

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

Yuki ONISHI, Koichi MASUYA, Kenji AMAYA  
Tokyo Institute of Technology, Japan

# Background

- 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.).

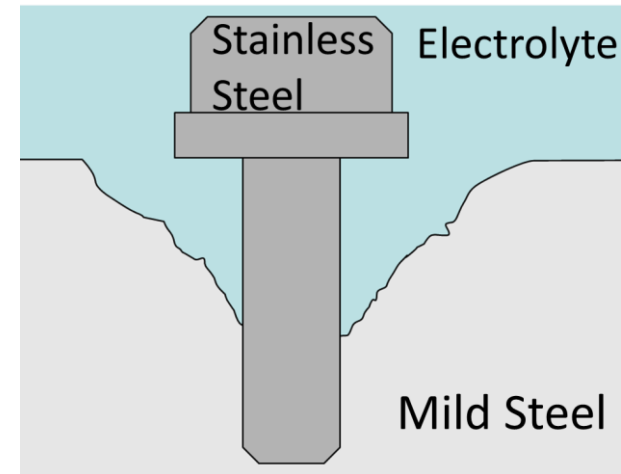


Fig. multi-material designed vehicle  
BMW Japan Corp.  
<http://www.bmw.co.jp/jp/ja/insights/corporation/bmwi/concept.html>

# 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**.

Fig. Galvanic corrosion  
TRANECT LTD  
[http://www.stainlesssteelbraid.co.uk/galvanic\\_corrosion.php](http://www.stainlesssteelbraid.co.uk/galvanic_corrosion.php)



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<sup>+</sup> ion is fast  $\Rightarrow \Delta t$  should be small.)

# Conventional Corrosion Simulations

	K. L. Heppner et al. <sup>[1]</sup>	S. Scheiner et al. <sup>[2]</sup>	Y. Onishi et al. <sup>[3]</sup>
Multi-physics	✓	✗	✓
Mass conservation	✗	✓	✓
Electroneutrarity	✓	✗	✓
Implicit integration	✗	✗	✗

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

[1] K. L. Heppner *et al.*, Corrosion Eng Sci Tec, Vol. 41, No. 2, pp. 110--121, 2006.

[2] S. Scheiner *et al.*, CMAME Vol. 198, No. 37-40, pp. 2898--2910, 2009.

[3] Y. Onishi *et al.*, Corrosion Science, Vol. 63, pp. 210--224, 2012.

# Objective

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

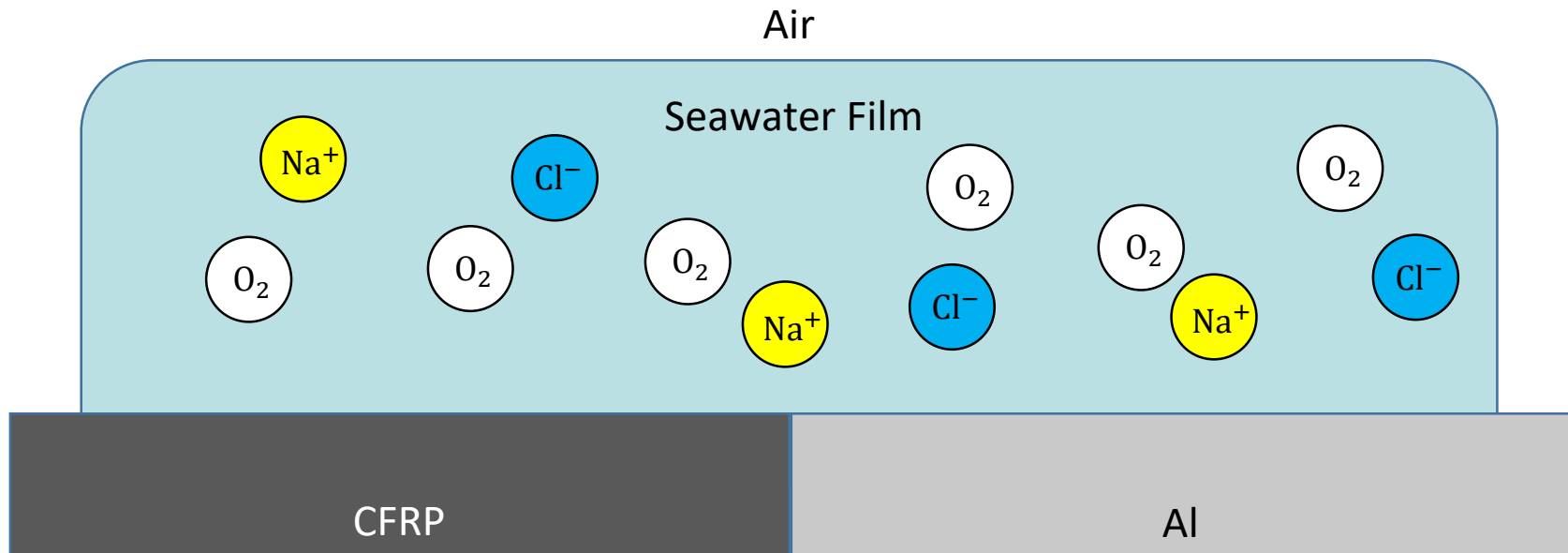
## **Table of Body Contents**

- 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

# Mechanism of Galvanic Corrosion in Issue

- 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.





# Mechanism of Galvanic Corrosion in Issue

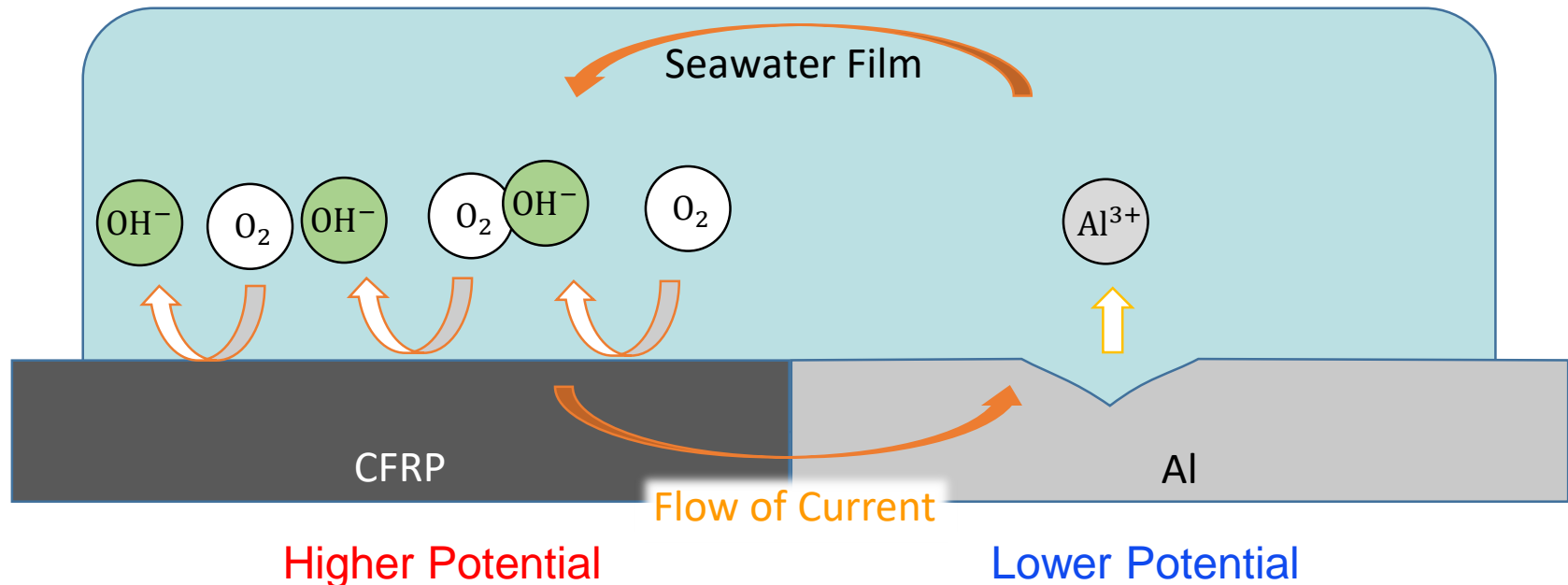
- As Al has lower natural potential than CFRP, Al is dissolved by the cell reaction.
- Electric current flows from CFRP to Al in the solid part.

## Chemical Reactions:

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

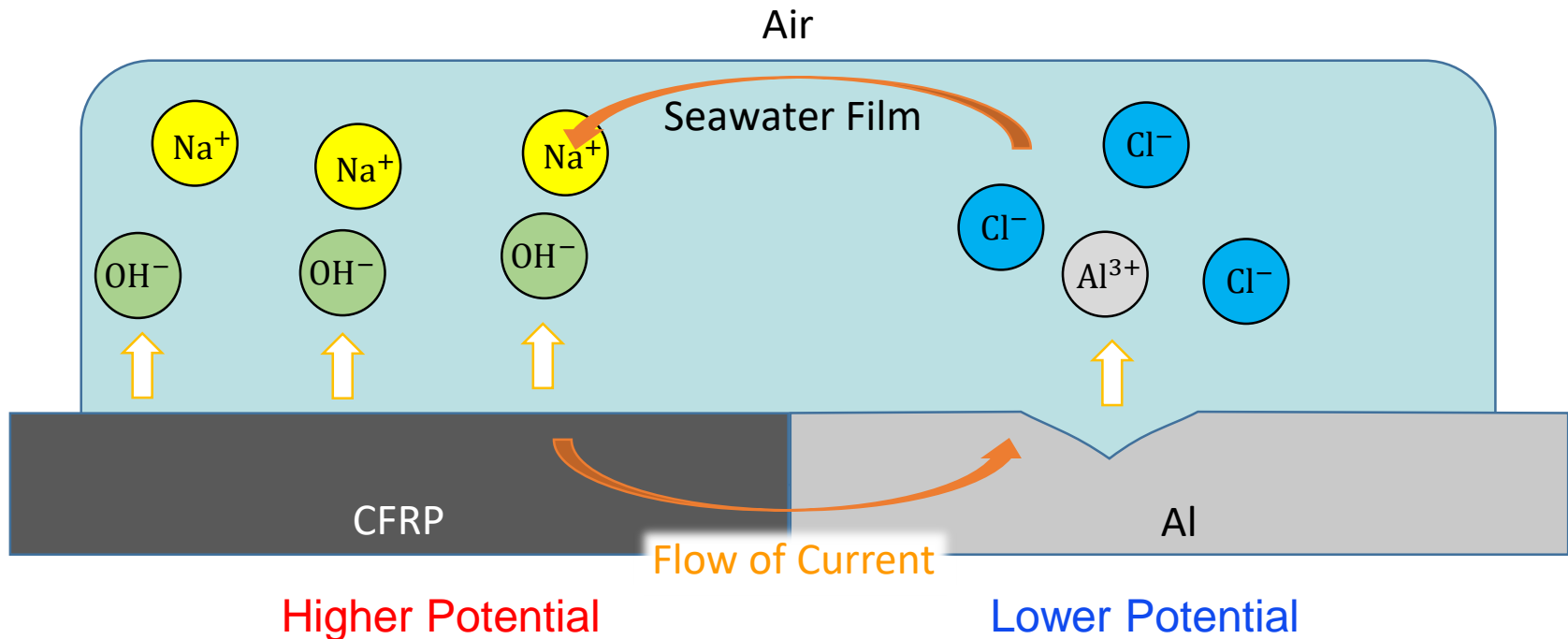
on CFRP:  $\text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^{-} \rightarrow 4\text{OH}^{-}$  (cathodic reaction)

Air



# Mechanism of Galvanic Corrosion in Issue

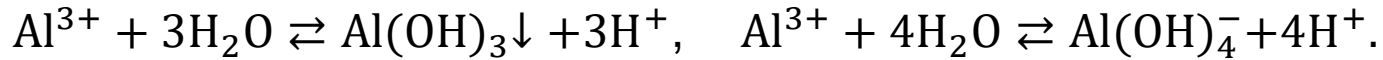
- The generated ions (hydroxide ions  $\text{OH}^-$  and aluminium ions  $\text{Al}^{3+}$ ) are electrically neutralized by the electrolyte ions,  $\text{Na}^+$  and  $\text{Cl}^-$ .
- Generation of  $\text{OH}^-$  makes the solution on the CFRP alkaline.



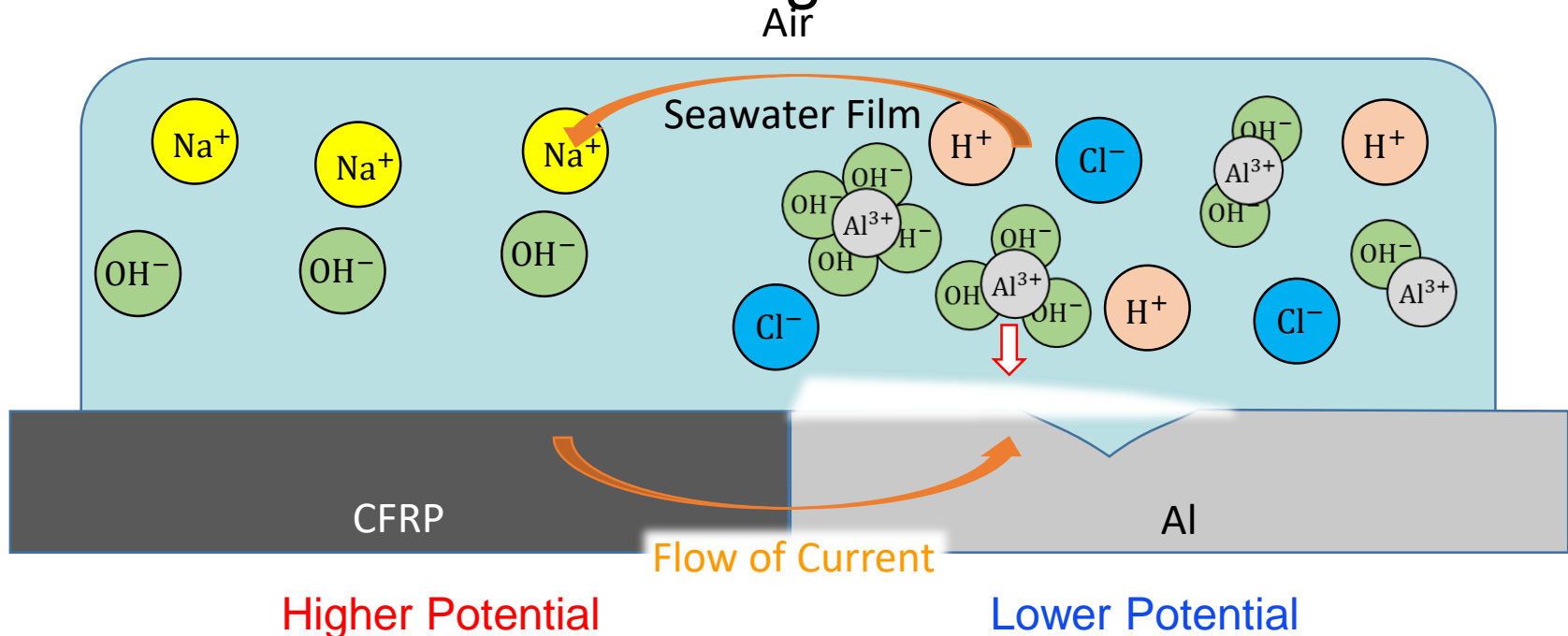
# Mechanism of Galvanic Corrosion in Issue

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

Chemical Reactions:



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



# Our Method to Solve the Corrosion Problem

# Governing Equations

## 1) Laplace equation in the electrostatic field

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

$\kappa$	Electrical conductivity (S m <sup>-1</sup> )
$\phi$	Electrostatic potential (V)
$J$	Current density (A m <sup>-2</sup> )
$C_i$	Molar concentration of ion $i$ (mol m <sup>-3</sup> )
$z_i$	Charge number of ion $i$
$u_i$	Mobility of ion $i$ (m <sup>2</sup> mol J <sup>-1</sup> s <sup>-1</sup> )
$F$	Faraday's constant (F m <sup>-1</sup> )
$D_i$	Diffusion coefficient of ion $i$ (m <sup>2</sup> s <sup>-1</sup> )

## 2) Mass transport equation

$$\frac{\partial C_i}{\partial t} = -\nabla \cdot \left( \underbrace{-z_i u_i C_i F \nabla \phi}_{\text{Electrophoresis}} - \underbrace{D_i \nabla C_i}_{\text{Mass diffusion}} + \underbrace{E_i(C_i)}_{\text{Chemical reaction}} \right)$$

We solve these 2 eqs. of the **multi-physics** problem with a **weak-coupling** method.

# Flowchart

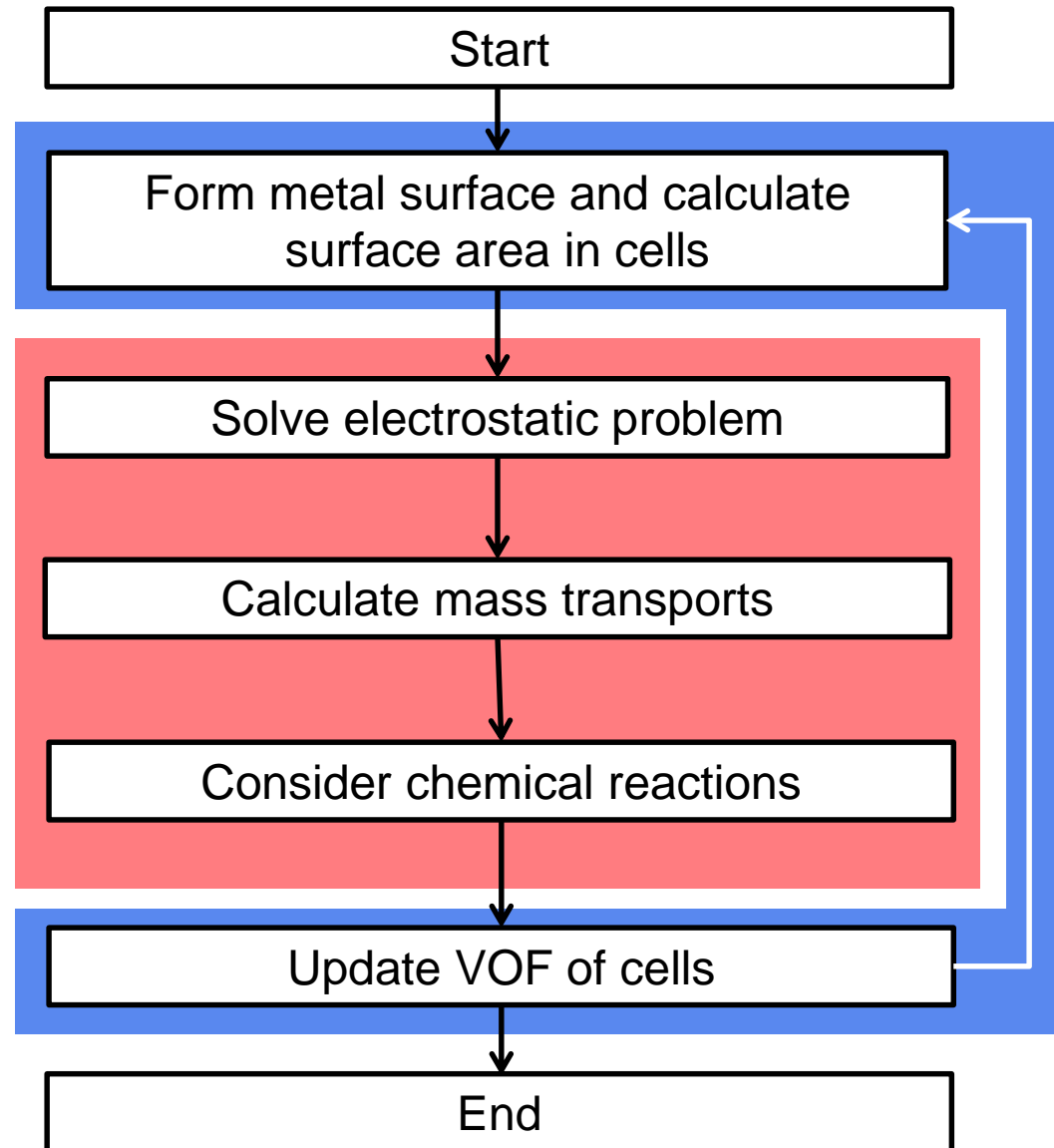
Our method adopts the voxel-based finite volume method (Voxel FVM).

## FVM

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

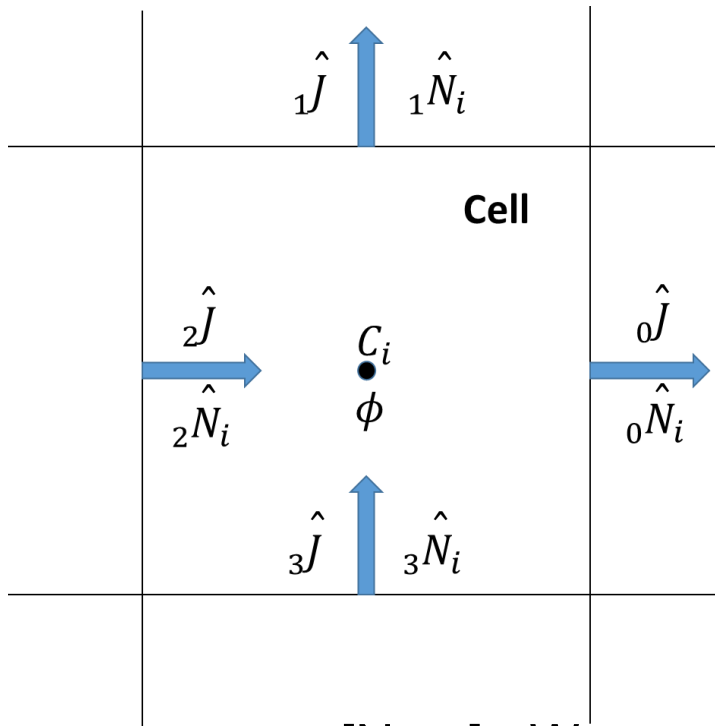
## Voxel method

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.**



$\hat{j}$	Normal current density ( $\text{A m}^{-2}$ )
$\phi$	Electrostatic potential (V)
$\hat{N}_i$	Normal molar flux density of ion $i$ ( $\text{mol m}^{-2} \text{s}^{-1}$ )
$C_i$	Molar concentration of ion $i$ ( $\text{mol m}^{-3}$ )

[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.

$$\hat{J} = F \sum_{i \in \text{II}} z_i \hat{N}_i .$$

$\hat{J}$	Normal current density (A m <sup>-2</sup> )
$F$	Faraday's constant (C mol <sup>-1</sup> )
$z_i$	Charge number of ion $i$
$\hat{N}_i$	Normal molar flux density of ion $i$ (mol m <sup>-2</sup> s <sup>-1</sup> )

- 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,  $\hat{N}_i$ 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

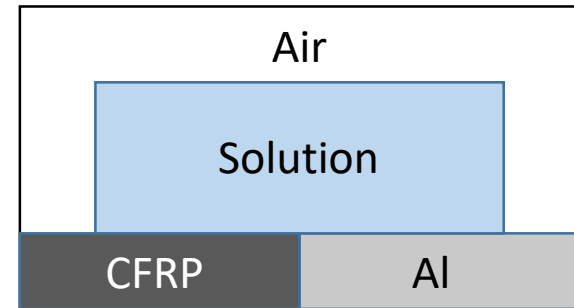
## Electrostatic analysis

On CFRP:  $\hat{j} = P_{\text{cathode}}(\phi, \text{pH}),$

On Al:  $\hat{j} = P_{\text{anode}}(\phi, \text{pH}),$

On Air:  $\hat{j} = 0.$

Polarization  
curve



Polarization curve represents relationship between  $(\phi, \text{pH})$  and  $\hat{j}$ .

## Mass transport analysis

On CFRP:  $\hat{N}_i = \frac{\lambda_i^{\text{CFRP}}}{F \sum_{k \in I} \lambda_k^{\text{CFRP}} z_k} \hat{j},$

On Al:  $\hat{N}_i = \frac{\lambda_i^{\text{Al}}}{F \sum_{k \in I} \lambda_k^{\text{Al}} z_k} \hat{j},$

On Air:  $\hat{N}_i = 0$  (except  $\text{O}_2$ ),

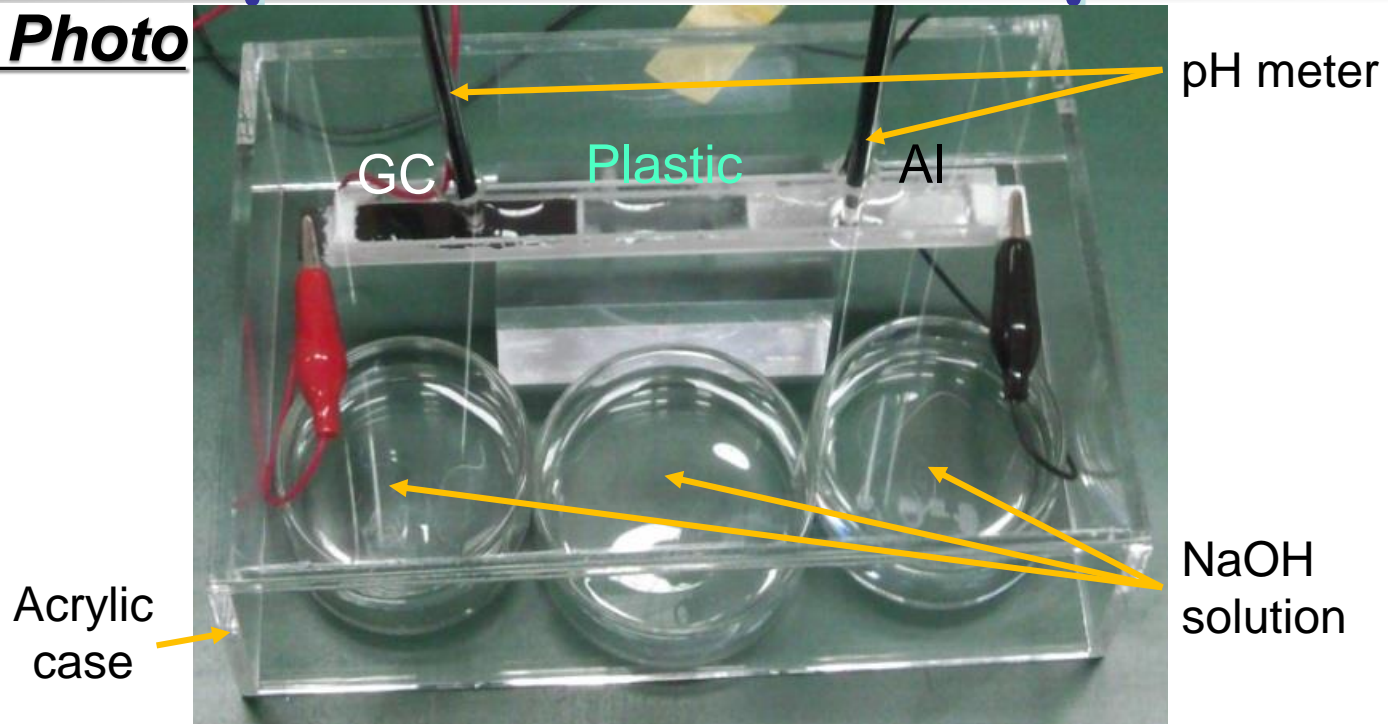
$C_{\text{O}_2} = \text{const.}$

$\hat{j}$	Normal current density ( $\text{A m}^{-2}$ )
$\phi$	Electrostatic potential (V)
$\hat{N}_i$	Normal molar flux density of ion $i$ ( $\text{mol m}^{-2}$ )
$\lambda_i^{\text{CFRP}}$	Reaction ratio on CFRP of ion $i$
$\lambda_i^{\text{Al}}$	Composition ratio of Al of ion $i$
$z_i$	Charge number of ion $i$
$F$	Faraday's constant ( $\text{C mol}^{-1}$ )

# Validation of Our Method

# Experimental Setup

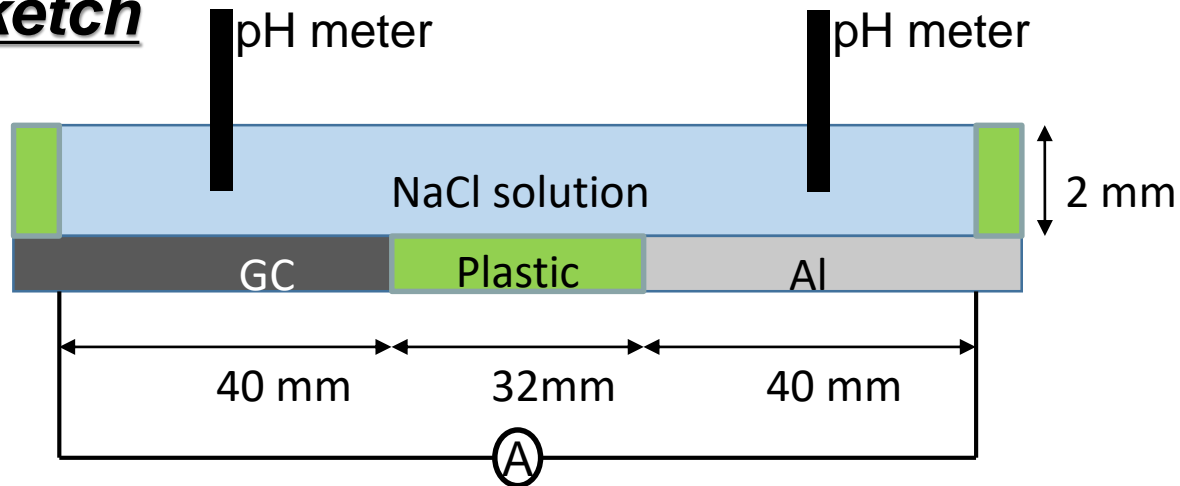
## Top View Photo



- 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 CO<sub>2</sub> removal and humidification.
- pH meters are set in the middle of each plate.

# Experimental Setup

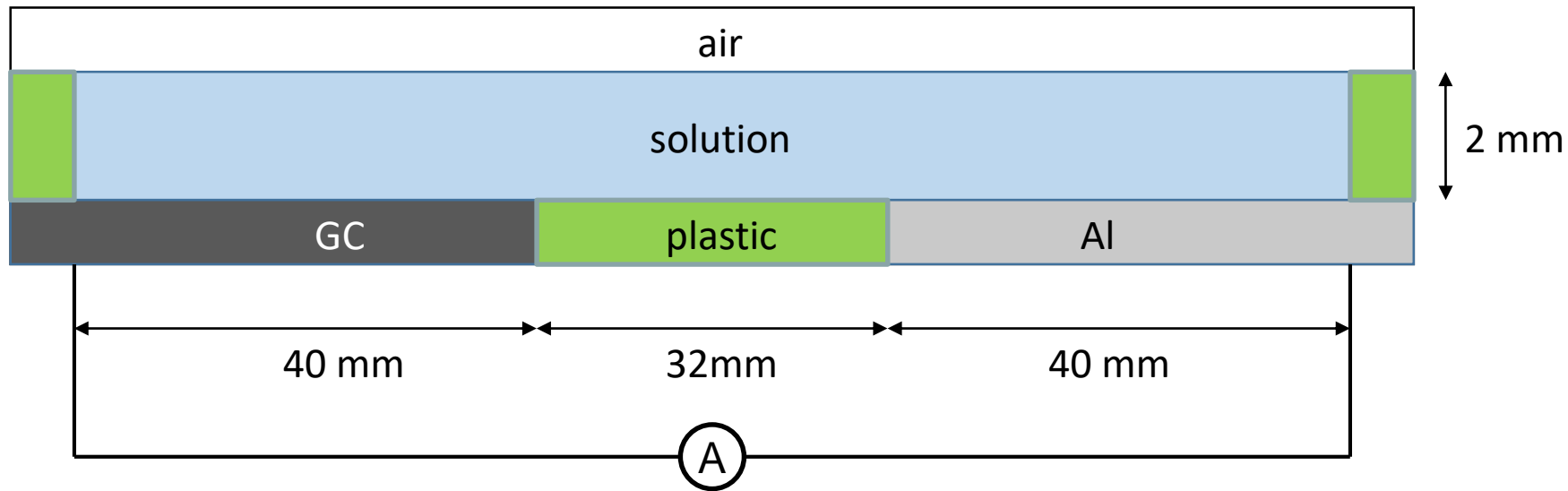
## Side view sketch



- 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.

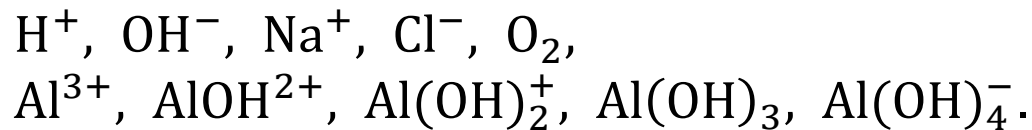
# Conditions of Numerical Analysis

## Analysis domain



■ Cell size: 1 mm × 1 mm.

■ Chemical species:

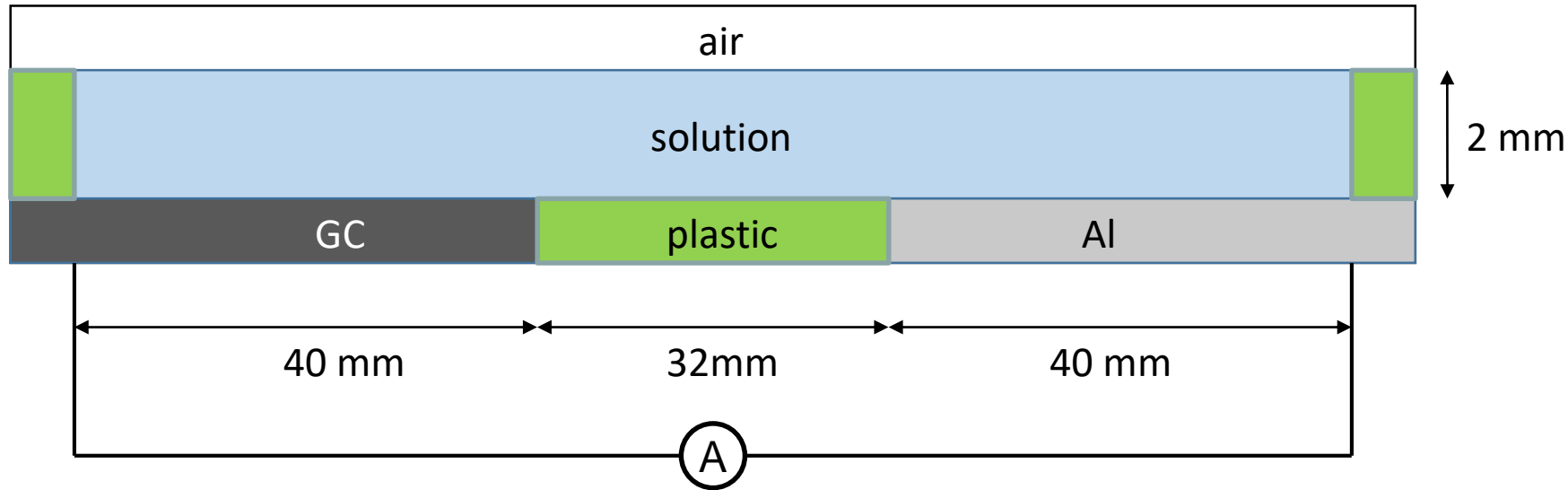


■ Initial conditions: concentrations of each ion.

■ 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.  $\text{Al}^{3+} + 2\text{H}_2\text{O} \rightleftharpoons \text{Al}(\text{OH})_2^+ + 2\text{H}^+$
3.  $\text{Al}^{3+} + 3\text{H}_2\text{O} \rightleftharpoons \text{Al}(\text{OH})_3\downarrow + 3\text{H}^+$
4.  $\text{Al}^{3+} + 4\text{H}_2\text{O} \rightleftharpoons \text{Al}(\text{OH})_4^- + 4\text{H}^+$
5.  $\text{H}^+ + \text{OH}^- \rightleftharpoons \text{H}_2\text{O}$

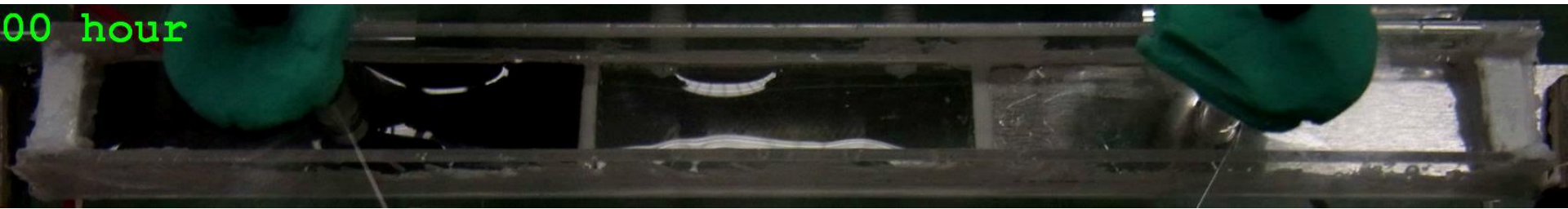
Simultaneous solutions are given by the bisection method.

Hydrolyses of Al ions

Ionization of  $\text{H}_2\text{O}$

# Interval Photo Movie of Experiment

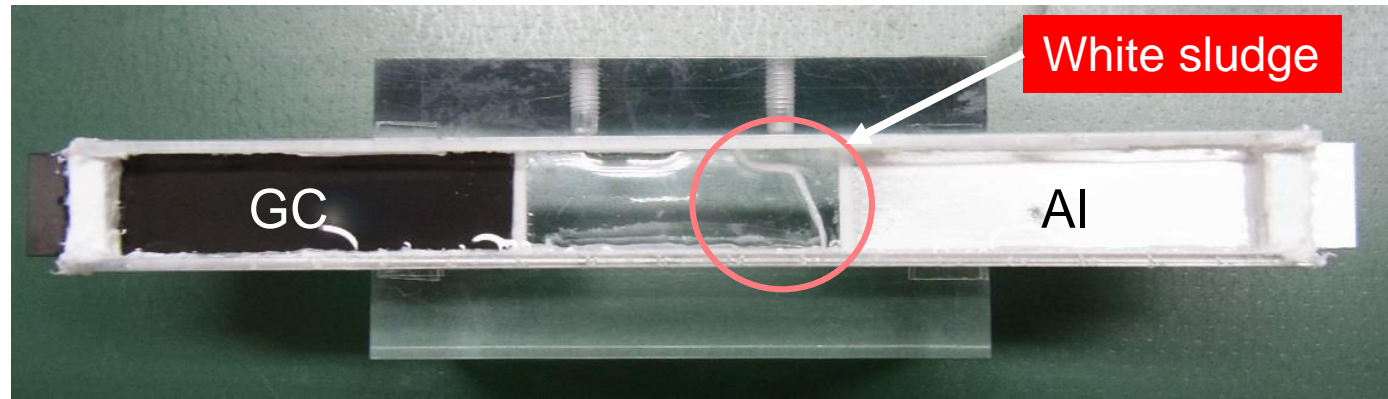
00 hour



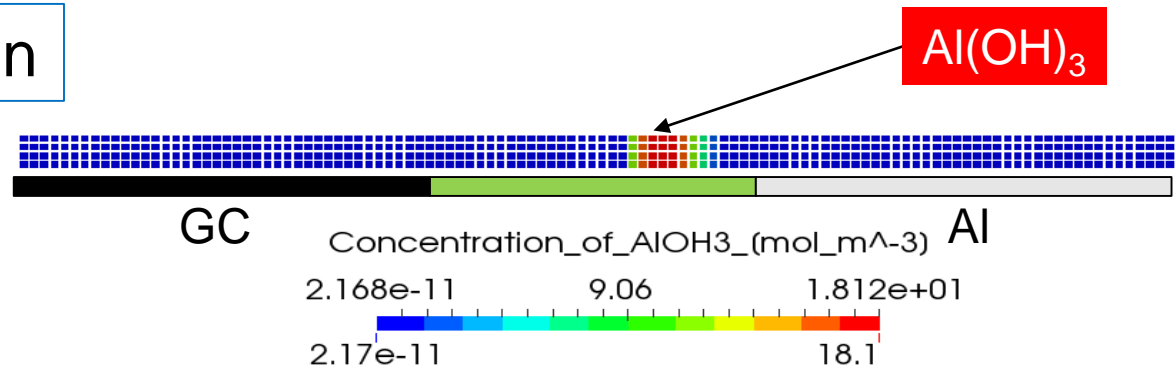


# Results ( $\text{Al}(\text{OH})_3$ at finish time)

Experiment



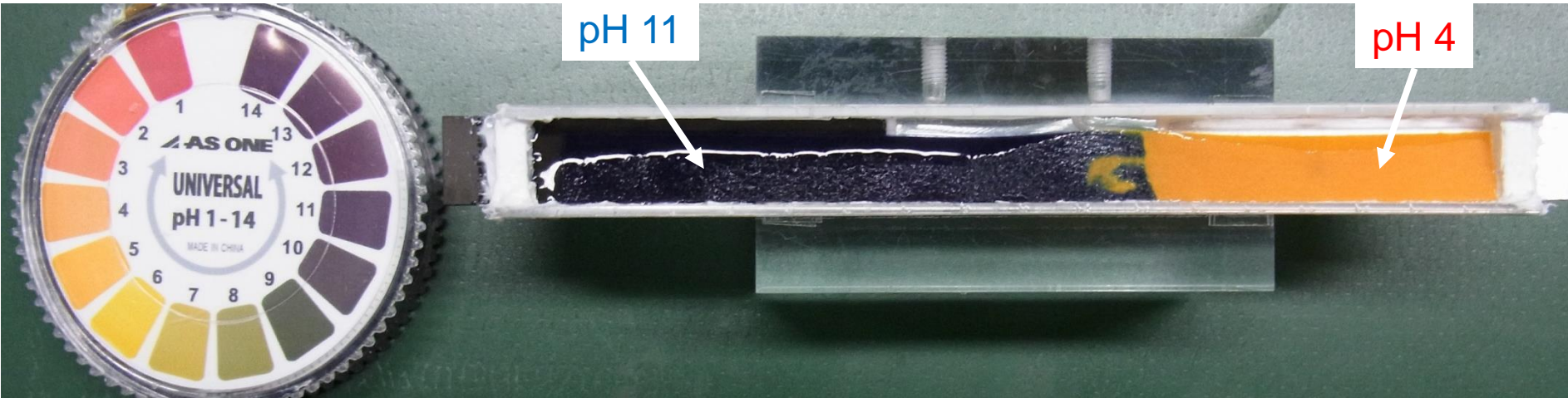
Numerical simulation



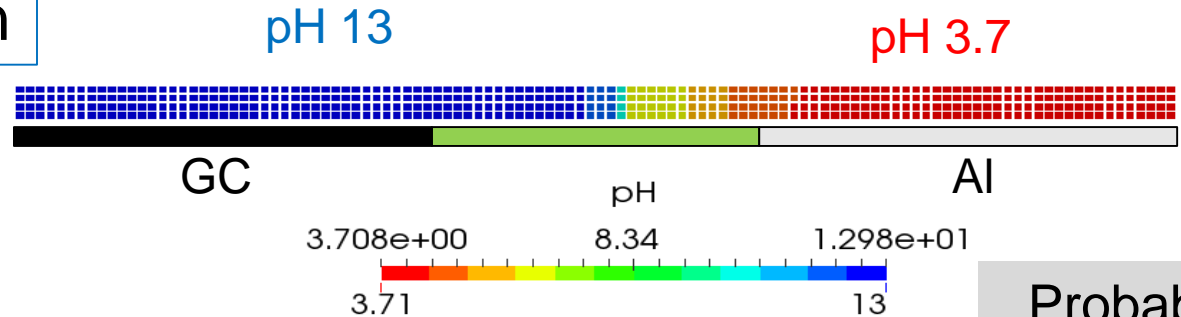
The position of  $\text{Al}(\text{OH})_3$  white sludge is well agreed.

# Results (pH at finish time)

## Experiment



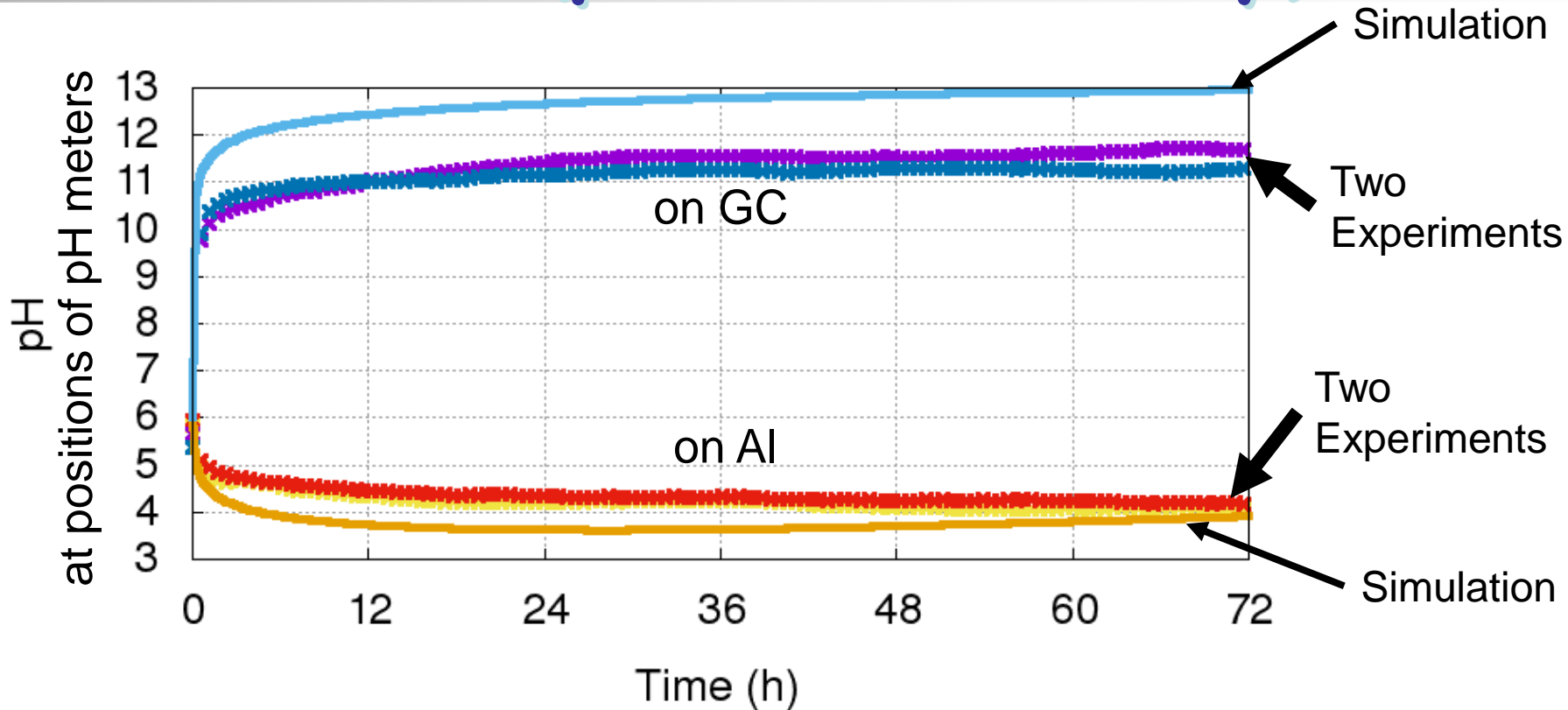
## Numerical simulation



The simulated pH on GC is a little high in comparison to the experimental result.

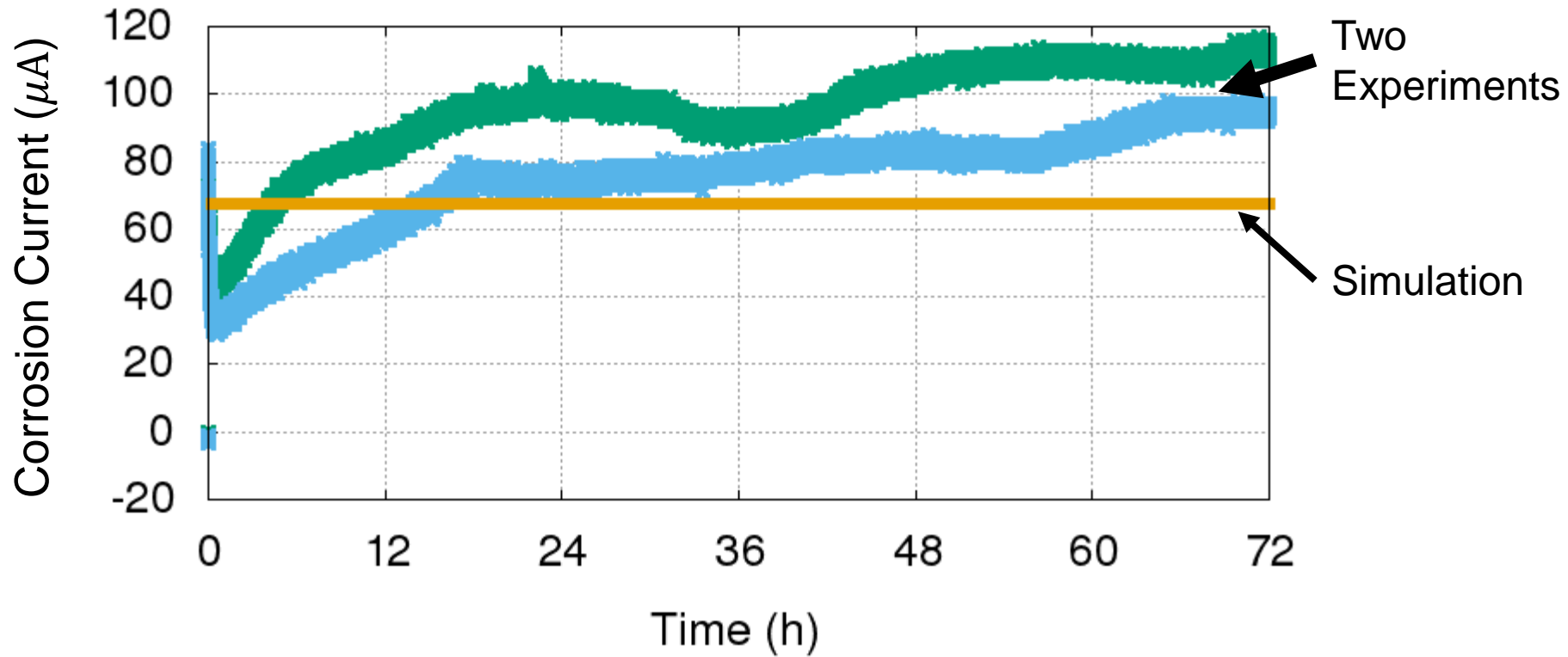
Probably due to unremoved CO<sub>2</sub>.

# Results (pH time history)



- The tendencies of pH change are successfully simulated.
- The quantitative agreement on GC is our future issue.

# Results (corrosion current time history)



- 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

Scheme	CPU Time	Speed (vs. Exp.)
Explicit time integration (our previous)	3 h 48 m 50 s	x 24
Implicit time integration (our new)	0 h 09 m 08 s	x 470

Our implicit scheme for mass transport analysis enables large  $\Delta t$  and thus is much faster than the conventional explicit scheme.

# Summary

# Summary

- A **multi-physics** simulator for **localized galvanic corrosion** was developed.
- It takes the followings into account.
  - > electrophoresis
  - > mass diffusion
  - > chemical reactions
  - > moving boundaries
  - > **mass conservation**
  - > **electroneutrality**
  - > **implicit time integration**
- 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.