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Evolution of Oxide Stability During Localized Corrosion of Model Al-Cu Alloys

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Motivation:

Mechanisms Governing Corrosion Initiation Are Not Clear

Corrosion is a Redox Reaction:

Aluminum Oxidation

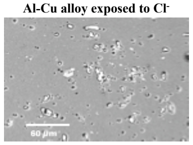
$Al = Al^{3+} + 3e^-$

Oxygen Reduction Reaction (ORR)

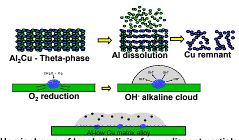
$2H_2O + O_2 + 4e^- = 4\ (OH)^-$

After long times: Propagation

Al-Cu alloy exposed to Cl^-



"Trenches" surround intermetallic particles



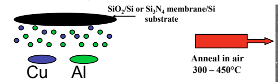
Hemispheres of local alkalinity from adjacent particles or dealloyed matrix overlap

Early stages: How does initial pH increase start? How does trenching evolve? Where does the ORR take place on the heterogeneous surface?

Approach:

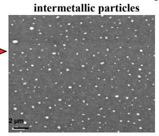
Model Alloy Thin Films and in-situ Microscopy Allow Observation of Earliest Stages of Corrosion

Electron-beam co-evaporation



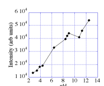
Expose to 10 mM NaCl + 0.3% H_2O_2 to initiate corrosion

SEM: uniform distribution of Al_2Cu intermetallic particles

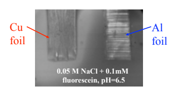


Al_2Cu precipitates at GB

Fluorescein as In-Situ pH Indicator Shows Spatial Distribution of Alkalinity



488 nm Ar laser excitation
548 nm fluorescein emission
Detect l > 515 nm - to VHS tape



Confocal Scanning Laser Microscope Image at R = 100kΩ

O reduction on Cu: $O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$

Al oxidation: $Al \rightarrow Al^{3+} + 3e^-$

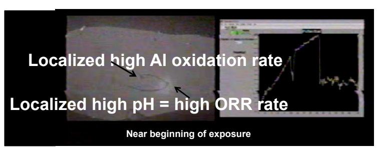
Al hydrolysis: $Al^{3+} + H_2O \rightarrow Al(OH)^{2+} + H^+$

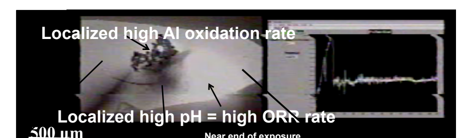
$Al^{3+} + 2H_2O \rightarrow Al(OH)_2^+ + 2H^+$

$Al^{3+} + 3H_2O \rightarrow Al(OH)_3 + 3H^+$

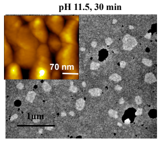
Results:

In-situ Fluorescence Microscopy Shows Localized Regions with High ORR Rate

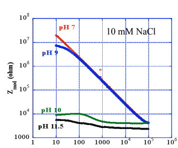




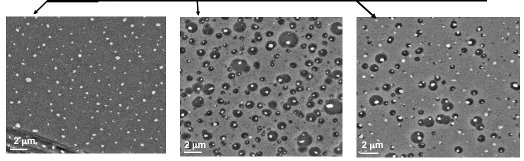
pH 11.5, 30 min



No attack observed for 30 min exposures up to pH 11.
At pH 11.5 breakdown sites are localized, Al_2Cu particles are passive



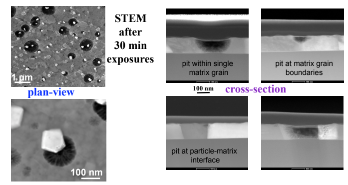
As pH 10 showed no surface attack, EIS suggests changes in passive oxide impedance



High pH, high ORR rate regions initiate in response to rapid Al oxidation at remote site, these regions grow macroscopically with time, oxide stability evolves with exposure

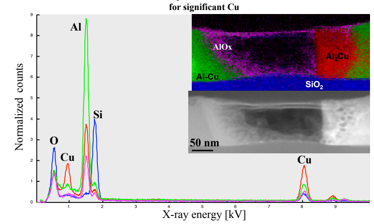
Results:

Localized Attack at Particles and on Matrix: Metastable Pitting

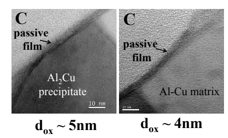


Attack proceeds radially from breakdown point beneath remnant oxide -morphology more like a traditional acidic pit than cathodic trenching

Pits contain Al-oxide corrosion product, remnant Al-oxide cover, no evidence for significant Cu

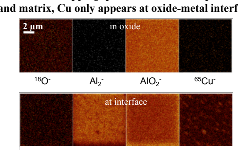


pH 11.5, 30 min exposure



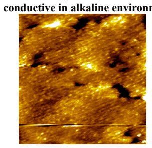
$d_{ox} \sim 5nm$ $d_{ox} \sim 4nm$

ToF-SIMS Mapping: pure Al-oxide above particles and matrix, Cu only appears at oxide-metal interface



(Seyeux, et. al. JECS, in reivew)

In-situ STM shows passive oxide is electronically conductive in alkaline environment



10 mM NaCl
pH 10.6
1 hr exposure

100 x 100 nm

Morphology, structure and composition are inconsistent with significant particle de-alloying or passive matrix dissolution: passive oxide governs ORR rate!

Impact: Understanding evolution of oxide stability during initial stages of localized corrosion is essential for developing accurate, predictive models and ultimately for guiding intelligent design of corrosion inhibition schemes

Future Work

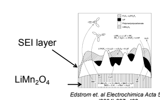
Tailored Oxide Surface Stability for Electrical Energy Storage

Our goal is to identify critical factors governing charge transfer and stability in order to guide optimization of surface properties for energy storage.

Background:
•Performance of Li+ battery electrodes is limited by stability and charge transfer rates determined by the solid-electrolyte interphase (SEI) layer that forms in-situ during potential cycling

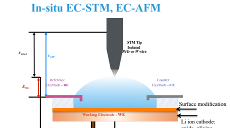
Approach:
•Determine mechanisms governing charge transfer and stability using model systems combined with in-situ characterization of SEI evolution during cycling

SEI formation: consumes active mass, inhibits Li+ mobility, electronically isolates nanoparticles

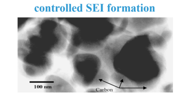


Edstrom et. al Electrochimica Acta 50 (2004) 397–403

In-situ EC-STM, EC-AFM



Tailored surfaces: controlled SEI formation



Nien, et. al. Journal of Power Sources 193 (2009) 822–827

Surface modification look promising, but which properties are critical?

Impact: Understanding evolution of electrode stability and charge transfer will allow optimization of surfaces for energy storage applications

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