Multi-physics Galvanic Corrosion Analysis for Carbon-Aluminium Structures under Saltwater Film

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The multi-material design of vehicles is recently in progress in order to reduce the weight.

Especially, carbon fiber reinforced plastics (CFRP) and aluminium alloys (Al) are coming into use.

As a result, galvanic corrosion occurs around the joint parts of different materials under saltwater film (e.g., seawater, solution of snow melting agents, etc.).

Fig. multi-material designed vehicle
BMW Japan Corp.
http://www.bmw.co.jp/jp/ja/insights/corporation/bmwi/concept.html
General Mechanism of Galvanic Corrosion

1. When multiple conductive materials with different ionization tendencies (or natural potentials) contact in electrolyte solution, an electric cell is formed.

2. The material with lower natural potential dissolves to the solution.

3. In addition, if the dissolved ions hydrolyze, pH of the solution becomes lower (acid).

4. Lower pH leads to further accelerated corrosion.

Evaluation of the corrosion rate in a variety of environments is important for safety engineering.
Issues in Corrosion Rate Evaluation

Issues in traditional Experimental Evaluation:

- A large number of tests are required.
- It costs high in terms of time and money.

Issues in recent Numerical Evaluation:

- A complicated multi-physics formulation is required. (i.e., electrostatics, mass transport, and chemical reactions.)
- A few constraints are difficult to be satisfied. (i.e., mass conservation and electroneutrality)
- Explicit time integration is easy to implement but slow due to the Courant (CFL) condition. (i.e., Speed of H⁺ ion is fast ⇒ Δt should be small.)
## Conventional Corrosion Simulations

<table>
<thead>
<tr>
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<tbody>
<tr>
<td>Multi-physics</td>
<td>✓</td>
<td>✗</td>
<td>✓</td>
</tr>
<tr>
<td>Mass conservation</td>
<td>✗</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>Electroneutrality</td>
<td>✓</td>
<td>✗</td>
<td>✓</td>
</tr>
<tr>
<td>Implicit integration</td>
<td>✗</td>
<td>✗</td>
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</table>

No standard method that satisfies all of the above has been established yet…

Objective

Developing a *fast* and *accurate* numerical *multi-physics* simulator for *localized galvanic corrosion* especially for CFRP/Al composite under a seawater film

**Table of Body Contents**

- Mechanism of galvanic corrosion on CFRP/Al composite under a seawater film
- Our method to solve the corrosion problem
- Validation of our method
- Summary
Mechanism of Galvanic Corrosion on CFRP/Al Composite under a Seawater Film
In seawater, sodium ions $\text{Na}^+$ and chloride ions $\text{Cl}^-$ are dominated.

There are sufficient oxygen molecules ($\text{O}_2$) in the seawater film because the interface between air and the seawater film is relatively large.
As Al has lower natural potential than CFRP, Al is dissolved by the cell reaction.

Electric current flows from CFRP to Al in the solid part.

Chemical Reactions:

on Al: \( \text{Al} \rightarrow \text{Al}^{3+} + 3e^- \) (anodic reaction)

on CFRP: \( \text{O}_2 + 2\text{H}_2\text{O} + 4e^- \rightarrow 4\text{OH}^- \) (cathodic reaction)
Mechanism of Galvanic Corrosion in Issue

- The generated ions (hydroxide ions OH⁻ and aluminium ions Al³⁺) are electrically neutralized by the electrolyte ions, Na⁺ and Cl⁻.
- Generation of OH⁻ makes the solution on the CFRP alkaline.
Mechanism of Galvanic Corrosion in Issue

- Hydrolysis of $\text{Al}^{3+}$ makes the solution on the Al acid.

**Chemical Reactions:**

$$\text{Al}^{3+} + \text{H}_2\text{O} \rightleftharpoons \text{AlOH}^2+ + \text{H}^+, \quad \text{Al}^{3+} + 2\text{H}_2\text{O} \rightleftharpoons \text{Al(OH)}_2^+ + 2\text{H}^+,$$

$$\text{Al}^{3+} + 3\text{H}_2\text{O} \rightleftharpoons \text{Al(OH)}_3↓ + 3\text{H}^+, \quad \text{Al}^{3+} + 4\text{H}_2\text{O} \rightleftharpoons \text{Al(OH)}_4^- + 4\text{H}^+.$$

- Aluminium hydroxide $\text{Al(OH)}_3$ precipitates(↓) on the Al surface as white sludge.

**Diagram:**

- Seawater Film
- Air
- Na$^+$
- Na$^+$
- Na$^+$
- OH$^-$
- OH$^-$
- OH$^-$
- H$^+$
- Cl$^-$
- Al$^{3+}$
- OH$^-$
- OH$^-$
- OH$^-$
- OH$^-$
- OH$^-$
- OH$^-$
- OH$^-$
- H$^+$
- Cl$^-$
- Al$^{3+}$

**Flow of Current:**

- CFRP
- Higher Potential
- Al
- Lower Potential
Our Method to Solve the Corrosion Problem
Governing Equations

1) Laplace equation in the electrostatic field

$$\kappa \nabla^2 \phi = \nabla J = 0$$

2) Mass transport equation

$$\frac{\partial C_i}{\partial t} = -\nabla \cdot (-z_i u_i C_i F \nabla \phi - D_i \nabla C_i) + E_i(C_i)$$

Electrophoresis  Mass diffusion  Chemical reaction

We solve these 2 eqs. of the multi-physics problem with a weak-coupling method.
Our method adopts the voxel-based finite volume method (Voxel FVM).

Corrosion rates are calculated with considering the multi-physics problem.

Metal shape and surface area are updated.
**Point 1: Mass Conservation**

- Voxels are used as the control volumes of FVM.
- Due to the adoption of FVM, mass conservation is perfectly satisfied.

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<table>
<thead>
<tr>
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<tbody>
<tr>
<td>$\mathbf{J}$</td>
<td>Normal molar flux density of ion $i$ (mol m$^{-2}$ s$^{-1}$)</td>
</tr>
<tr>
<td>$\mathbf{N}$</td>
<td>Normal molar flux density of ion $i$ (mol m$^{-2}$ s$^{-1}$)</td>
</tr>
<tr>
<td>$\phi$</td>
<td>Electrostatic potential (V)</td>
</tr>
<tr>
<td>$C_i$</td>
<td>Molar concentration of ion $i$ (mol m$^{-3}$)</td>
</tr>
</tbody>
</table>

[Note] We currently focus on 2D problems, this cell is not a voxel but a pixel in this study.
Point 2: Electroneutrality

The following equation should be considered as an additional constraint of the mass transport analysis.

\[ \hat{J} = F \sum_{i \in \Pi} z_i \hat{N}_i. \]

- \( \hat{J} \): Normal current density (A m\(^{-2}\))
- \( F \): Faraday’s constant (C mol\(^{-1}\))
- \( z_i \): Charge number of ion \( i \)
- \( \hat{N}_i \): Normal molar flux density of ion \( i \) (mol m\(^{-2}\) s\(^{-1}\))

In mass transport analysis, \( \hat{N}_i \)'s are treated as unknowns and the solution is corrected with a projection method (similar to MAC method in CFD).

Due to this treatment, electroneutrality is perfectly satisfied.
Point 3: Implicit Time Integration

In mass transport analysis with implicit scheme, $\tilde{N}_i$'s are treated as unknowns and the solution is given by solving a matrix equation for each time step.

- The formulation becomes complicated,
- The analysis requires a matrix solver. BUT,
- CFL condition needs not to be satisfied and thus large $\Delta t$ is acceptable.

**In total, implicit scheme is faster than explicit scheme.**
**Boundary Conditions**

**Electrostatic analysis**

On CFRP: \( \dot{J} = P_{\text{cathode}}(\phi, \text{pH}), \)

On Al: \( \dot{J} = P_{\text{anode}}(\phi, \text{pH}), \)

On Air: \( \dot{J} = 0. \)

Polarization curve represents relationship between \((\phi, \text{pH})\) and \(\dot{J}\).

**Mass transport analysis**

On CFRP: \( \dot{N}_i = \frac{\lambda_i^{\text{CFRP}}}{F \sum_{k\in I} \lambda_k^{\text{CFRP}} z_k} \dot{J}, \)

On Al: \( \dot{N}_i = \frac{\lambda_i^{\text{Al}}}{F \sum_{k\in I} \lambda_k^{\text{Al}} z_k} \dot{J}, \)

On Air: \( \dot{N}_i = 0 \) (except \(O_2\)), \(C_{O_2} = \text{const.}\)

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \dot{J} )</td>
<td>Normal current density ((\text{A m}^{-2}))</td>
</tr>
<tr>
<td>( \phi )</td>
<td>Electrostatic potential ((\text{V}))</td>
</tr>
<tr>
<td>( \dot{N}_i )</td>
<td>Normal molar flux density of ion (i) ((\text{mol m}^{-2}))</td>
</tr>
<tr>
<td>( \lambda_i^{\text{CFRP}} )</td>
<td>Reaction ratio on CFRP of ion (i)</td>
</tr>
<tr>
<td>( \lambda_i^{\text{Al}} )</td>
<td>Composition ratio of Al of ion (i)</td>
</tr>
<tr>
<td>( z_i )</td>
<td>Charge number of ion (i)</td>
</tr>
<tr>
<td>( F )</td>
<td>Faraday’s constant ((\text{C mol}^{-1}))</td>
</tr>
</tbody>
</table>
Validation of Our Method
- Glassy carbon (GC) is used instead of CFRP for simplicity.
- Plastic plate is inserted between GC and Al plates.
- NaOH solution is put in an acrylic case with the test piece for CO₂ removal and humidification.
- pH meters are set in the middle of each plate.
Size of each electrode is 40 mm × 10 mm.
- Thickness of the NaCl solution film is 2 mm.
- Strength of NaCl solution is 0.5 wt%.
- Corrosion current is measured by ammeter.
- The test time is 72 hours.
- Two tests are conducted.
**Analysis domain**

- **Cell size:** 1mm × 1 mm.
- **Chemical species:**
  \[ \text{H}^+, \text{OH}^-, \text{Na}^+, \text{Cl}^-, \text{O}_2, \]
  \[ \text{Al}^{3+}, \text{AlOH}^2+, \text{Al(OH)}_2^+, \text{Al(OH)}_3, \text{Al(OH)}_4^- \].
- **Initial conditions:** concentrations of each ion.
- **Electro conductivity:** constant \( \kappa \) of 1.0 wt% NaCl solution (\( \neq 0.5 \) wt%).
**Conditions of Numerical Analysis**

**Analysis domain**

- **Chemical Reactions:**
  1. \( \text{Al}^{3+} + \text{H}_2\text{O} \rightleftharpoons \text{AlOH}^{2+} + \text{H}^+ \)
  2. \( \text{Al}^{3+} + 2\text{H}_2\text{O} \rightleftharpoons \text{Al(OH)}_2^{+} + 2\text{H}^+ \)
  3. \( \text{Al}^{3+} + 3\text{H}_2\text{O} \rightleftharpoons \text{Al(OH)}_3^{-} + 3\text{H}^+ \)
  4. \( \text{Al}^{3+} + 4\text{H}_2\text{O} \rightleftharpoons \text{Al(OH)}_4^{-} + 4\text{H}^+ \)
  5. \( \text{H}^+ + \text{OH}^{-} \rightleftharpoons \text{H}_2\text{O} \)

Simultaneous solutions are given by the bisection method.

Hydrolyses of Al ions

Ionization of \( \text{H}_2\text{O} \)
Interval Photo Movie of Experiment
Results \((\text{Al(OH)}_3\) at finish time\)

**Experiment**

- White sludge

**Numerical simulation**

- \(\text{Al(OH)}_3\)

The position of \(\text{Al(OH)}_3\) white sludge is well agreed.
Results (pH at finish time)

Experiment

The simulated pH on GC is a little high in comparison to the experimental result. Probably due to unremoved CO₂.
• The tendencies of pH change are successfully simulated.
• The quantitative agreement on GC is our future issue.
The magnitude of simulated current is approximately agreed with the average of the experimental results.

Yet, the increasing tendency of current could not be reproduced by our present model.

The increase in current is probably due to the increase of electro conductivity.
## CPU Time

### CPU Time for the 72 h corrosion analysis

<table>
<thead>
<tr>
<th>Scheme</th>
<th>CPU Time</th>
<th>Speed (vs. Exp.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Explicit time integration (our previous)</td>
<td>3 h 48 m 50 s</td>
<td>x 24</td>
</tr>
<tr>
<td>Implicit time integration (our new)</td>
<td>0 h 09 m 08 s</td>
<td>x 470</td>
</tr>
</tbody>
</table>

Our implicit scheme for mass transport analysis enables large $\Delta t$ and thus is much faster than the conventional explicit scheme.
Summary
A multi-physics simulator for localized galvanic corrosion was developed.

It takes the followings into account.

- electrophoresis
- chemical reactions
- mass conservation
- implicit time integration
- mass diffusion
- moving boundaries
- electroneutrality

A validation test with GC/Al composite revealed that our method was able to reproduce the distributions of pH and white sludge, and corrosion current approximately.

A practical method for localized galvanic corrosion analysis is almost established.

Thank you for your kind attention.