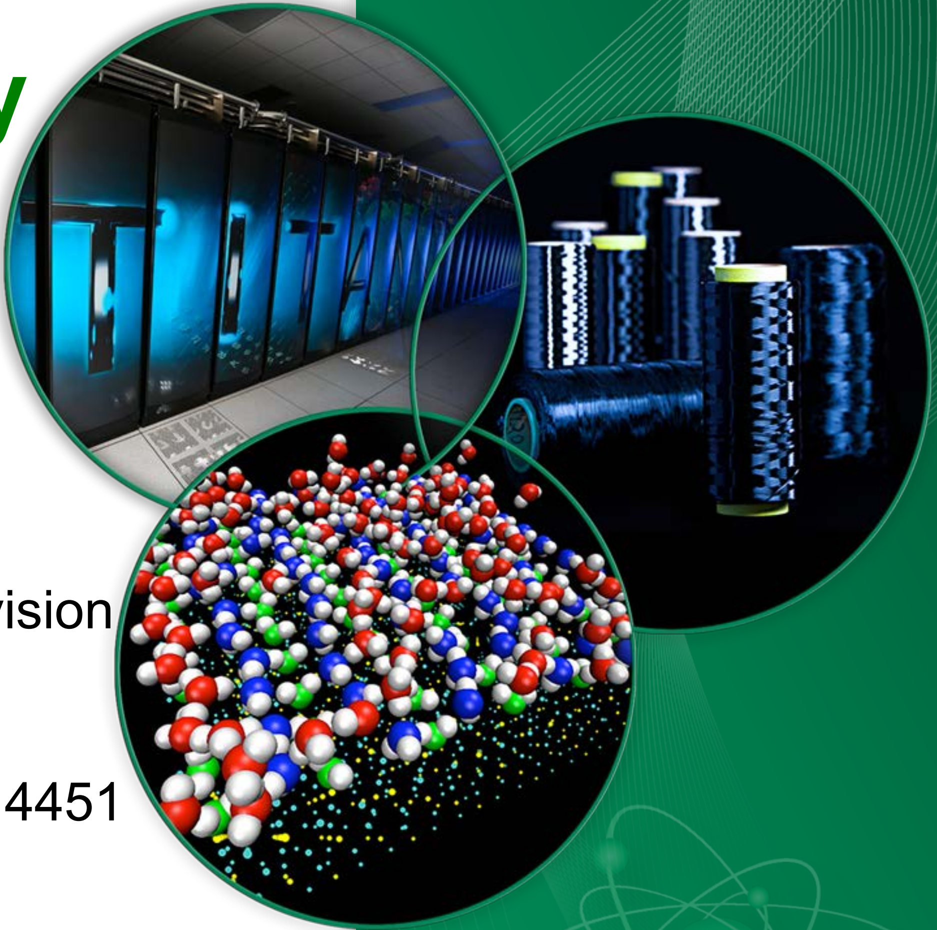
Corrosivity and passivity of metastable Mg alloy

---An Introductory Study to Future Stainless Mg Alloys



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Project ID # LM096

Overview: Project

Timeline

- Project start: Nov. 2013
- Project end: Sept. 2015
- ~85 Percent complete

Budget

- Total project funding
  - $600k DOE share
- $600k received in FY13

Barriers

- Lightweight Materials Barrier H: Maintenance, Repair, and Recycling
- Lightweight Materials Barrier C: Performance (corrosion resistance)
- 50% vehicle body/chassis weight reduction target will require low-cost, corrosion-resistant Mg alloys

Partners

- U. Montana (collaborator)
- GM R&D Center Corp.

Relevance and Objective: Improve Mg Alloy Corrosion Resistance

- Mg and carbon fiber have the highest potential to achieve targeted 50% weight reduction in vehicle body and chassis
- Poor corrosion resistance is a major challenge to achieve widespread adoption of Mg alloys in vehicle applications
- Development of passivated stainless Mg alloys may permanently solve the poor corrosion, particularly the galvanic corrosion problem
- **Objective**: explore the possibility and feasibility of forming a stainless Mg alloy

Issues to address

- Can a Mg alloy be passivated by a supersaturated Passivating Element (PE) in the matrix phase?
- If yes, what is the PE threshold level?
- How is a surface film affected by the substrate Mg alloy?

Difficulty

❖ Key ---passivity of matrix phase
❖ Difficulty ---solubility of PE in the matrix phase

- Limited solubility of PE in Mg
- Traditional metallurgy ---impossible to obtain a passive matrix

Milestones: Focus on passivity and corrosivity measurement

- ✓ **FY 2015** Complete XRD, XPS, electrochemistry, and TEM study of at least 3 sputtered Mg-Ti compositions relative to pure Mg (3/31/15): **Met**

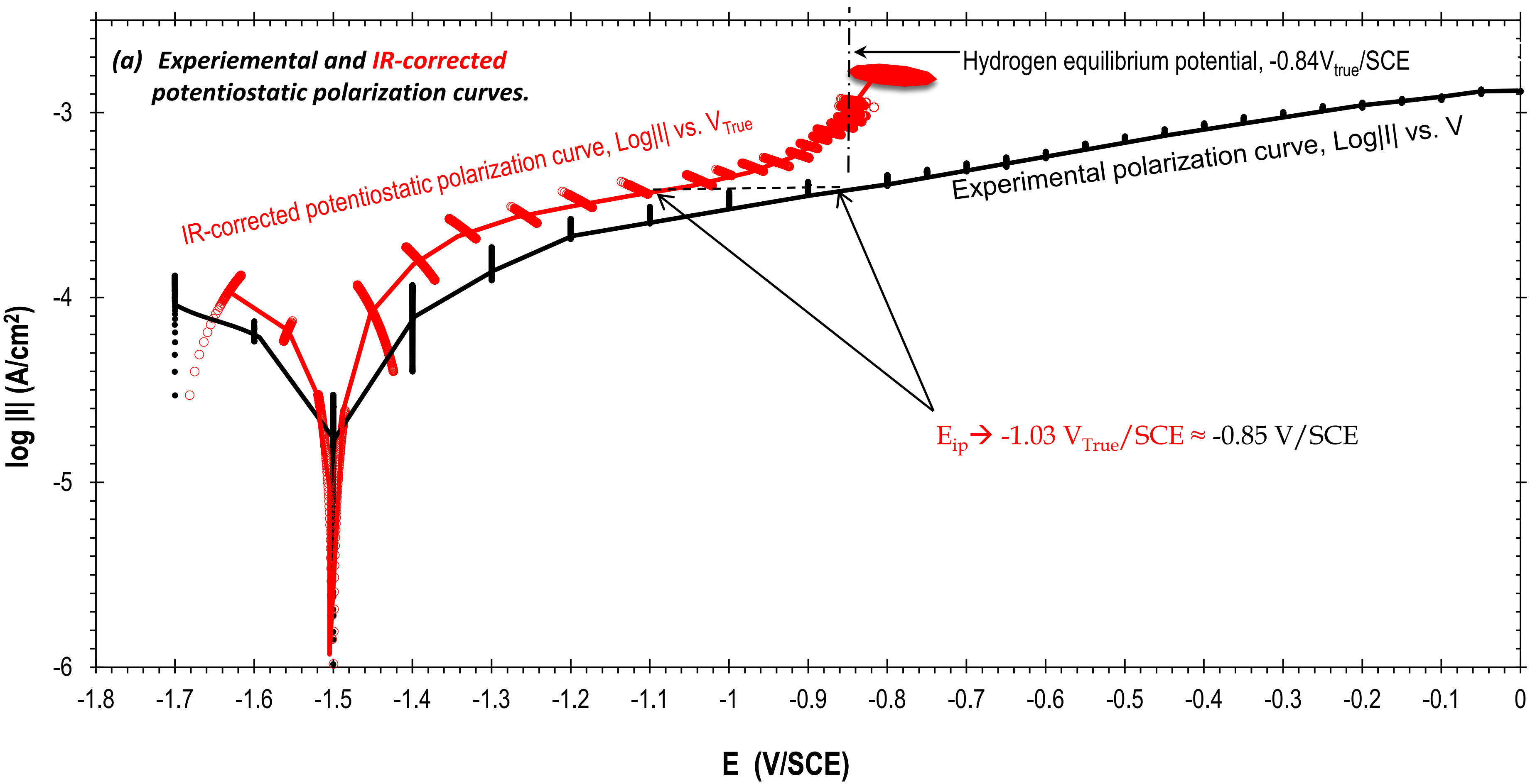
- ✓ **FY 2015** Submit journal paper on Mg-Ti system (6/30/15): **On Track**

- ✓ **FY 2015** Complete electrochemical and XPS screening assessment in sputtered Mg-Cr system, submit journal paper if results warrant (9/30/15): **On Track**

Approach/Strategy: passivity of Mg-matrix phase with strong passivating element

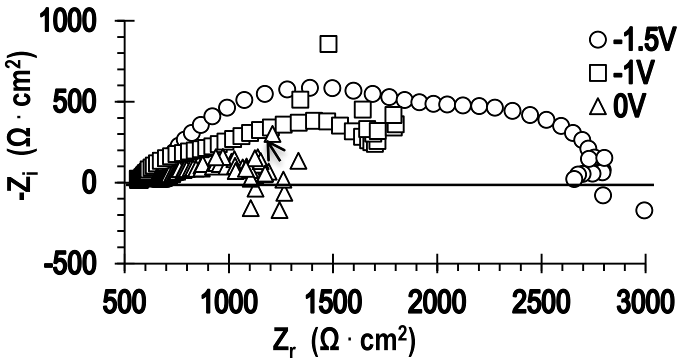
- To find out whether Mg alloys can become passive or not by alloying approach, magnetron-sputtering was employed to form single phase Mg-X (X-strong passivating elements, such as Ti, Cr, Al)
  - Selected strong passivating elements
  - Non-equilibrium process
  - Metastable single phase
  - Pure Mg as bench mark
- Immersion and polarization curve measurements to detect corrosivity and passivity
- SEM,TEM, XPS, XRD to characterize the alloys and surface films
- Correlation of alloy composition, film characteristics and passivity/passivity

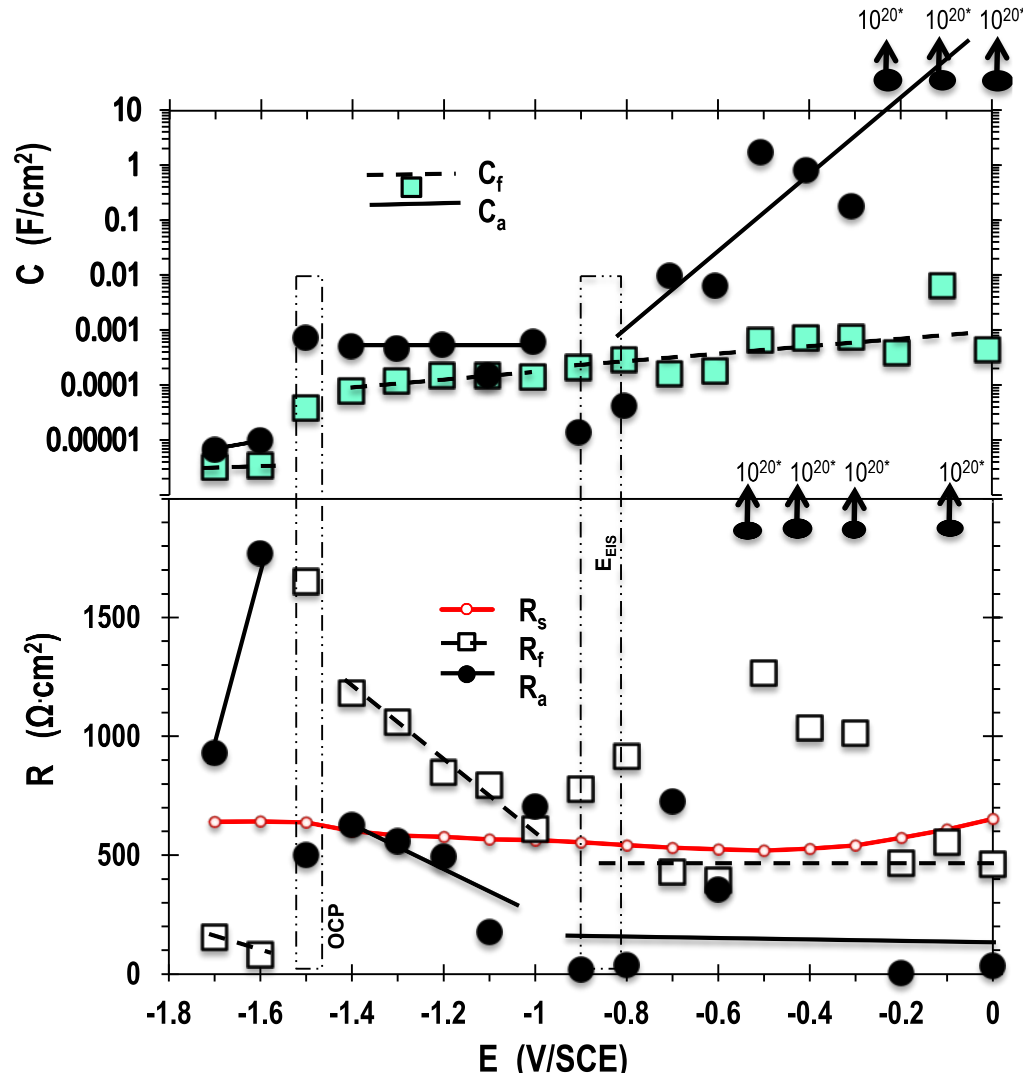
Ingot pure Mg in saturated $Mg(OH)_2$ solution



Polarization curves, even after IR-correction, shows that Mg cannot become passive by strong anodic polarization. Anodic dissolution rate increases with with increasing potential.

AC-impedance confirmation





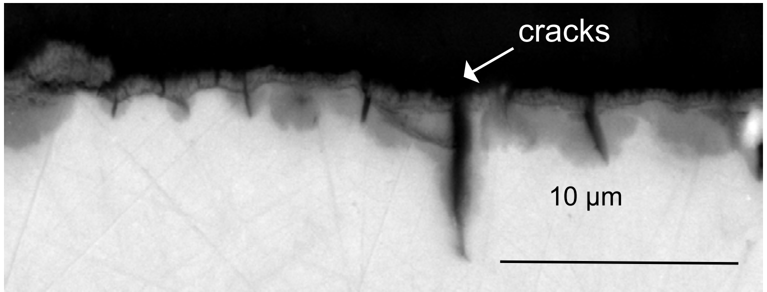
- Active dissolution behavior of Mg in the non-corrosive solution
- The film becomes more porous and thicker at a higher anodic polarization potential

SEM cross-sections of Mg in saturated $Mg(OH)_2$ for 24 hours

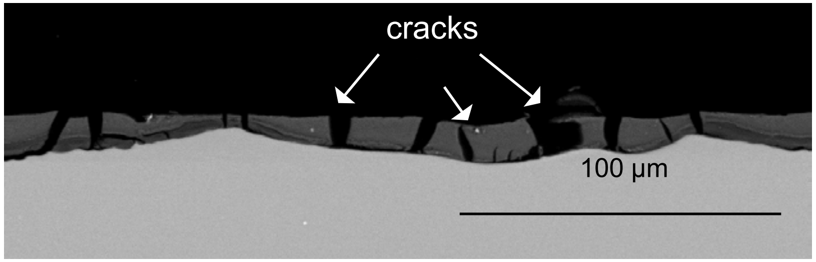
(A) Film is thick, cracked, not protective

(B) Film becomes thicker with increasing potential

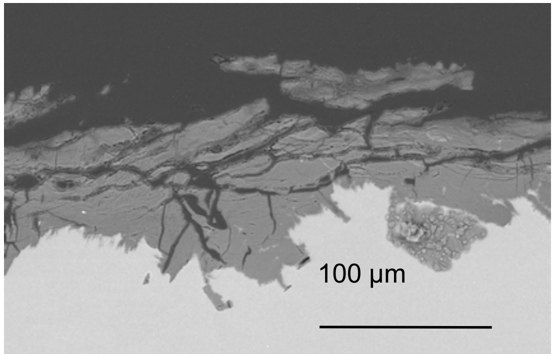
(C) Film ruptures at high potential



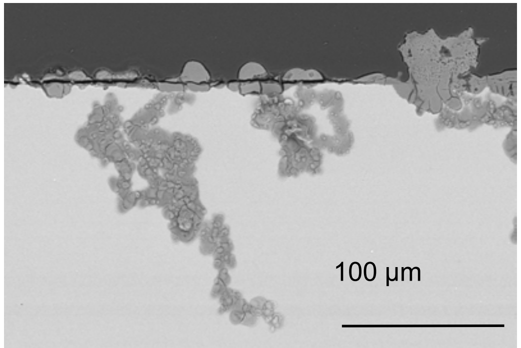
(A) BSE SEM, OCP



(B) BSE SEM, -1 V/SCE

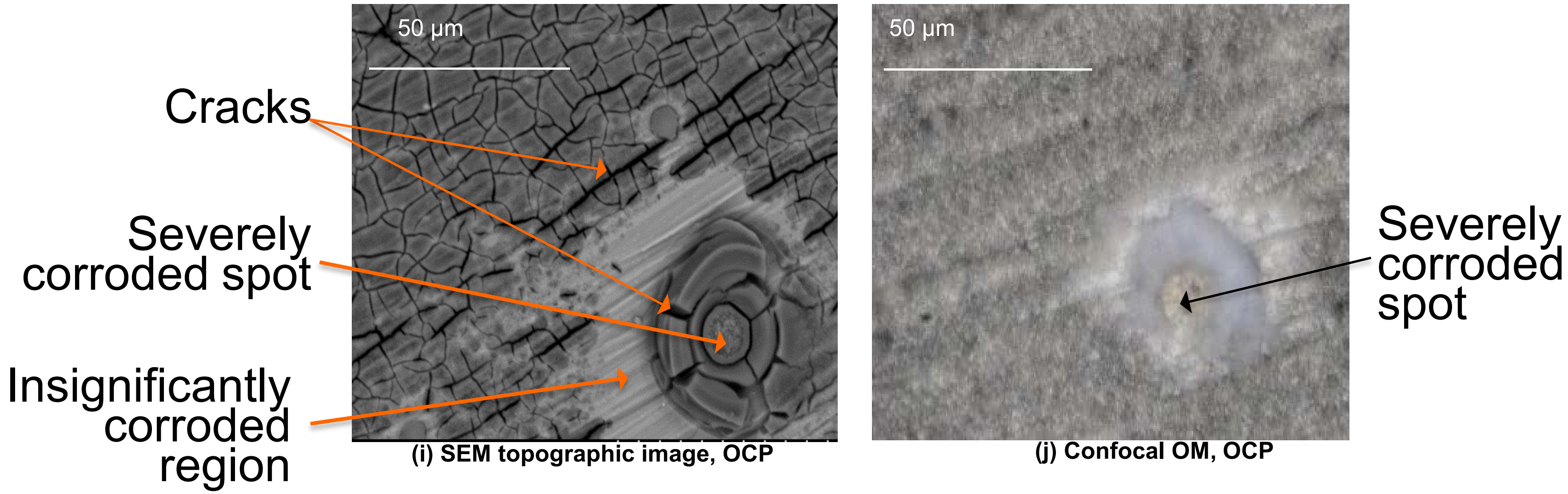


(C) BSE SEM, 0 V/SCE



(d) BSE SEM. 0 V/SCE

SEM and OM topographic images of Mg after immersion in saturated $Mg(OH)_2$

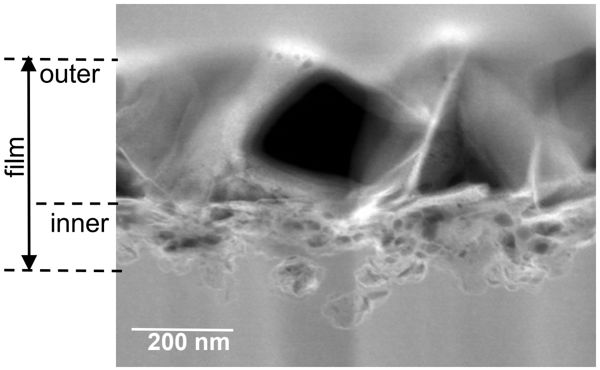


(i) SEM topographic image, OCP

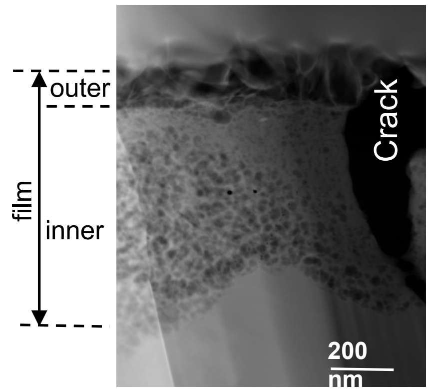
(j) Confocal OM, OCP

- Cracks might be formed during film formation or SEM/TEM examination
- A severely corroding spot may cathodically protect its surrounding areas → non uniform corrosion damage

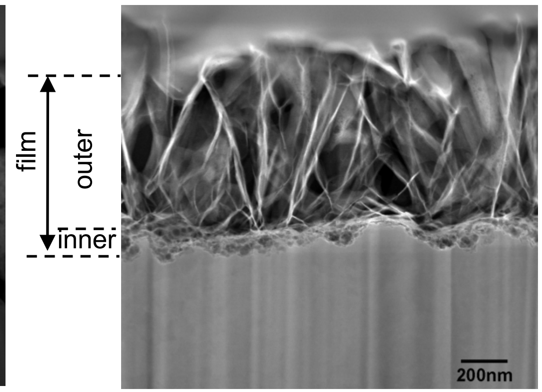
TEM cross-sections of Mg in saturated $Mg(OH)_2$ for 24 hours



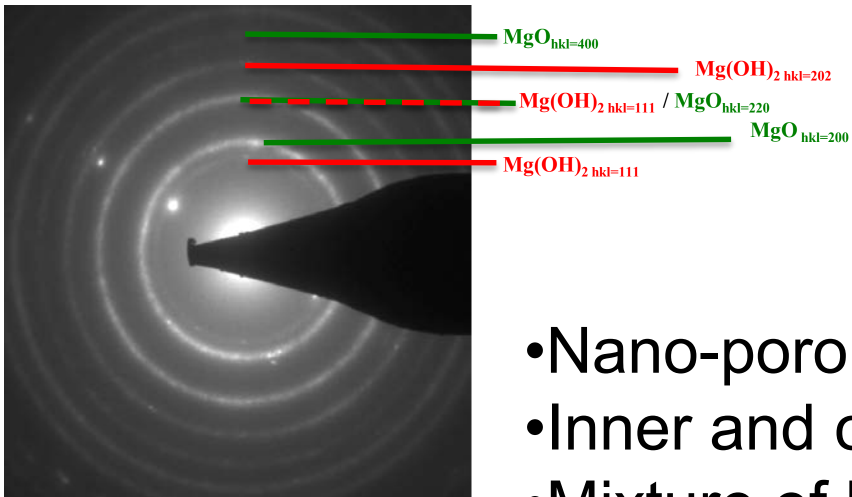
(e) HAADF STEM, OCP



(f) HAADF STEM, -1 V/SCE



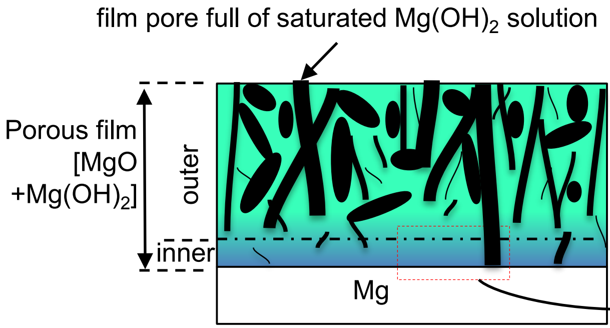
(g) HAADF STEM, 0 V/SCE



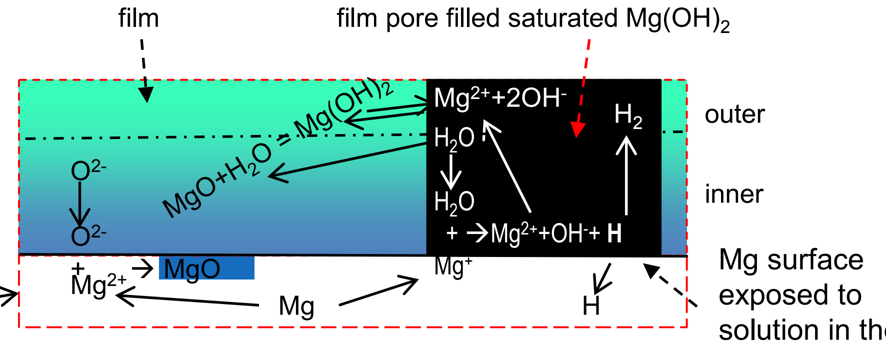
(h) Electron diffraction pattern

- Nano-porous
- Inner and outer layers
- Mixture of MgO and $Mg(OH)_2$

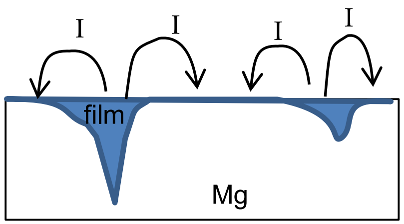
Film formation and corrosion model



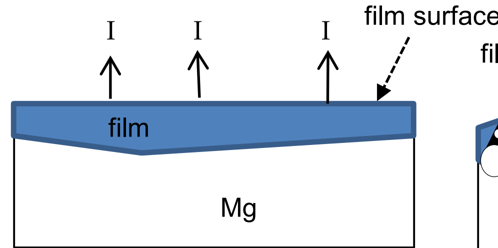
(a) Schematic illustration of micro-view of the surface film on Mg



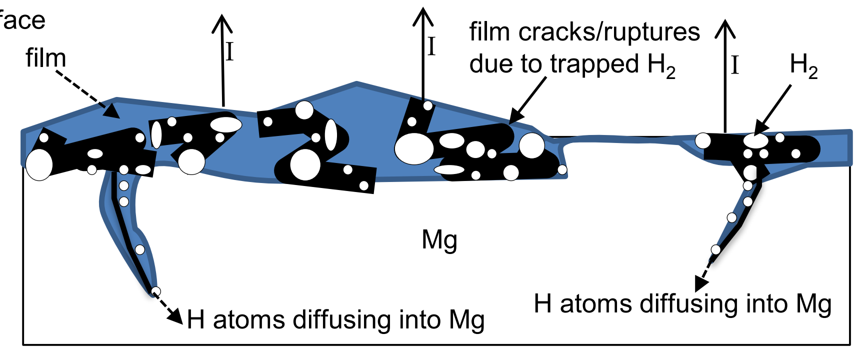
(b) Schematic illustration of the enlarged area from the section as shown in Fig.4(a) and the reactions involved in the film formation and dissolution



(c) Schematic illustration of current distribution and macro-view of the film formation on Mg around OCP



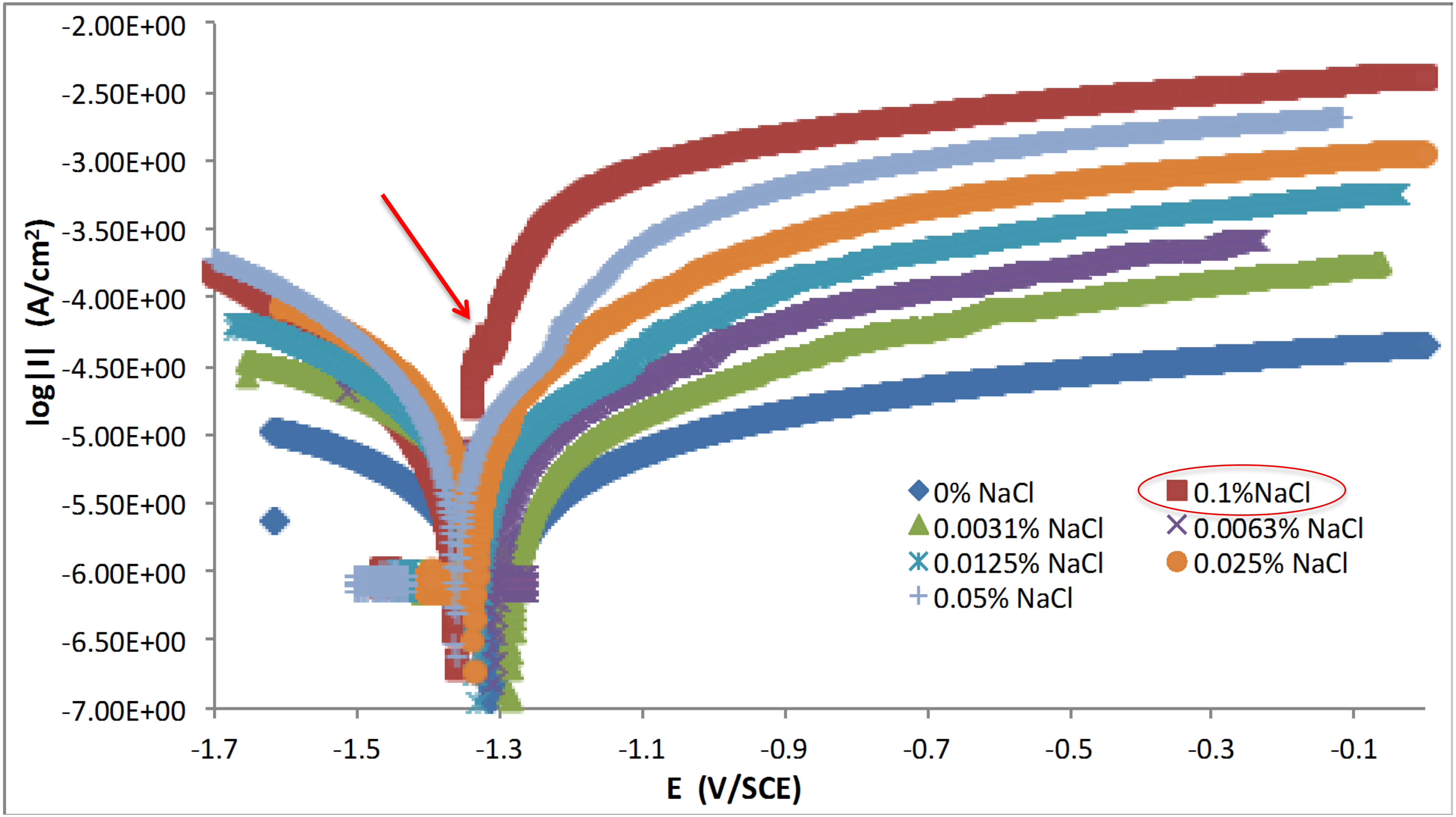
(d) Schematic illustration of current distribution and macro-view of the film formation on Mg at an anodic potential, e.g., -1V/SCE



(e) Schematic illustration of current distribution and macro-view of the film formation on Mg at a very positive potential, e.g., 0V/SCE

- Electrochemical dissolution and hydrogen at exposed surface area
- Chemical oxidation on non-exposed area
- $Mg(OH)_2$ mainly deposited from solution, and MgO & $Mg(OH)_2$ conversion in film
- Film ruptured due to anodic hydrogen evolution

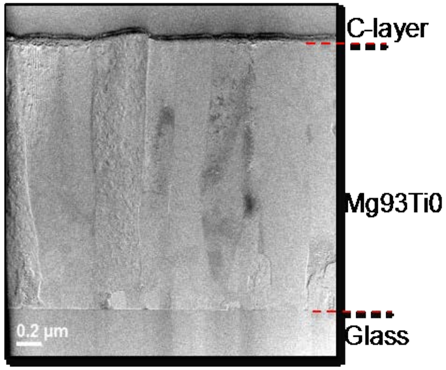
Solution selection for Mg-Ti alloy passivity measurement



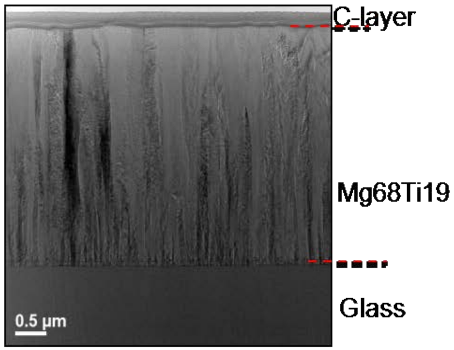
0.1wt.% NaCl + saturated $Mg(OH)_2$ selected (with clear passivity breakdown feature)

Magnetron-sputtered Mg-Ti alloys

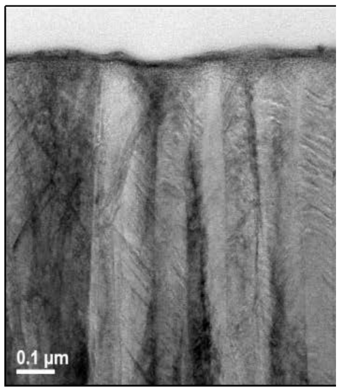
Name scheme	Composition (at.%) Time(s)	Mg	O	C	Ti
Mg93Ti0	960	**93.4**	3.8	2.8	**0.0**
Mg68Ti19	1320	**68.5**	4.7	7.5	**19.3**
Mg52Ti38	1320	**52.3**	3.3	6.4	**38.0**
Mg28Ti51	1320	**28.3**	9.9	10.4	**51.4**



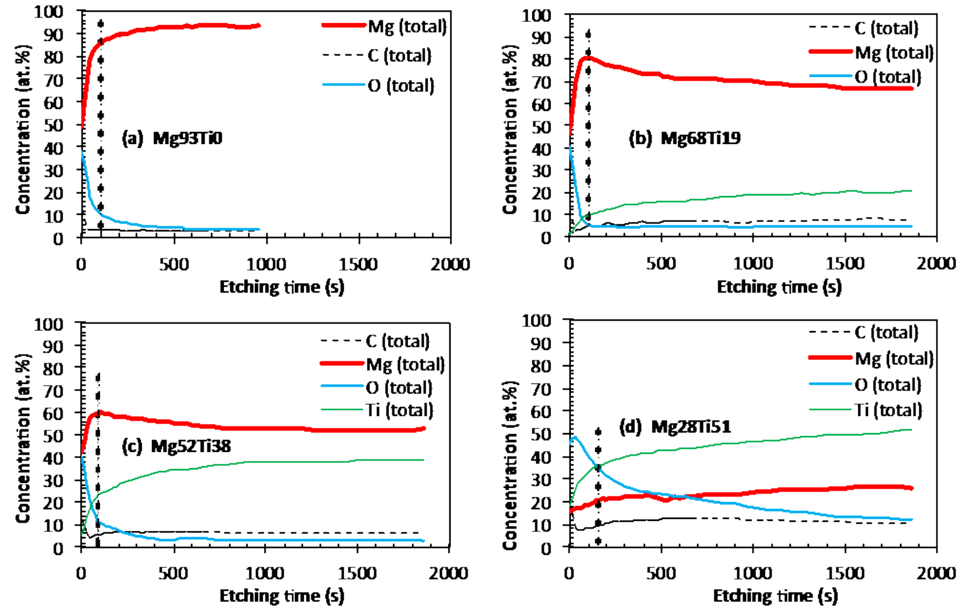
(a) Mg93Ti0



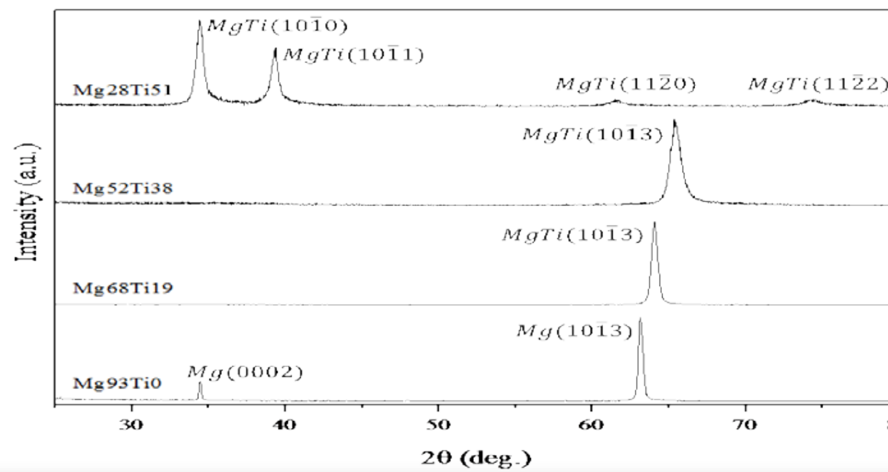
(b) Mg68Ti19



(c) Mg52Ti38

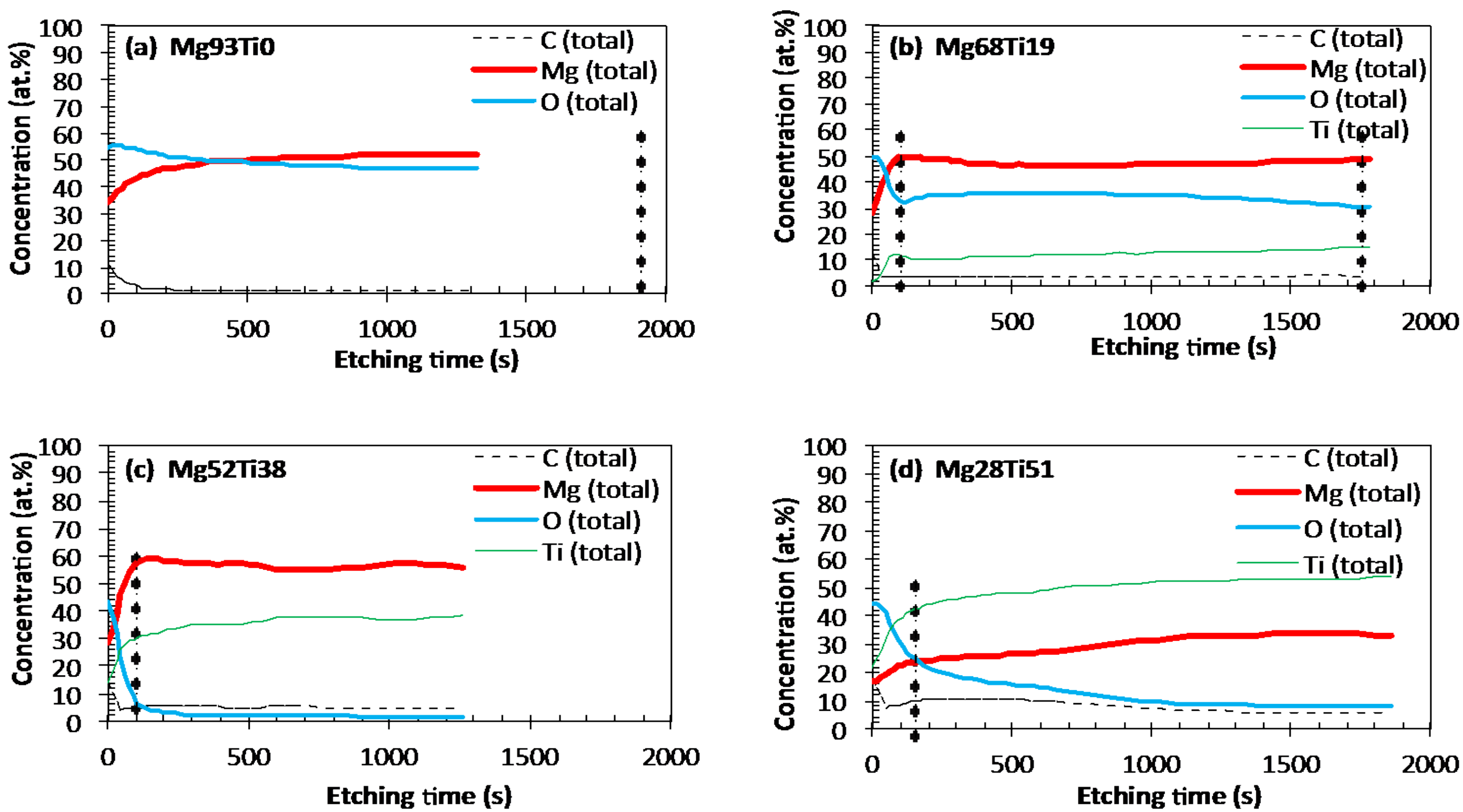


- Some O and C are included in the alloy
- There is always a thin oxide/hydroxide film on the surface
- Vertically grown grains
- Crystal orientation and single phase alloy



Single phase Mg-Ti solid solution alloys simulating the Mg matrix phases

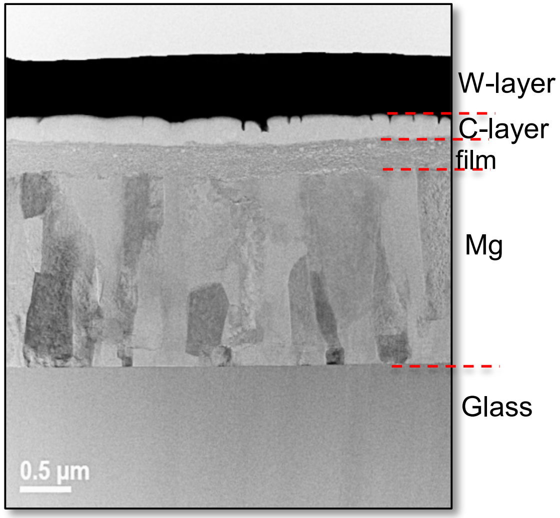
Compositions of the surface films formed after 5 hours of immersion in the testing solution

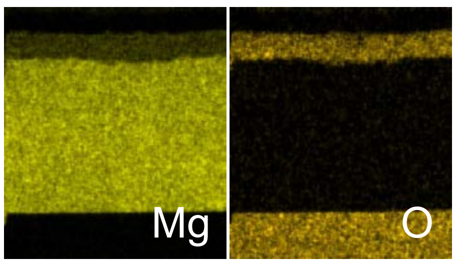


- Mg93Ti0: thick surface film mainly MgO
- Mg68Ti19: mixture of thick surface film and uncorroded areas (?MgO/OH?)
- Mg52Ti38: thin surface film (?MgOH/O?)
- Mg28T51: thin surface film (?MgOH/O?)

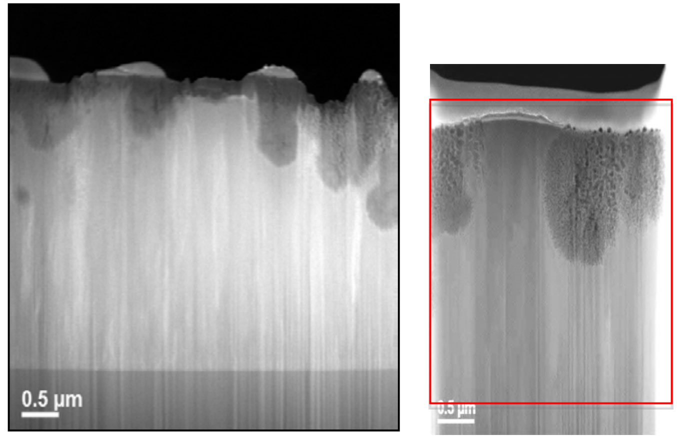
TEM cross-sections of the surface films after 5 hours of immersion in the testing solution

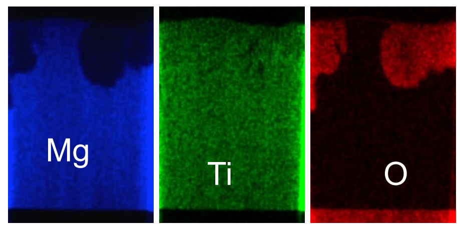
Mg93Ti0 TEM



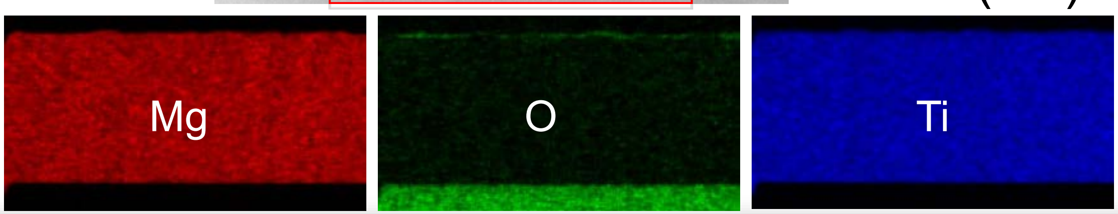


Mg68Ti19 TEM



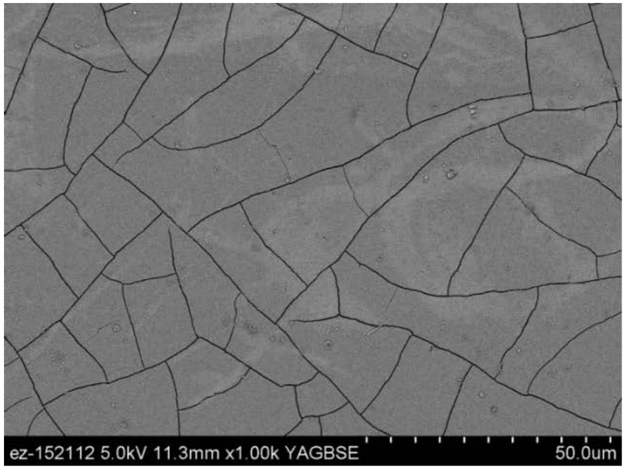


Mg52Ti38 TEM

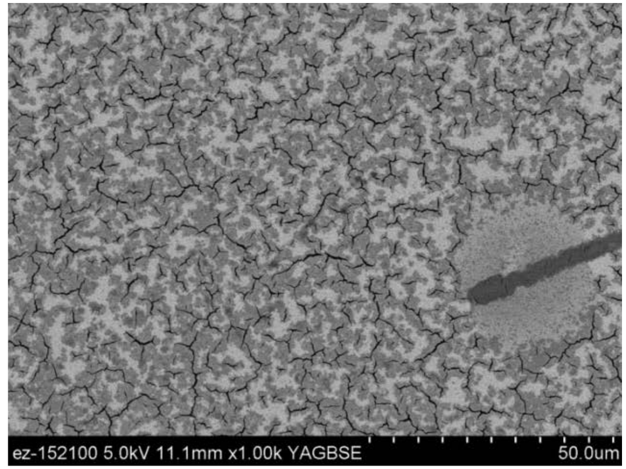


- Mg93Ti0: thick surface film (Mg/O)
- Mg68Ti19: non uniform thick surface film coverage/corrosion damage (Ti/O)
- Mg52Ti38: thin surface film (O?)

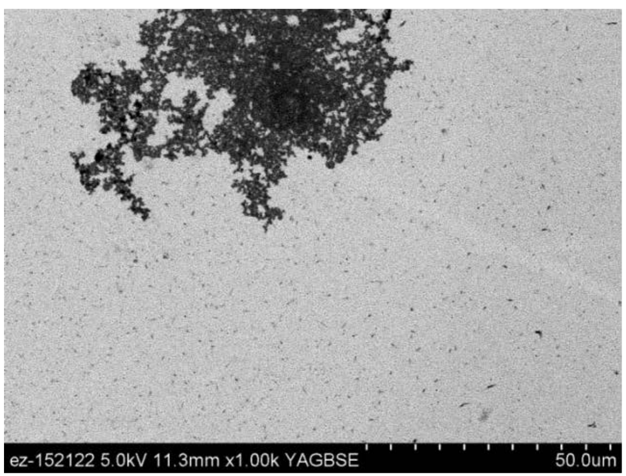
Immersed Surface Morphologies after 5 hours of immersion in the testing solution



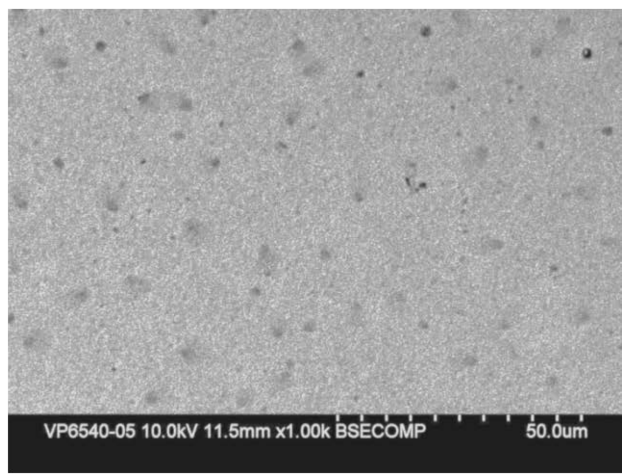
(a) Mg93Ti0



(b) Mg68Ti19



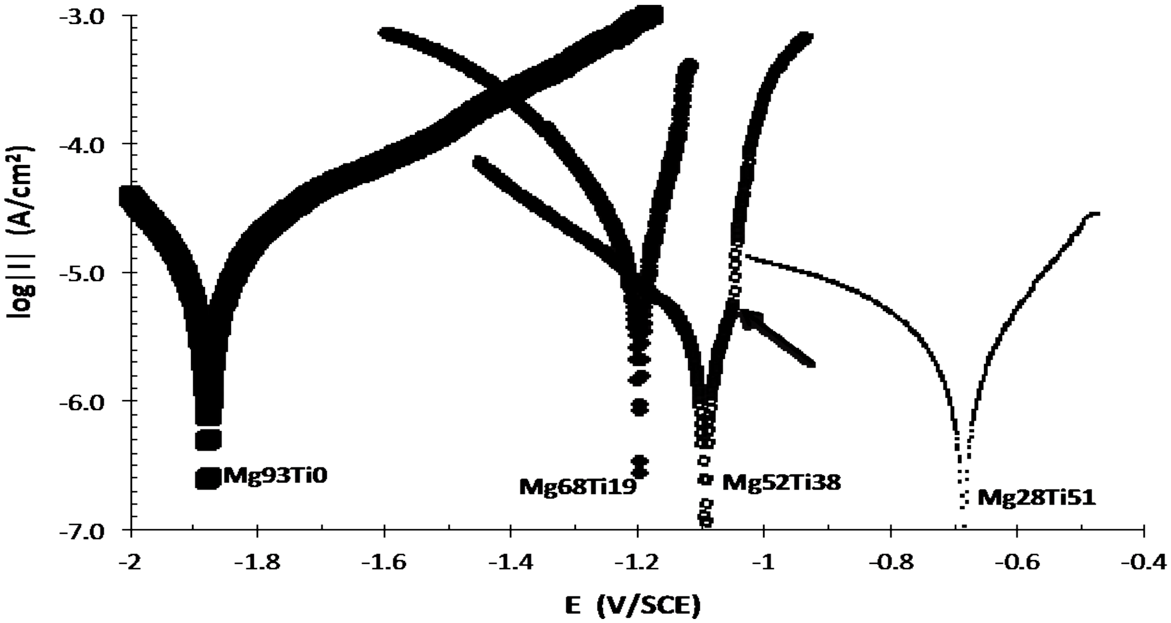
(c) Mg52Ti38



(d) Mg28Ti51

- Cracks formed on Mg93Ti0 and Mg68Ti19
- Some corrosion damage/cracks on Mg52Ti38
- Almost non-corrosion on Mg28Ti51

Uniformly magnetron-sputtered MgTi alloys in the testing solution



- Sputtered Mg more active than ingot Mg
- Active dissolution at ~19%Ti
- Active-passive at ~39%Ti
- Passivated at ~51%Ti
- Anodic current density decreases with increasing Ti content
- Cathodic current density does not always decrease with increasing Ti content

Responses to previous year reviewers' comments

- This project was not reviewed last year

Collaboration and coordination

- GM R&D Center
  Anil Sachdev
  ---helped select alloying elements and will provide a GM alloy

- University of Montana State University
  Paul E. Gannon, Phil Himmer, Quinn Andrews
  ---magnetron-sputtering Mg-X alloys for this project

Future work in FY2015

(Project ends in Sept. 2015)

- Initial Mg-Cr alloy synthesized and under evaluation
- The corrosivity/passivity of Mg-Cr alloys will be measured
- SEM, TEM, XRD and XPS characterization of Mg-Cr
- Key milestone: a paper on Mg-Cr passivity (9/30/2015)

Challenge

- Cr passivating ability may be stronger than Ti, but
- Cr is heavier than Ti, and thus the amount of Cr alloying cannot be too high

Summary

- ✓ Pure Mg cannot become passive in a non-corrosive solution even by anodic polarization

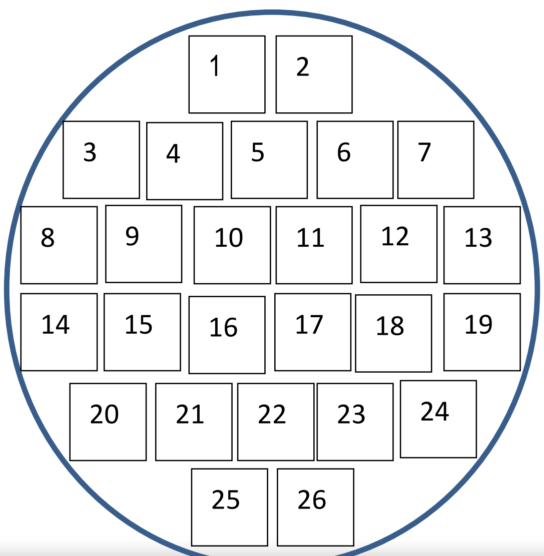
- ✓ Ti alloying can significantly reduce the anodic dissolution rate of Mg. Complete passivity can be achieved after the Ti content is high enough and the Mg-Ti alloy becomes Ti based.

- ✓ A continuous thin protective passive film can only be formed on a Ti based Mg-Ti alloy with a Ti crystal structure. On a low Ti-containing alloy with Mg crystal structure, the surface film is thick but not protective. When the Ti content is neither high enough nor too low, a thin film may be formed on some local surface areas, while on the other areas the film is a thick non-protective corrosion product layer.

Technical Back-Up Slides

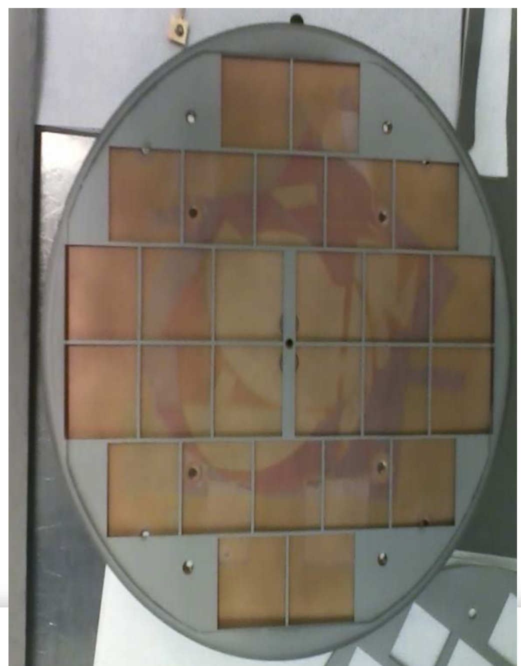
Magnetron sputtering MgTi alloys

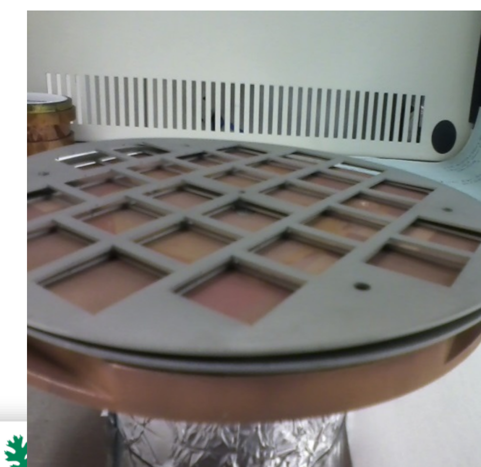
Sample holder in Vapor Deposition Chamber



2nd layer that holds samples onto bottom plate

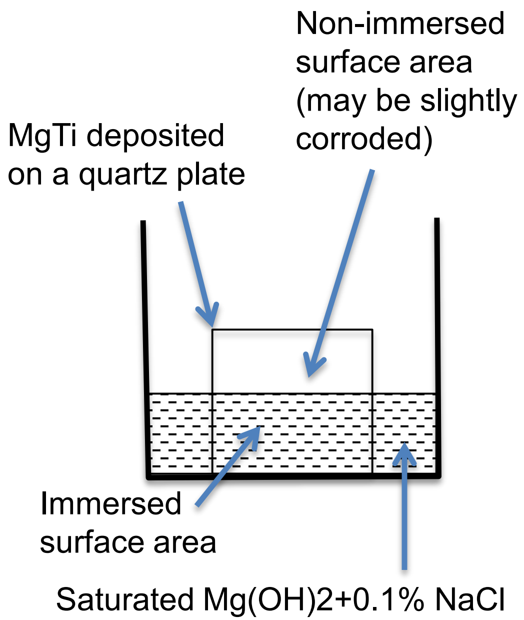
1st layer that samples are inserted into



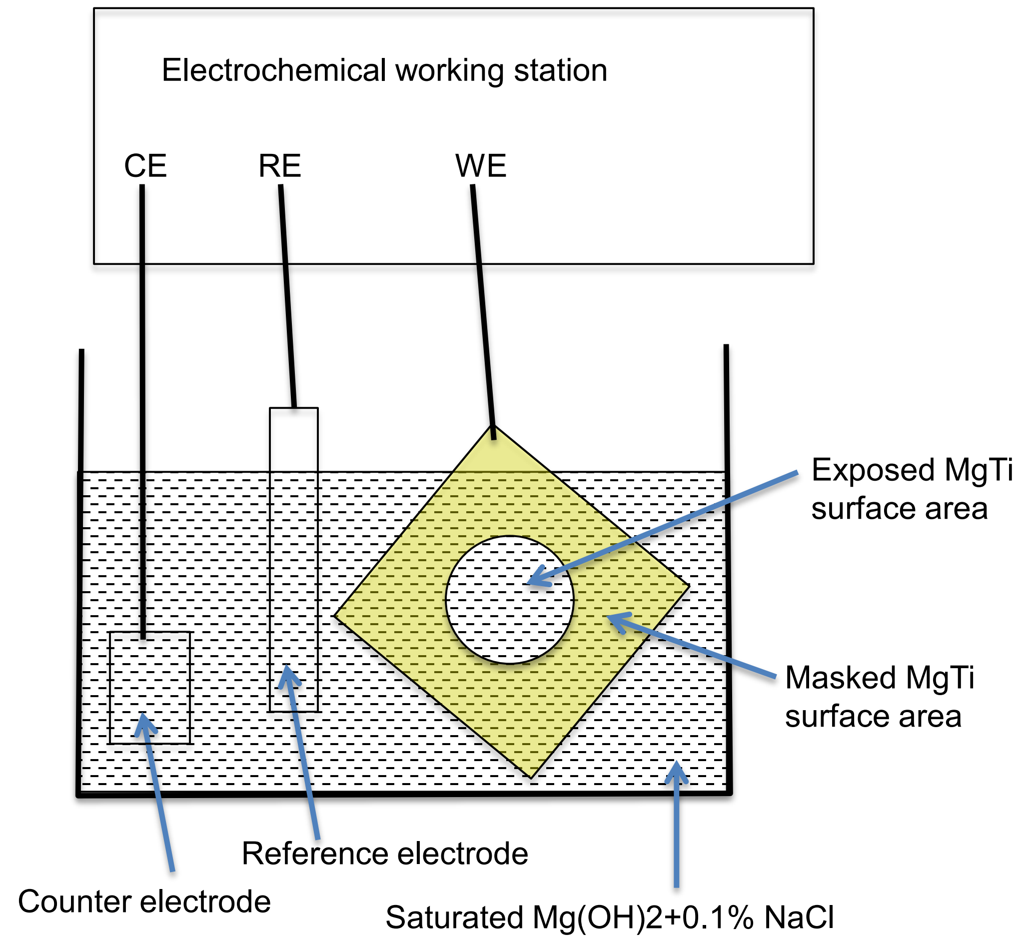


Setups for Immersion Corrosion and Electrochemical Tests

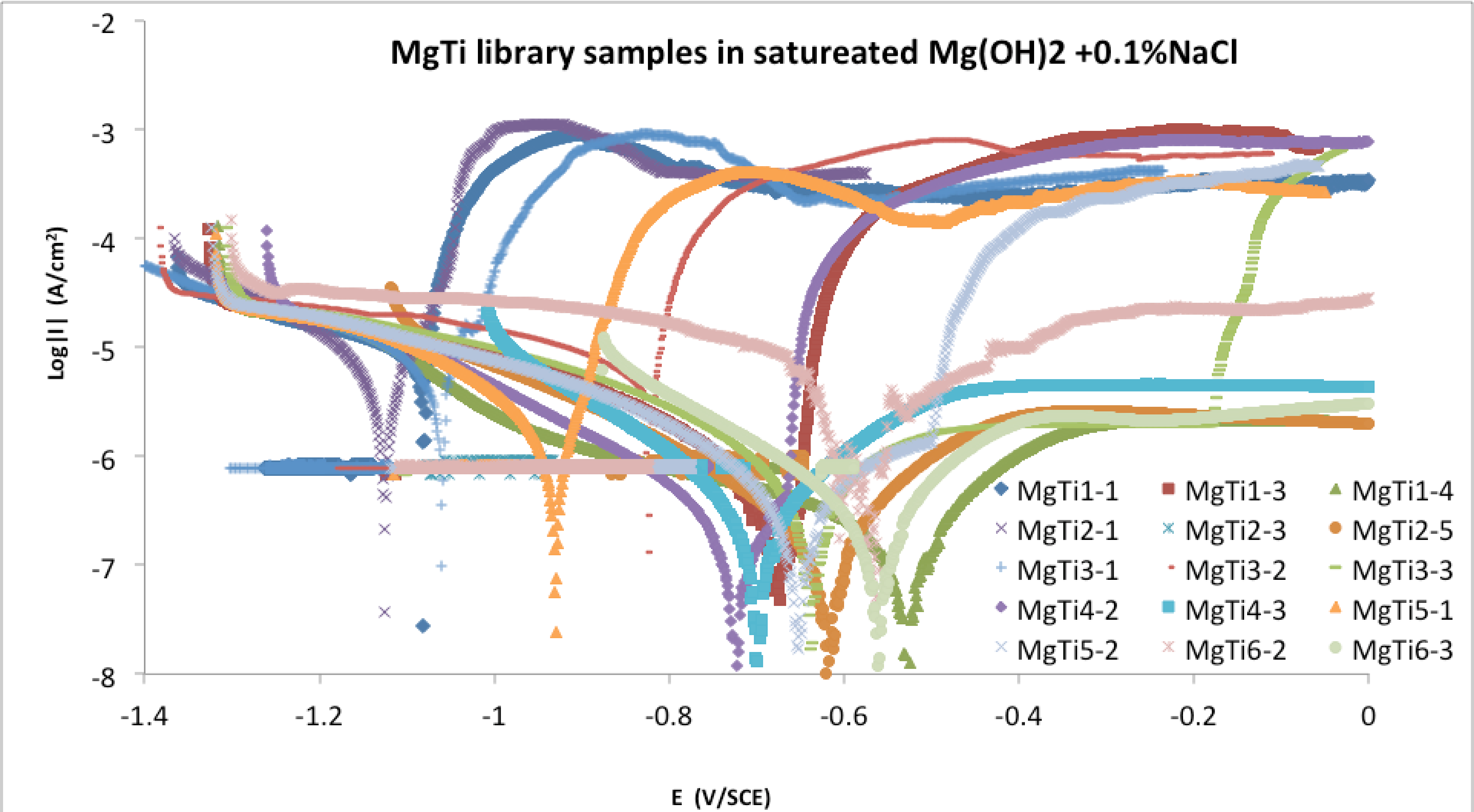
Immersion test



Electrochemical tests

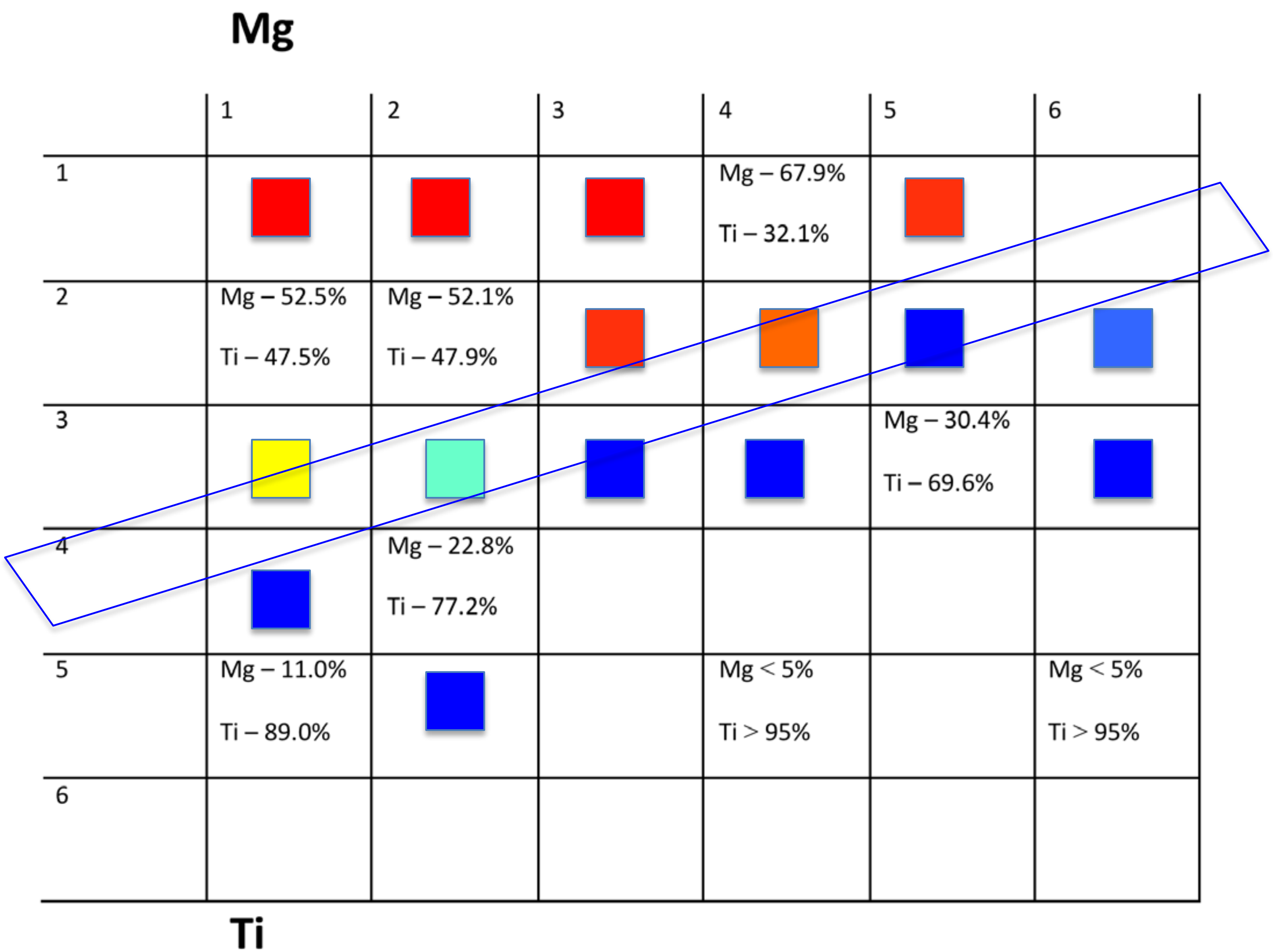


Polarization curves of library



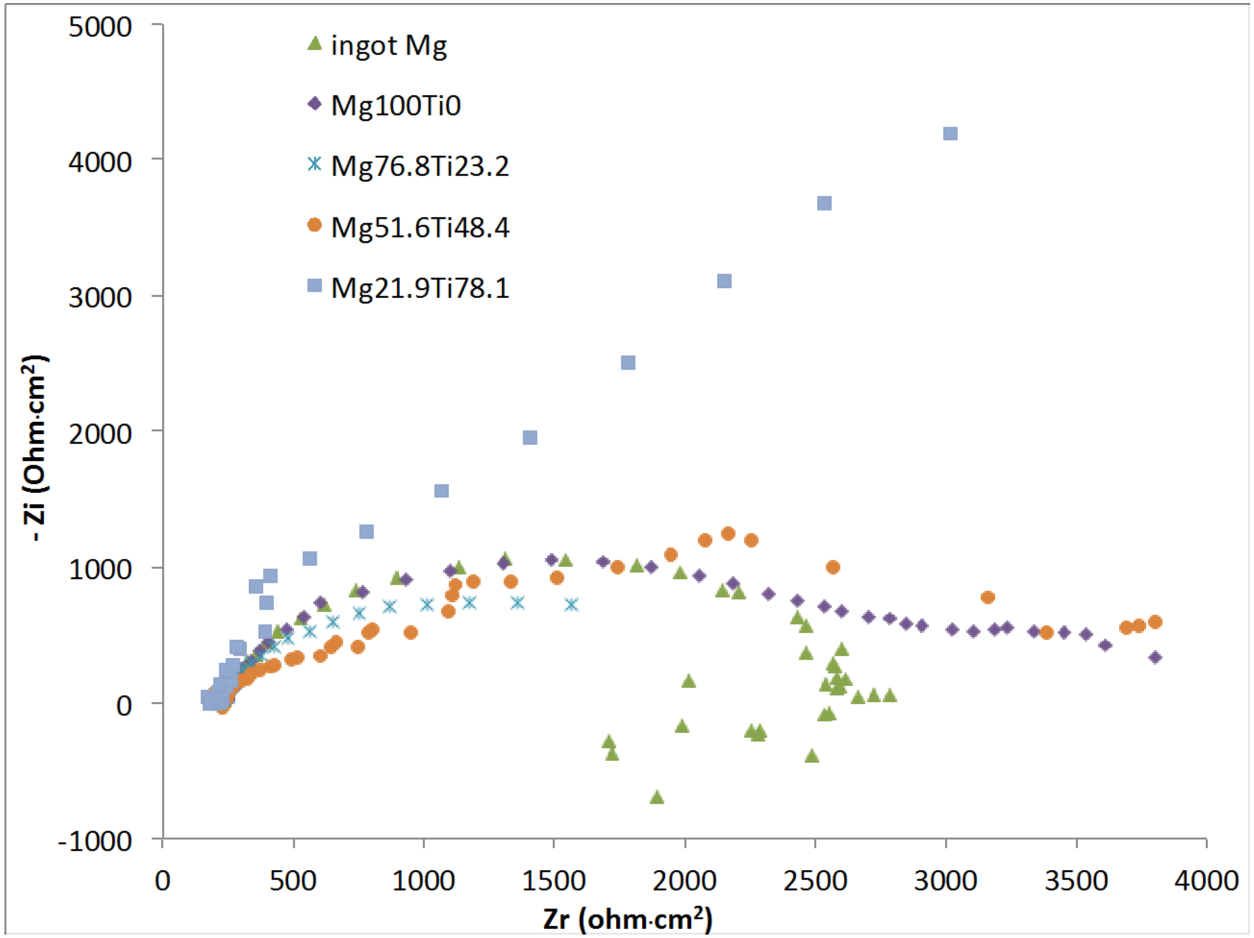
active, transitive, and passive

Passivated/unpassivated composition



Very roughly, 3 zones: active; transitive; passive

Active-passive dissolution confirmed by EIS



- EIS resistance extremely large at 51%Ti

- EIS resistance a few thousand Ohm when Ti<50%