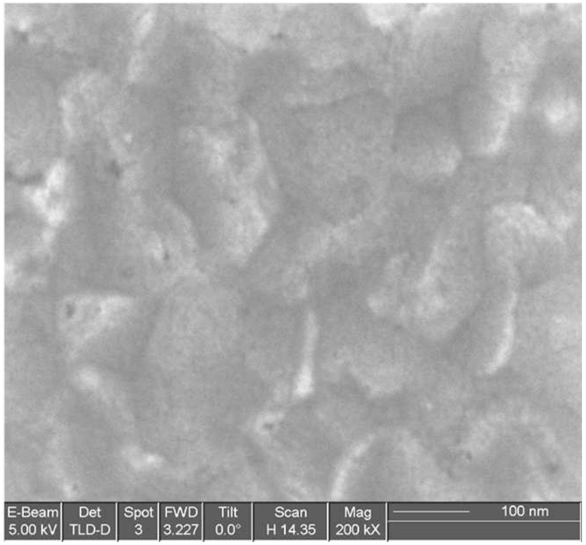
pH 5.9
ρ 8x10^{10} cm^{-2}
d_{avg} 5 nm
d_{max} <12 nm



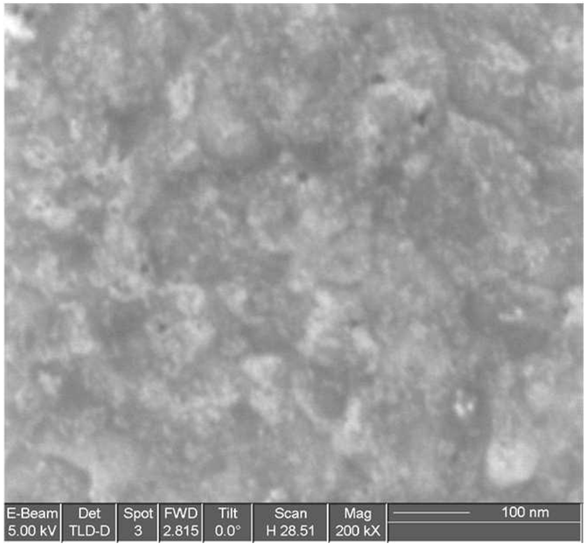
pH 6.4
ρ 4x10^{10} cm^{-2}
d_{avg} 4 nm
d_{max} <10 nm



pH 7.0
ρ 8x10^{9} cm^{-2}
d_{avg} 10 nm
d_{max} >10 nm



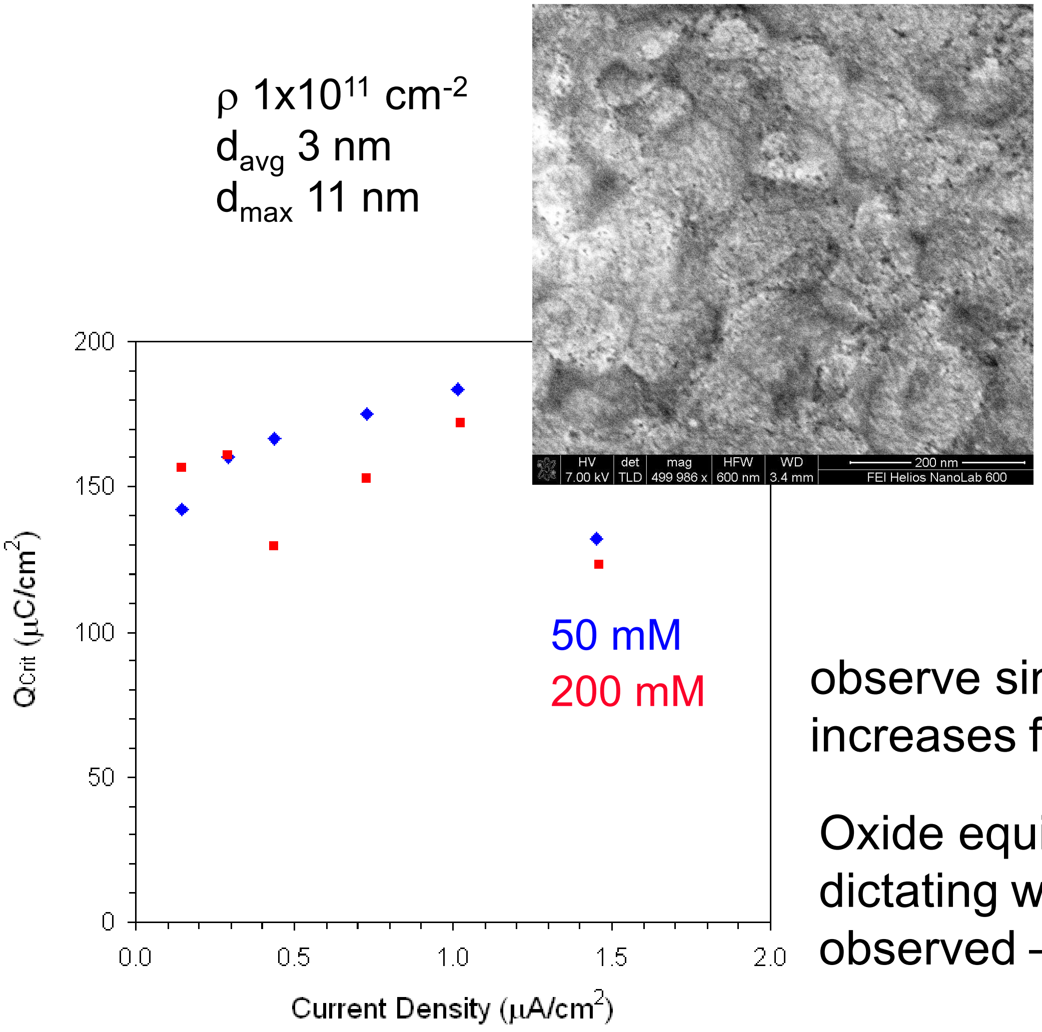
pH 8.0
ρ 4x10^{9} cm^{-2}
d_{avg} 10 nm
d_{max} >10 nm

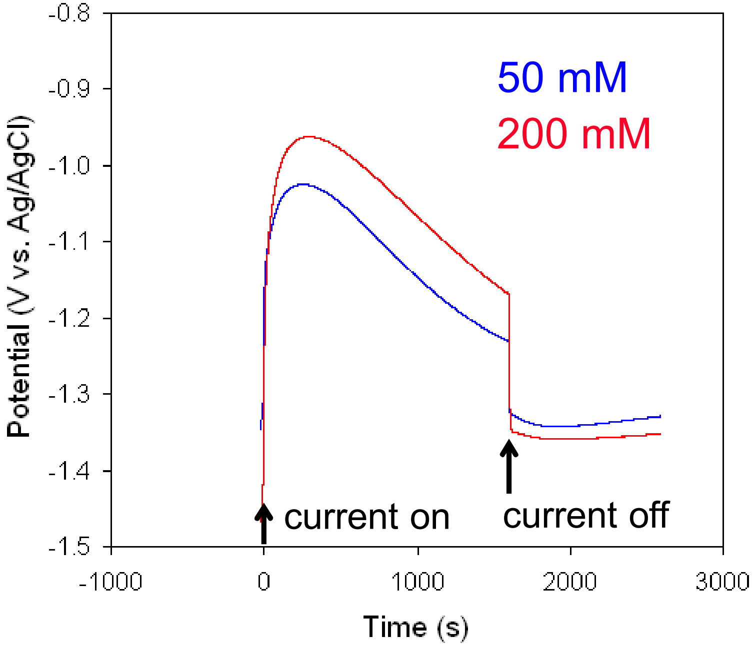


Chloride appears to have little effect on void nucleation at lower pH values

200 mM Cl$^-$, pH 5.9, 0.7 $\mu A \cdot cm^{-2}$

ρ 1x10^{11} cm^{-2}
d_{avg} 3 nm
d_{max} 11 nm

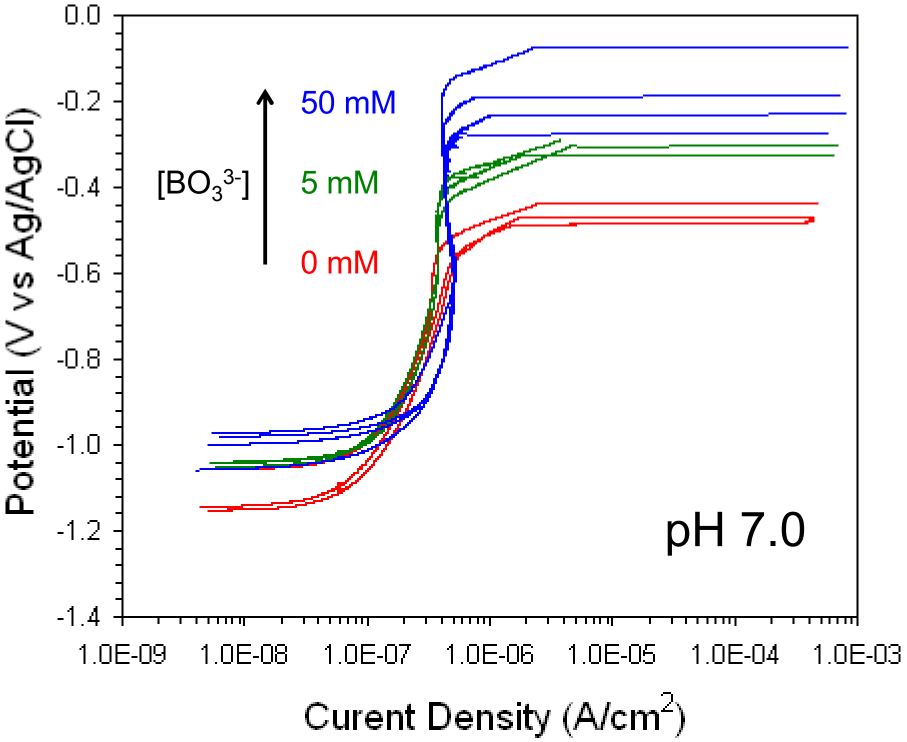




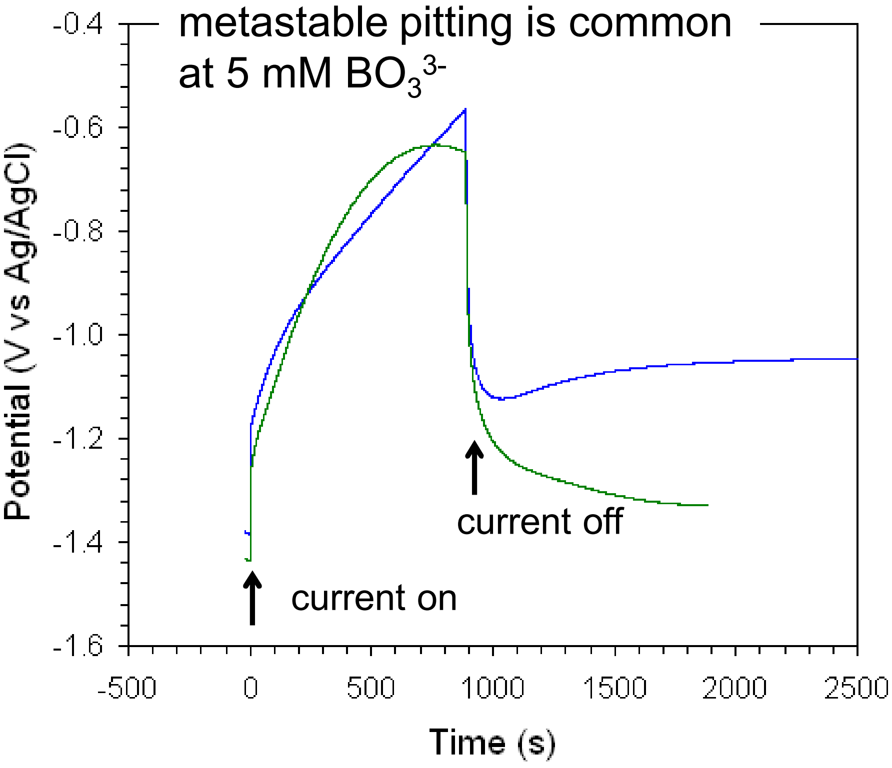
observe similar ΔR_p decreases and ΔC_{ox} increases for equivalent 50 mM polarization

Oxide equilibration time plays a key role in dictating whether a defect response is observed – metastable pitting

The presence of borate produces several significant changes in the polarization characteristics of the oxide



retards pre-stable pitting activity



induces a transition from a defect response to a oxide growth response

Borate displaces chloride at the outer:inner layer interface

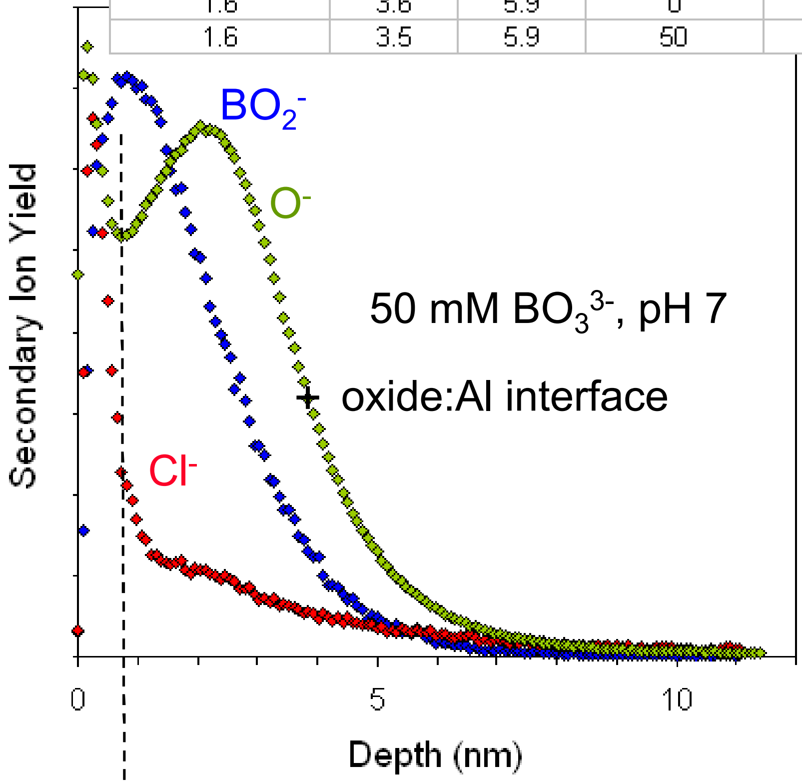
Q ($mC \cdot cm^{-2}$)	d_{ox} (nm)	pH	[BO_3^{3-}] (mM)	[Cl^-] (cm^{-3})	[BO_2^-] (cm^{-3})
0	2.9	7	0	1.0E+20	9.1E+18
0	3.5	7	5	1.1E+20	8.0E+18
0	2.9	7	50	3.3E+19	1.2E+19
1.6	3.5	7	0	2.3E+20	1.3E+19
1.6	4.0	7	5	1.5E+20	1.2E+19
1.6	3.9	7	50	2.9E+19	2.0E+19
1.6	3.6	5.9	0	2.4E+20	5.6E+18
1.6	3.5	5.9	50	7.8E+19	3.9E+19

equil. 3x

high pH 8x

low pH 3x

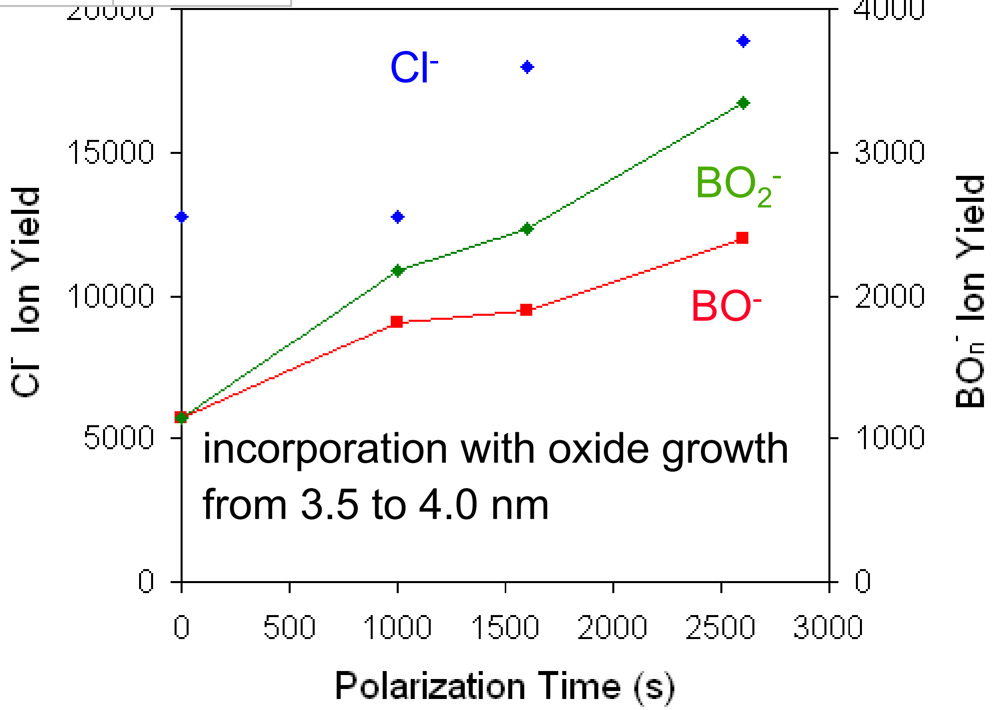
trends in Cl^- displacement with [BO_3^{3-}] for each class



50 mM BO_3^{3-}, pH 7

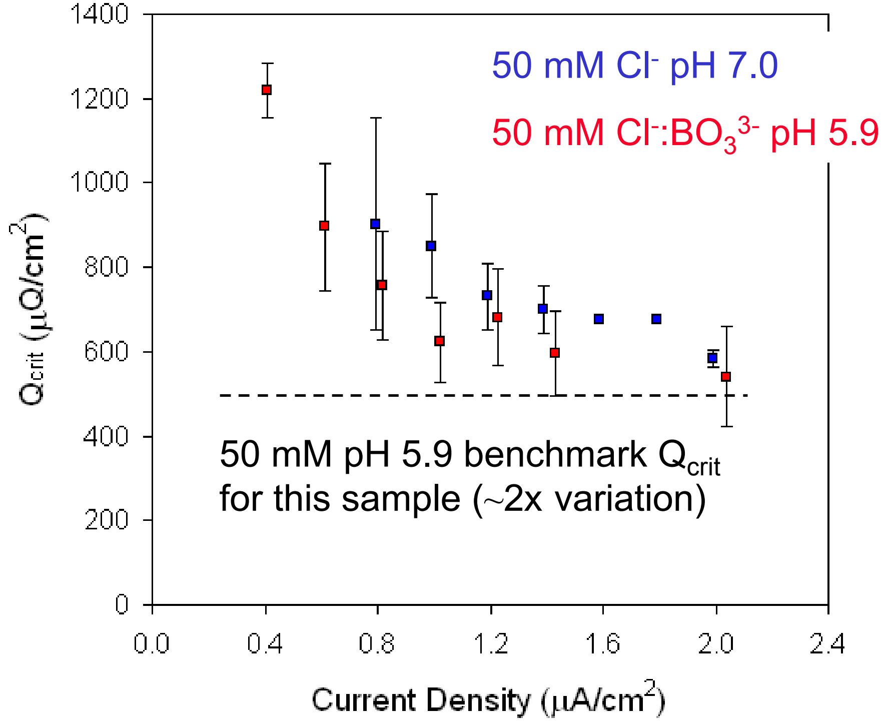
oxide:Al interface

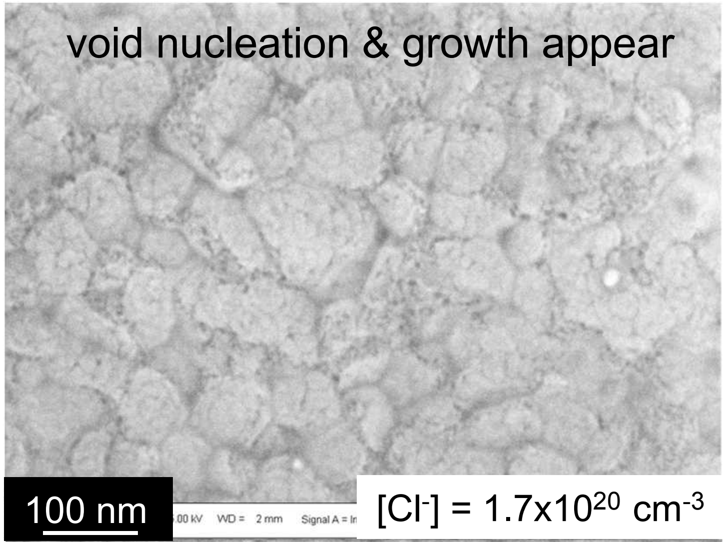
outer:inner layer interface



incorporation with oxide growth from 3.5 to 4.0 nm

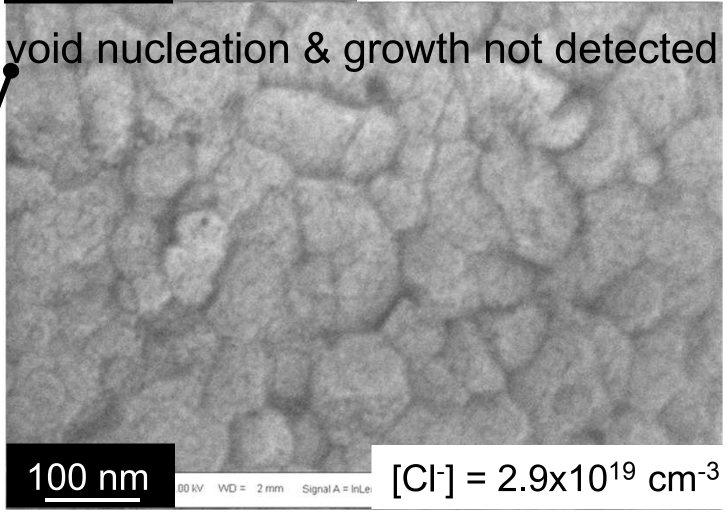
Decreasing the pH low enough restores the defect response of the passive oxide





void nucleation & growth appear

[Cl$^-$] = 1.7x10^{20} cm^{-3}



void nucleation & growth not detected

[Cl$^-$] = 2.9x10^{19} cm^{-3}

in select cases electrolyte factors are unable to drive void nucleation – SIMS shows Cl$^-$ displacement

surface Cl$^-$ is critical for efficient void nucleation

Conclusions

- Void nucleation and growth is enhanced at low pH

  consistent with a suppression of the O vacancy filling reaction

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

  higher pH results highlight the defect nature of the polarization response

- A chloride impact on void nucleation is not observed for the concentration range studied

  a critical surface concentration is required for void growth > 2.9×10^{19} cm^{-3}

- Borate exerts a significant impact on void nucleation and growth

  displacement of chloride is correlated with a transition to oxide growth

  pitting is inhibited due to growth of the oxide