FEM based studies of a Mg/Al hybrid component joint regarding corrosion prediction

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COMSOL CONFERENCE
ROTTERDAM 2013

Helmholtz-Zentrum Geesthacht
Centre for Materials and Coastal Research

Comsol History

Year	Reference	Image
2007	D. Höche, M. Shinn, J. Kaspar, G. Rapin and P. Schaaf, Laser pulse structure dependent texture of FEL synthesized TiN_x coatings; Journal of Physics D: Applied Physics, Vol. 40(3): 818-825, 2007. D. Höche, G. Rapin and P. Schaaf, FEM simulation of the laser plasma interaction during laser nitriding of titanium; Applied Surface Science, Vol. 254(4): 888-892, 2007.	
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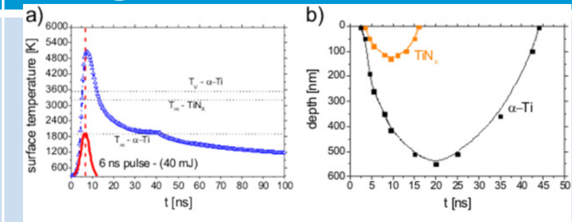
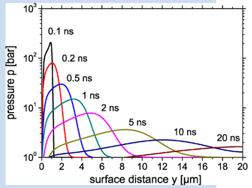
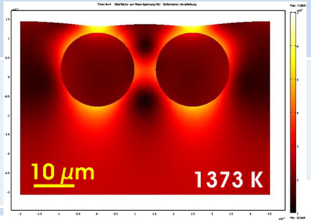
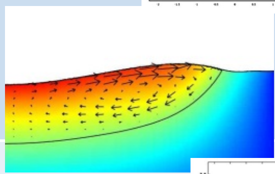
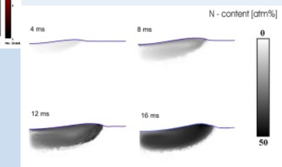
2009	D. Höche, M. Shinn, S. Müller, G. Rapin and P. Schaaf, Marangoni convection during free electron laser nitriding of titanium; Metallurgical Material Transaction B, Vol. 40(4): 497-507, 2009.	
2012	D. Höche and J. Isakovic, Level-set modeling of galvanic corrosion of magnesium; Mg2012 conference in Vancouver, Symposium Simulation and Modeling, 08.-13.07.2012, Proceedings 2012.	
2013	S. Klink, D. Höche, F. La Mantia, W. Schuhmann; FEM modelling of a coaxial three-electrode test cell for electrochemical impedance spectroscopy in lithium ion batteries, Journal of Power Sources, Vol. 240: 273-280, 2013 D. Höche and J. Isakovic; Mikrogalvanische Korrosion am Magnesium-Aluminium System - Detaillierte elektrochemische Einblicke mittels FEM - Simulationen, Chemie Ingenieur Technik, online, 2013. D. Höche; Towards the simulation based design of Mg/Al hybrid component joints in terms of corrosion prevention, Proceedings EuroCORR, Estoril, 2013.	

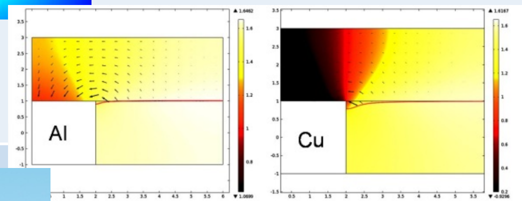


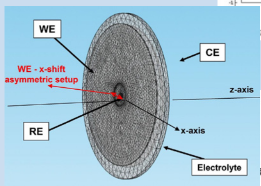


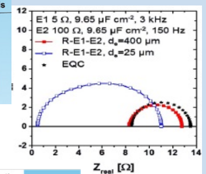


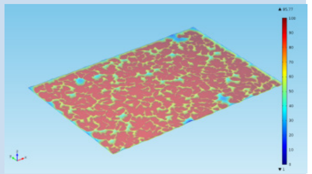


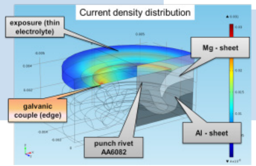










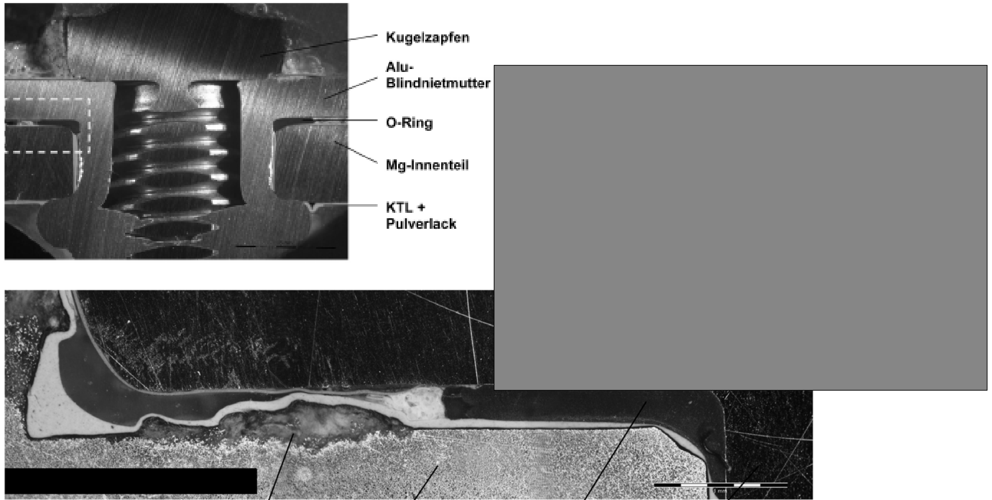


Corrosion in multi-material design

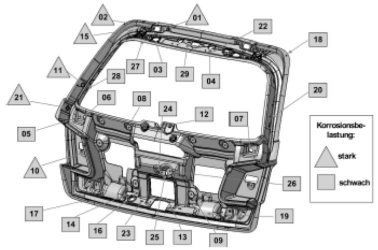
- galvanic corrosion (AA, Mg, Steel, CFK)
- under paint corrosion
- crevice corrosion (gap, edge, scratch)
- localised corrosion / filiform corrosion

Anti-corrosive lightweight design needs:

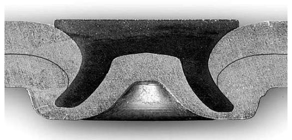
- Constructive corrosion protection
  - component selection (non-metallic)
  - avoiding galvanic contacts
  - spacer distances etc.
- Active corrosion protection
  - optimized coating systems (hybrid)
  - superior pre-treatments
- Corrosion resistant materials / alloys



H. Schreckenberger, P. Izquierdo, S. G. Klose, **D. Höche** et.al.; Materialwissenschaft und Werkstofftechnik, 2010.



P. Izquierdo, S.G. Klose,, **D. Höche**, et.al.; World Magnesium Conference. Hongkong, 2010.



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Aims of simulation action

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Application on engineering tasks

→ Assisting engineers in Multi-Material-Design (combination of different materials) under corrosion protection aspects

→ Corrosion prediction for **Multi-Material-Joints** *(welds, rivets, clinches)* = minimising the need of corrosion protection action *(coatings, etc.)*

→ Tailoring of various properties like spacing distances

Most common advantages

→ Reduction of development expenses and periods

→ Improved planning ability due to tailored properties

→ Simulation based safeguarding of corrosion protection action

Objective:

Computer-Aided Engineering (CAE) in terms of corrosion protection

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Anti-corrosive simulation based design

1. **Challenge** → the model development chain

Joining technology	welds (FSW, Laser, arc) clinches, rivets, adhesive	selfpierce punch rivet
Geometry	sheets, casts, crevices, spacers, exposed area	2 sheets and a rivet
Materials M1, M2, Mx	bulk materials, AA, Mg alloys, steels, CFK...	bulk Mg and Al sheet, Al rivet
Surface state	bare, cleaned, etched, conversion coated, top coat	bare
Environmental Exposure	liquid couluum, thin film, flow, splashes	thin film

scientific aspects

- materials state (as received)
- scratches, artefacts
- Impurities

- galvanic corrosion
- crevices
- under paint corrosion

- electrical properties (conductivity)
- electrochemical response

- interface chemistry
- Faraday reaction
- passivation, layer growth

- ion concentration, pH
- conductivity
- transport mechanism

Chose the **correct** interdisciplinary approach including the correct physics / chemistry

Self-pierce punch rivet model problem (Al in Mg)

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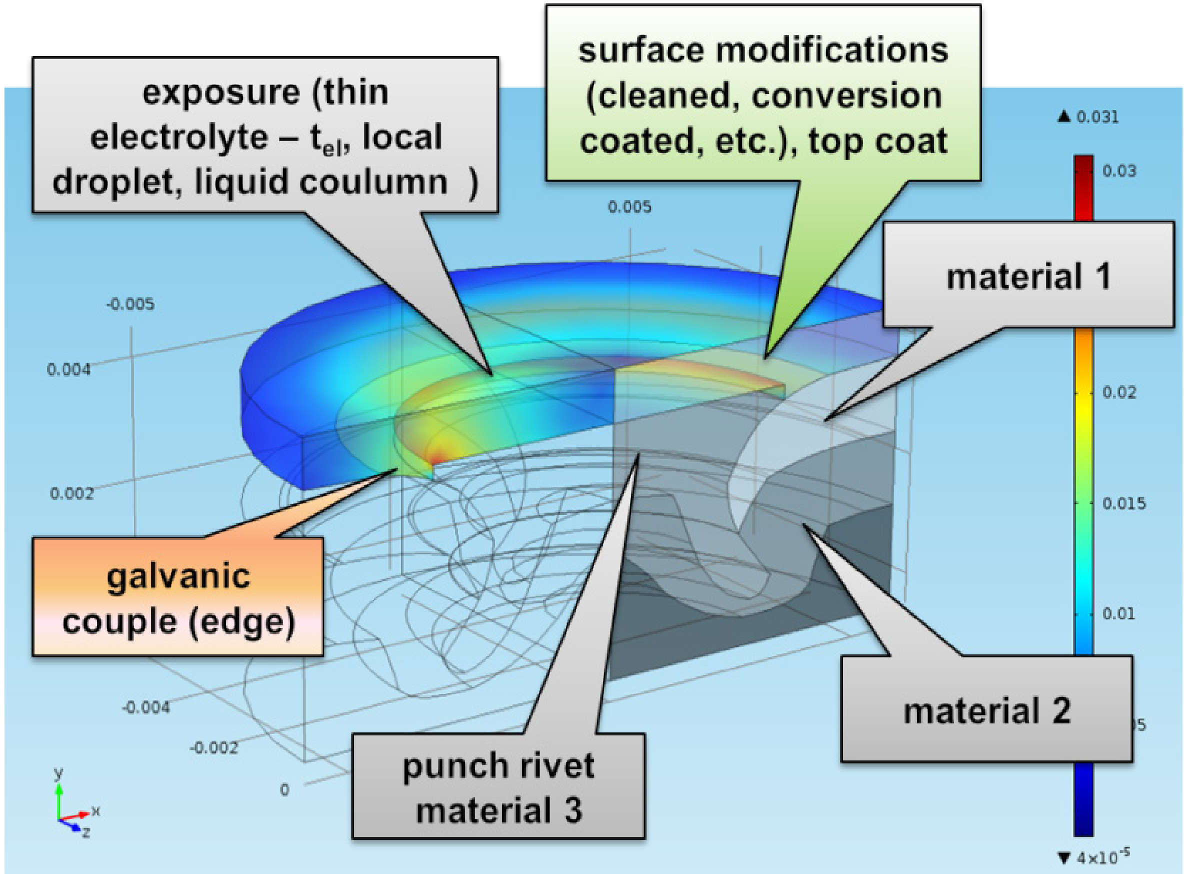
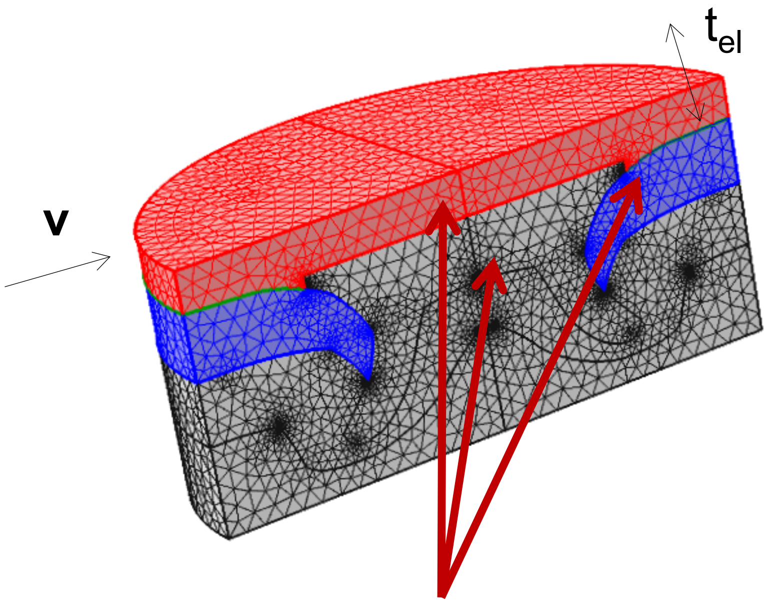


Geometry setup:

use symmetries



reduce to "active" domains

- Try to figure out **all** aspects → develop the model starting with most "weighted" issue.
- Keep it **as easy as possible** (checking requirements in context to limitations and assumptions)

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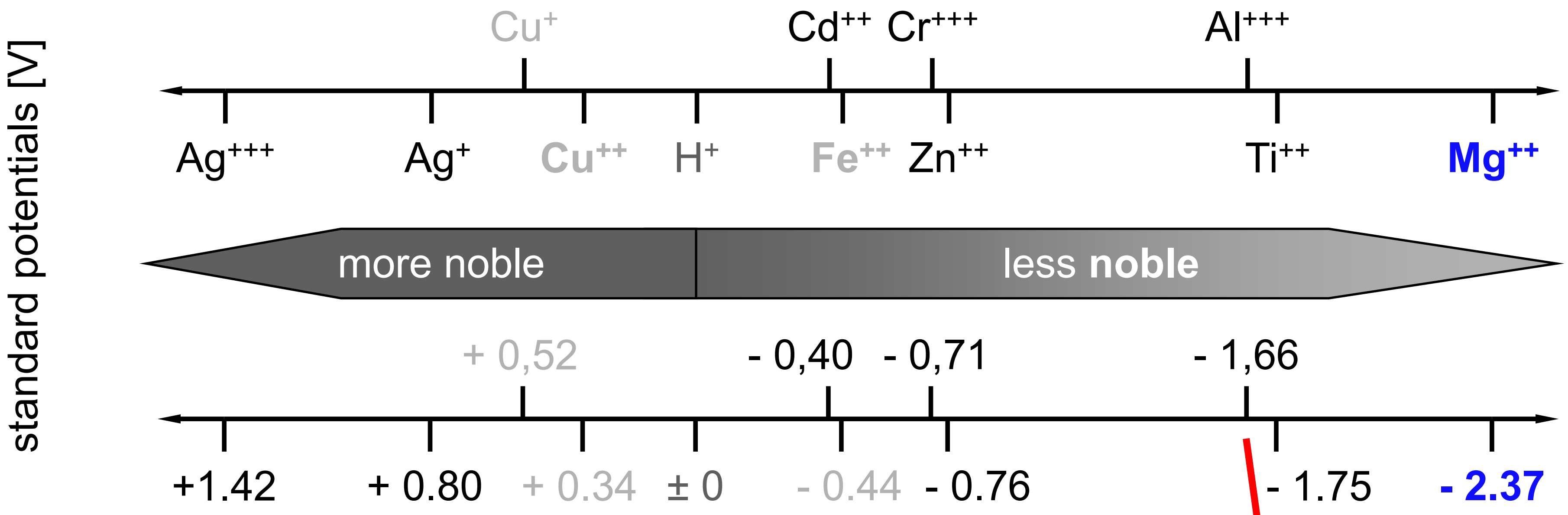
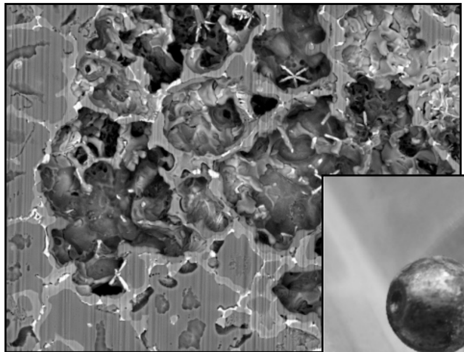
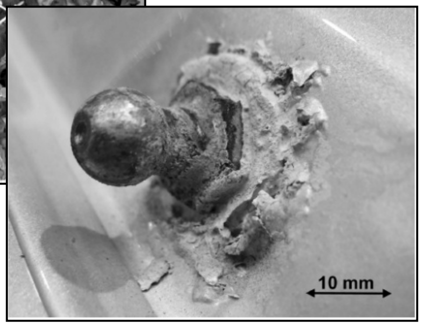
Most „weighted“ problem

Galvanic couples in Mg based engineering



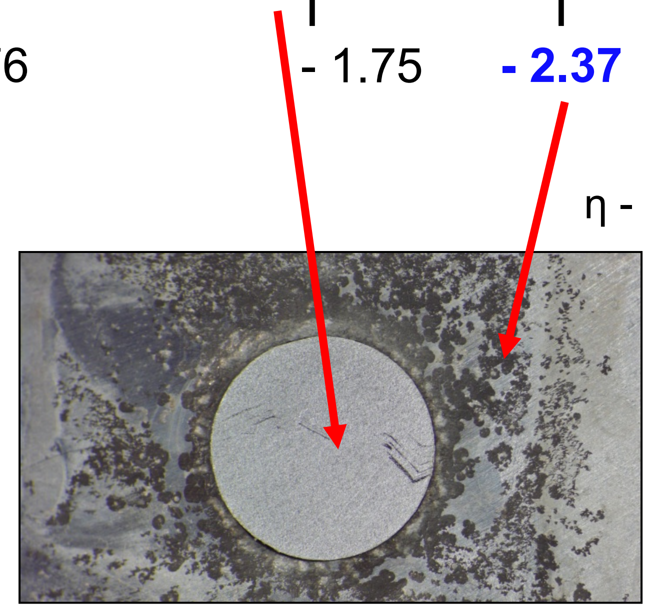


micro



macro

η - overpotentials



General rules – galvanic couples

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- **ratio of cathode area to anode area / <u>area rule</u>**
- galvanic corrosion will **become more severe** over time once it is initiated.
- affected zone can be relatively large and galvanic corrosion may be caused by a **remote cathode metal** (spacing aspects).
- **avoid** that the anode is **electrically connected** to the cathode (not possible).
- relative positions of electrodes → corrosion products from the Mg anode can be transferred to the cathode, corrosion could be slightly reduced through an "**alkalisation effect**". (being simulated)
- Corrosion products from the cathode on the Mg surface (e.g. by convection) leading to a **"passivation" or "poisoning" effect**, which could either slightly, ameliorates or deteriorates the galvanic corrosion. (very important)
- A **"shortcut" effect** can be caused by the accumulation of corrosion products → accelerating galvanic corrosion unexpectedly at a remote area.

G. Song, B. Johannesson, S. Hapugoda, D. StJohn, Corrosion Science. 46 (2004) 955-977.

Mathematical approach

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Nernst:

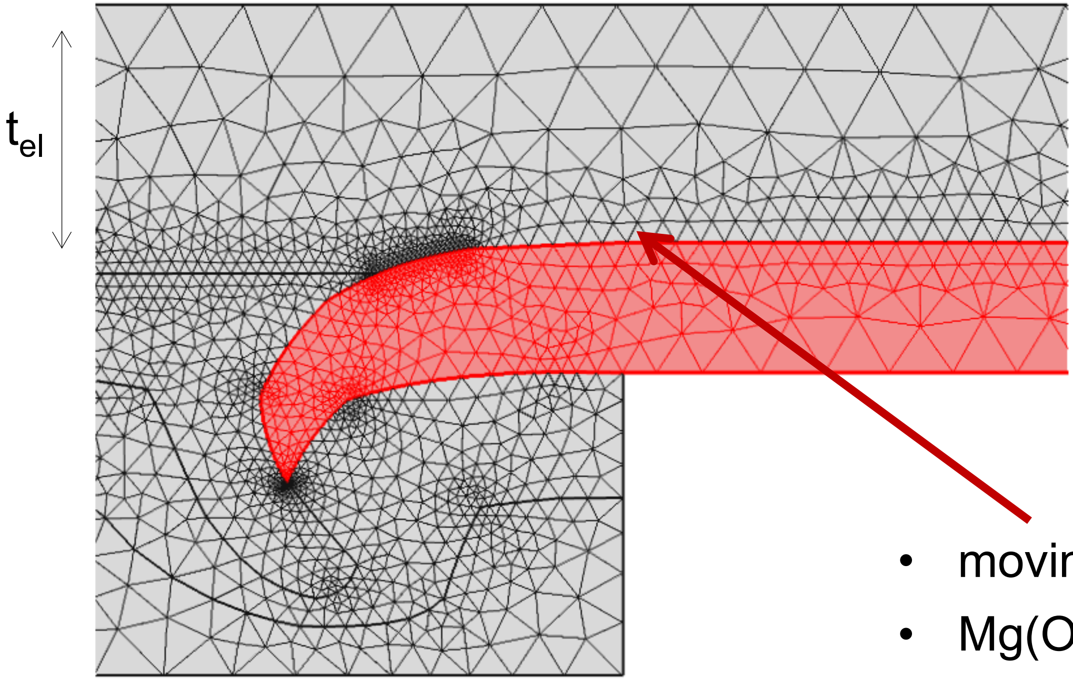
$$\frac{\partial c_i}{\partial t} + \nabla\left(-D_i \nabla c_i - z_i u_{mob} F c_i \nabla U_{el}\right) + \mathbf{u}\cdot\nabla c_i = R_{i,tot}$$

water autoprotolysis

$$H_2O \Leftrightarrow H^+ + OH^-$$

$$R_{OH^-} = R_{H^+} = k_f - k_b(c_{H^+} c_{OH^-})$$

Faraday:



$$j_{el} = F\sum z_i N_i$$

$$i_{el} = -\sigma\cdot\nabla U$$

- moving interface
- $Mg(OH)_2$ precipitation
- anodic dissulution

Specimens:
(to be extended)

species	Mg^{2+}	OH^-	H^+	Na^+	Cl^-	O_2
D $[m^2/s]*10^{-9}$	0.71	5.27	9.31	1.33	5.27	1.98
C_0 $[mol/m^3]$	0	10^{-4}	10^{-4}	42	42	0.233

Mathematical approach

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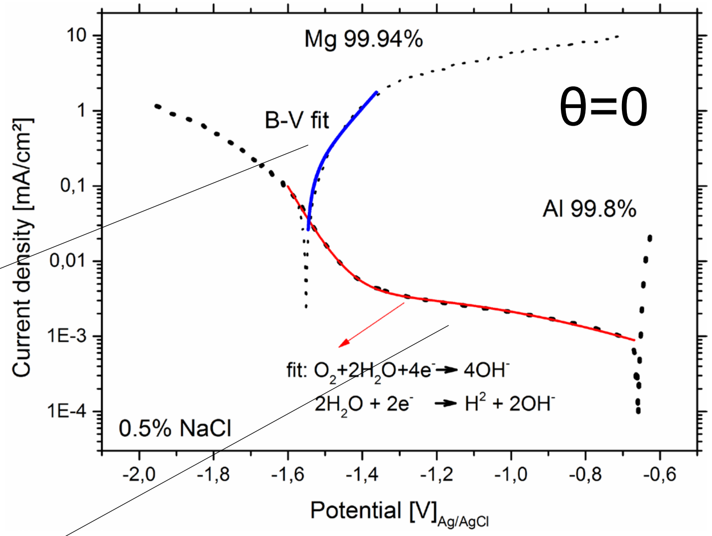
to be used: (in 4.2a)

- Tertiary Current Distribution, Nernst-Planck Interface
  - modified boundary conditions (weak form) to include the reduced flux due to layer growth
- Surface Reactions Interface
- Deformed Geometry and Moving Mesh Interface (ALE)
- Mathematics Interface
  - 3 ODE's for surface coverage, layer thickness and porosity

Boundary conditions – electrode response

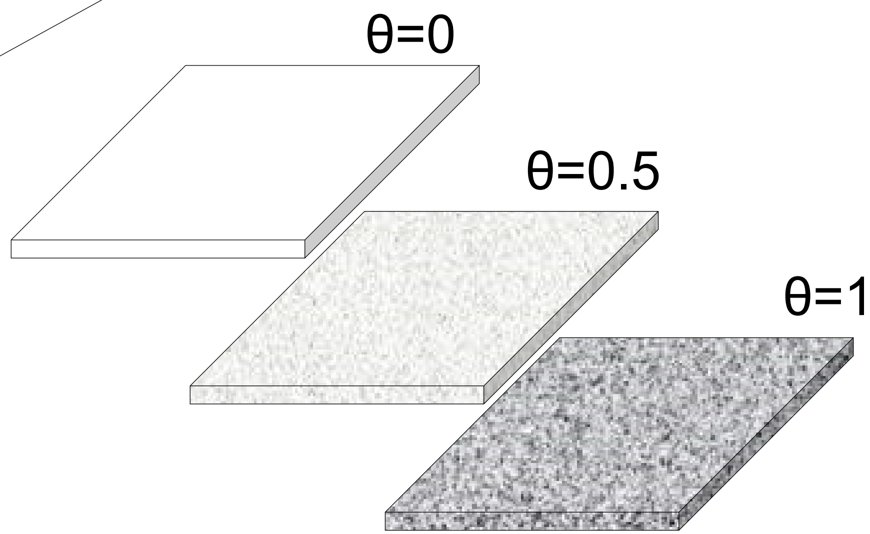
anodic: Mg dissolution	$Mg \rightarrow Mg^{2+} + 2e^-$
cathodic: oxygen reduction water electrolysis	$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$ $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$
global reaction:	$Mg + 2H_2O \rightarrow Mg^{2+} + 2OH^- + H_2$



$$i_{anode} = (1-\theta+\varepsilon\theta)\cdot i_0\left(e^{\left(\frac{z\alpha_a F\eta}{RT}\right)} - e^{\left(-\frac{z\alpha_c F\eta}{RT}\right)}\right)$$

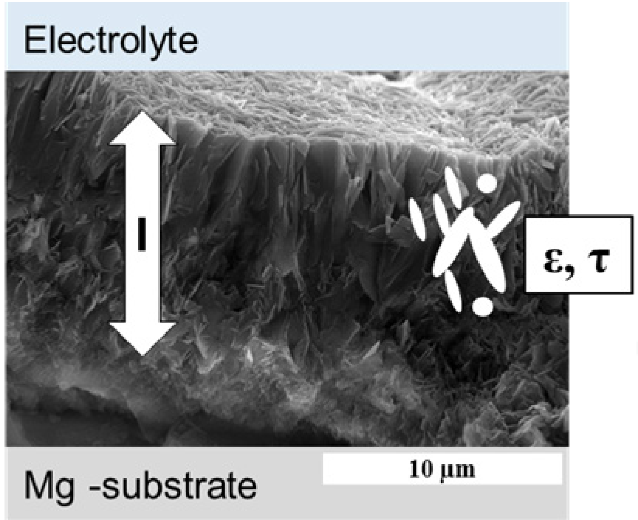
→ Tafel does not work

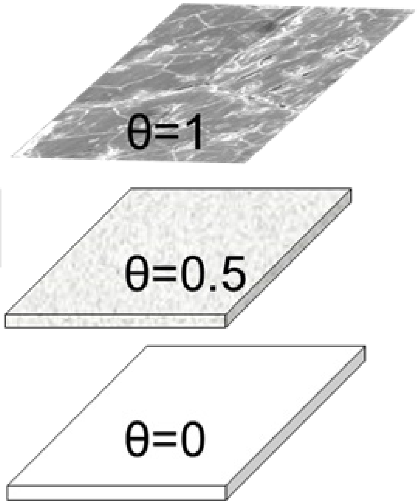
$$i_{cathode} = (1-\theta+\varepsilon\theta)\cdot\frac{i_0 e^{\left(-\frac{z\alpha_c F\eta}{RT}\right)}}{1-\left(\frac{i_0}{i_d}\right)\left[1-i_0 e^{\left(-\frac{z\alpha_c F\eta}{RT}\right)}\right]} + (1-\theta+\varepsilon\theta)\cdot i_{0H}\cdot 10^{\left(-\frac{\eta_H}{\beta}\right)}$$



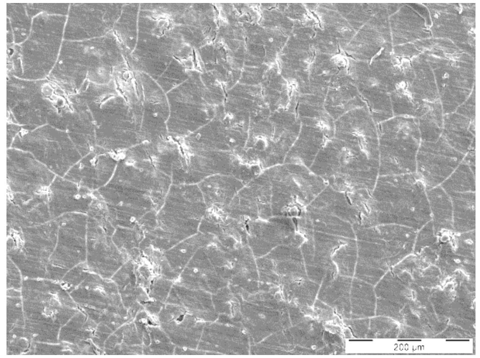
→ self induced corrosion layer growth

Boundary conditions – surface coverage





HP_Mg 0.1 NaCl 96h



200 µm

Surface coverage θ:

$$\frac{d\theta}{dt} = -\frac{1}{l(1-\varepsilon)}\left(\frac{R_{Mg^{2+}} M_{Mg(OH)_2}}{\rho_{Mg(OH)_2}}\right) \qquad R_{Mg^{2+}} = -(1-\theta)\,\mathrm{k}_{Mg(OH)_2}(\mathrm{c}_{Mg^{2+}}\, c_{OH^-}^2 - \mathrm{K}_{Mg(OH)_2})$$

Reduced flux:

$$\mathbf{n}\cdot(\mathbf{N}_{total} - \mathbf{N}_{eff})_i = \mathbf{n}\cdot\mathbf{N}_{i-red} = D_i\left(\theta - \frac{\theta}{N_M}\right)\left(-\nabla \mathbf{c}_i - \frac{z_i F}{RT} c_i \nabla \mathbf{U}_{el}\right)$$

Interface velocity:

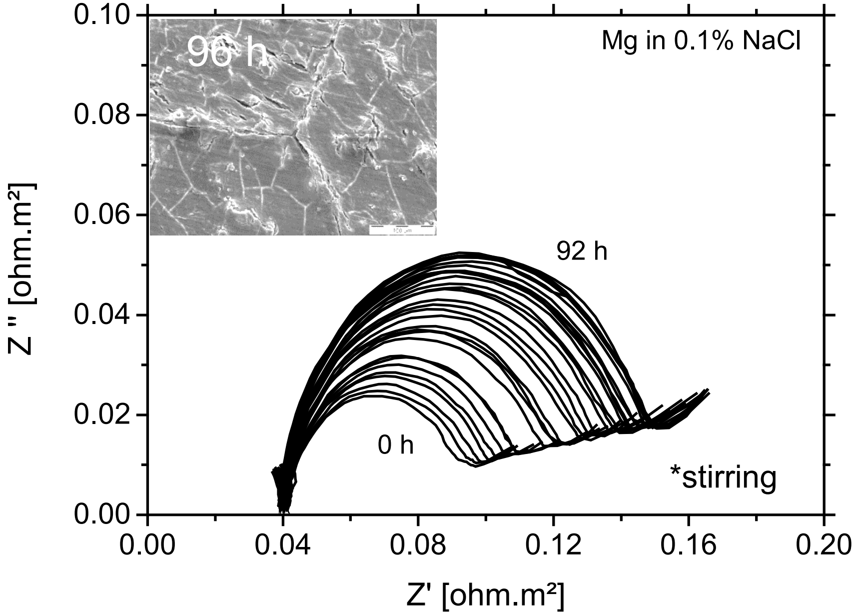
$$\mathbf{u}_{total}\cdot\mathbf{n} = -\frac{M}{zF\rho}\cdot i_{Mg}(\theta) + u_{layer} \quad \text{with} \quad u_{layer} = \frac{R_{Mg(OH)_2} M_{Mg(OH)_2}}{(1-\varepsilon)\rho_{Mg(OH)_2}}$$

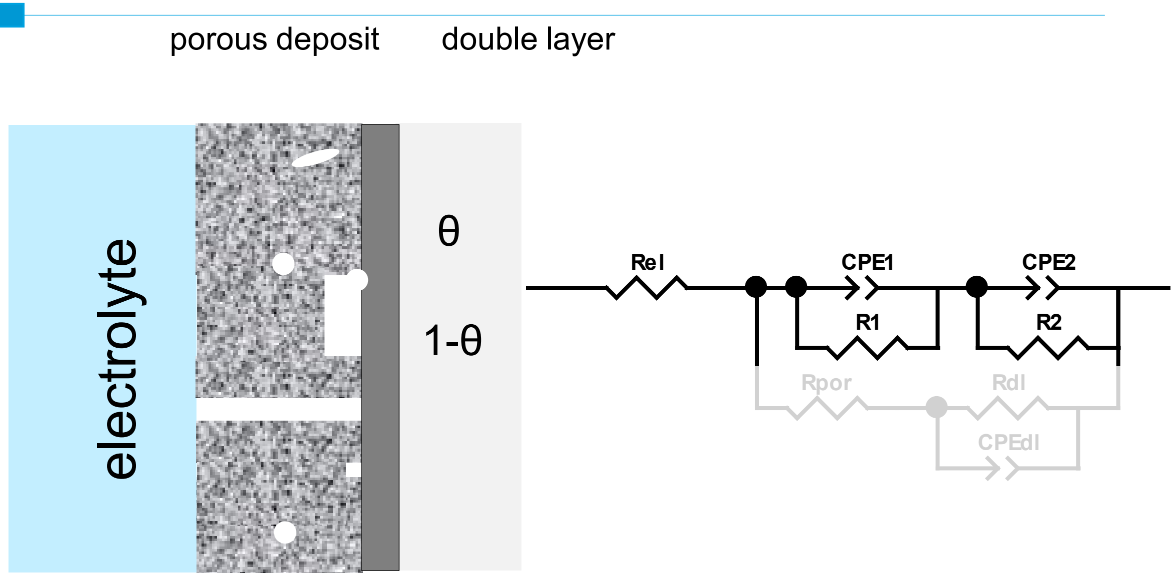
anodic dissolution — deposit growth

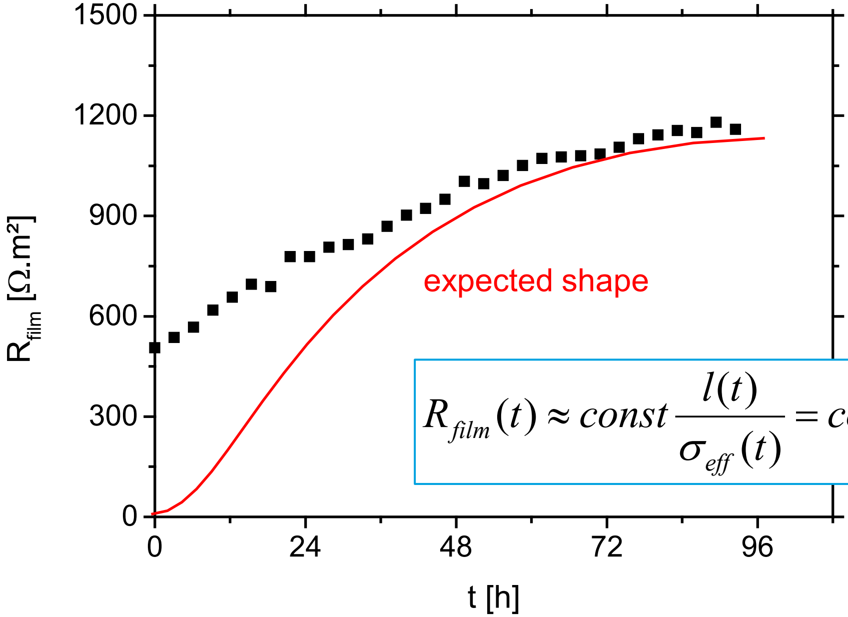
Assumptions and limitations

- Al is non-corroding (anodic branch is neglected)
- dilute solution theory is applicable
- precipitates do not dissolve
- hydroxide formation occurs at the interface
- limited number of chemical specimens and reaction products
- non-technical alloys
- without localised effects (pitting / Cl^-)
- …..

Results – checking the model







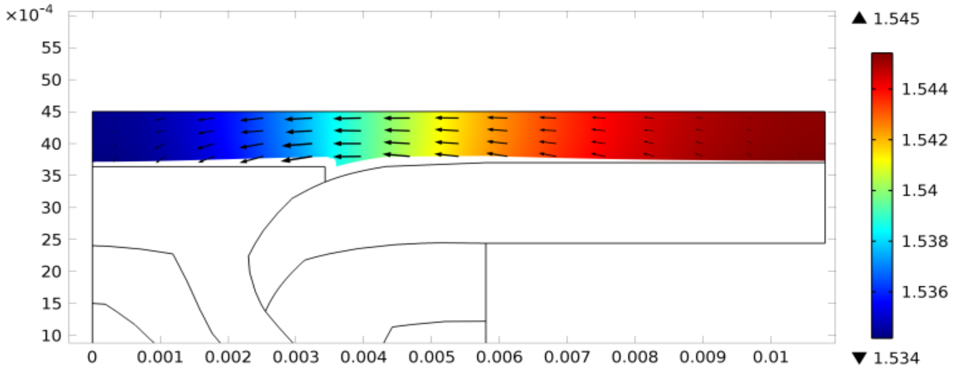
$$R_{film}(t) \approx const\,\frac{l(t)}{\sigma_{eff}(t)} = const\,\frac{l(t)}{\sigma\theta(t)s^{n}\varepsilon^{2}}$$

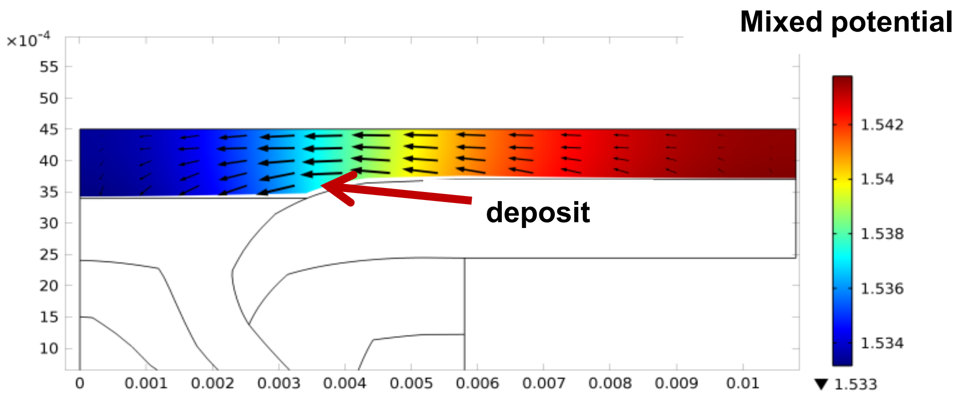
→ θ>0 at t=0 (native layer)

Results – Geometry aspects

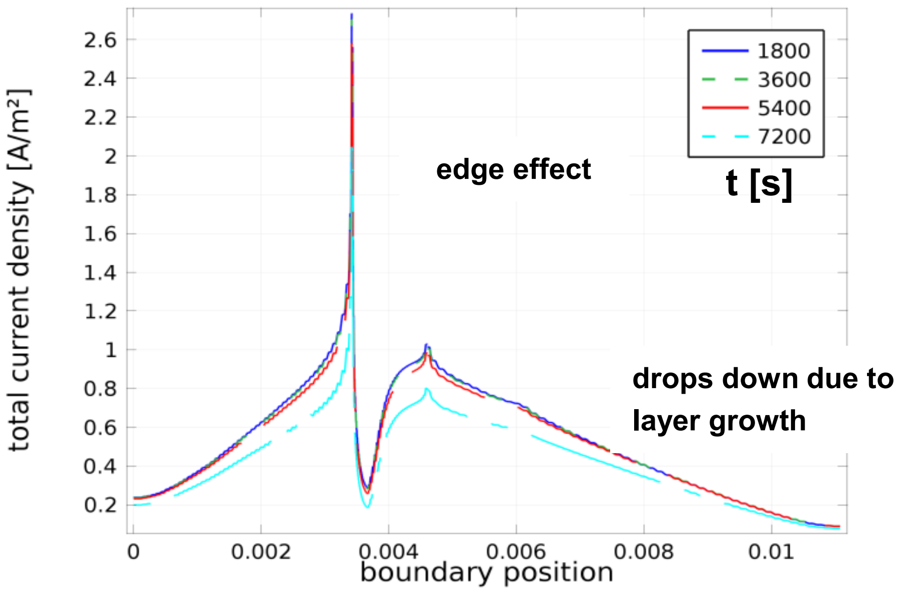
first results without reducing flux:

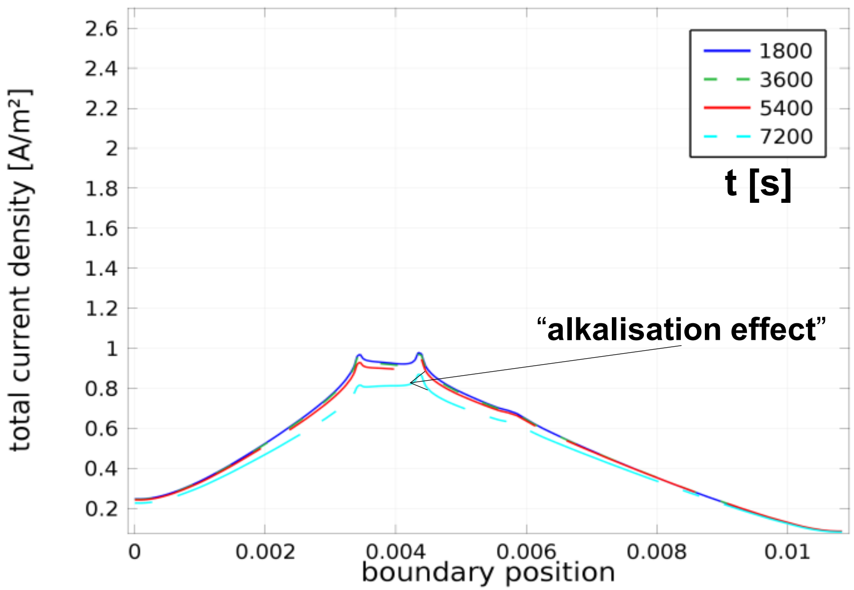
e.g. different head shape:





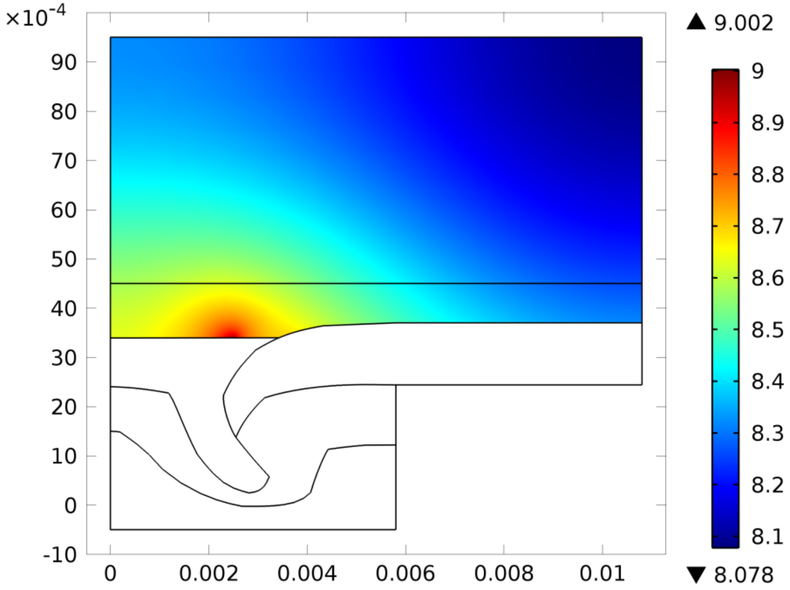
minimizing the corrosion current density:





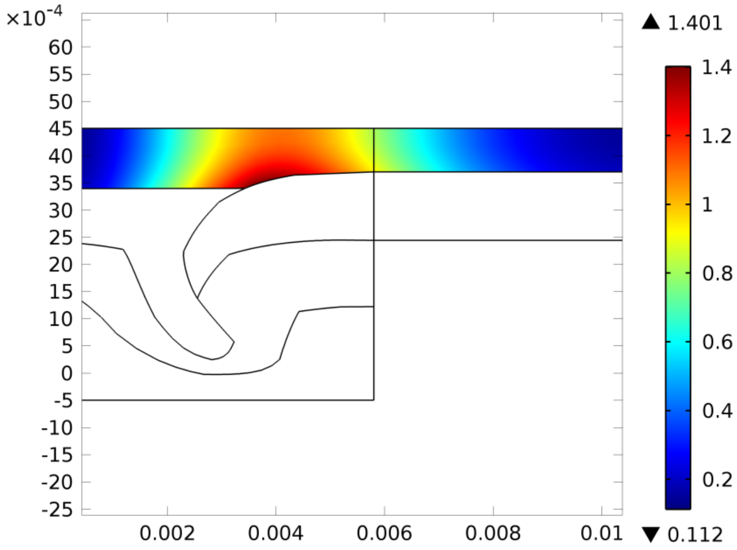
Results – Possible studies

pH - development



accelerating pre-developments and designing the layout

ion concentrations (c_Mg^{2+} [mol/m³])



Alloys…

- Aspects of galvanic corrosion can be predicted
- Environmental exposure modelling still needs to be setup
- Surface treatments and coatings have to be tackled separately

Need of further extensions

- addition of further chemical specimens
- improved layer model including the MgO aspects
- predicting localised corrosion issues
- correlation to functionality (e.g. strength, stiffness)
- Al activity has to be taken into account especially at high pH values (>12 hydroxide species)
- …..

Results and issues of the model study

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beside the previous explained aspects by Song et.al:

- sharp edges and gradients should be avoided due to local “critical” increases in the current density arising in discontinues anodic “dissolution” currents
- the relative position of the cathode should be “below” the anode to force precipitation of chemical products → decrease in the cathodic current
- θ=1 for a non-porous structure would stop corrosion → **the engineer should try to find an alloy system achieving (1- θ + θε) → 0**

Modelling issues:

- physical and chemical correct time depended boundary conditions
- capacitive double layer, layer growth is still to strong, convective effects
- pH and conductivity variations / migration
- re - dissolution effects

Summary

- Simulations can **assist** the design regarding corrosion protection
- Chose of the model depends on requirements (careful)
- Simplified parameter studies are possible and can save experimental effort
- Many process parameters still have to be implemented
- The whole simulation based design approach requires interdisciplinary working and should be tackled in modules

⇨ **there is still much to do**

Thank you