ENGINEERING
TEXAS A&M UNIVERSITY

TEXAS A&M ENGINEERING EXPERIMENT STATION

# Marine corrosion and extreme environment capabilities for basic and applied research for NACE consortia

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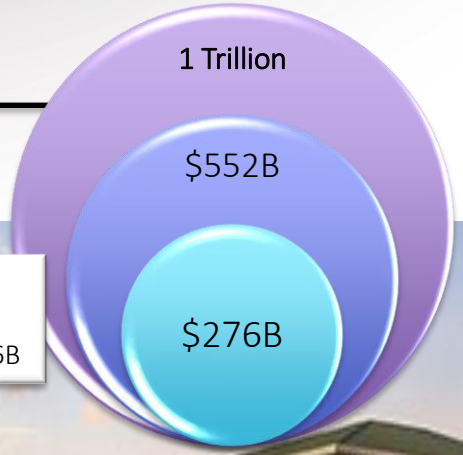
Texas A&M University

# National Corrosion and Materials Reliability Laboratory

TEXAS A&M ENGINEERING EXPERIMENT STATION

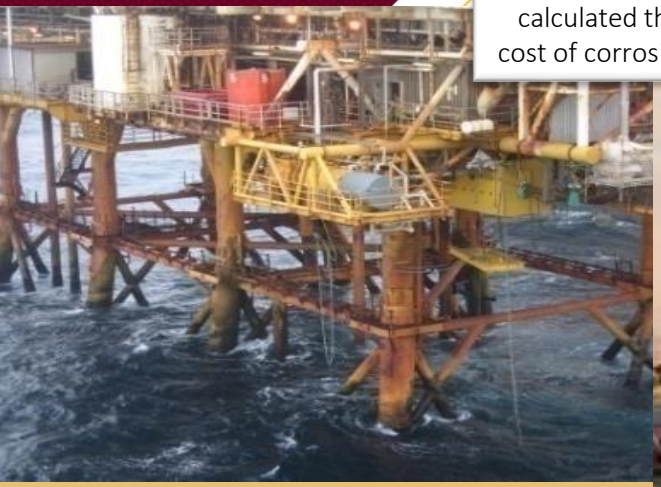
## Cost of corrosion




Fast forward to 2013, with inflation the direct cost is now over $1 Trillion annually in U.S.

In 1998 a NACE study calculated the directed cost of corrosion at $276B

"NCMRC includes state of the art facilitates to host leaders in corrosion and materials through mentoring and research that solves tomorrow's industrial challenges"



## National Corrosion and Materials Reliability Laboratory (NCMRL)

## How can we help industry?

- Being a World Class Corrosion Education and Research Center
- Bridging the gap between fundamental research (science) and technology (engineering)
- Corrosion Minor and certificate

# NCMRL-Main Laboratory

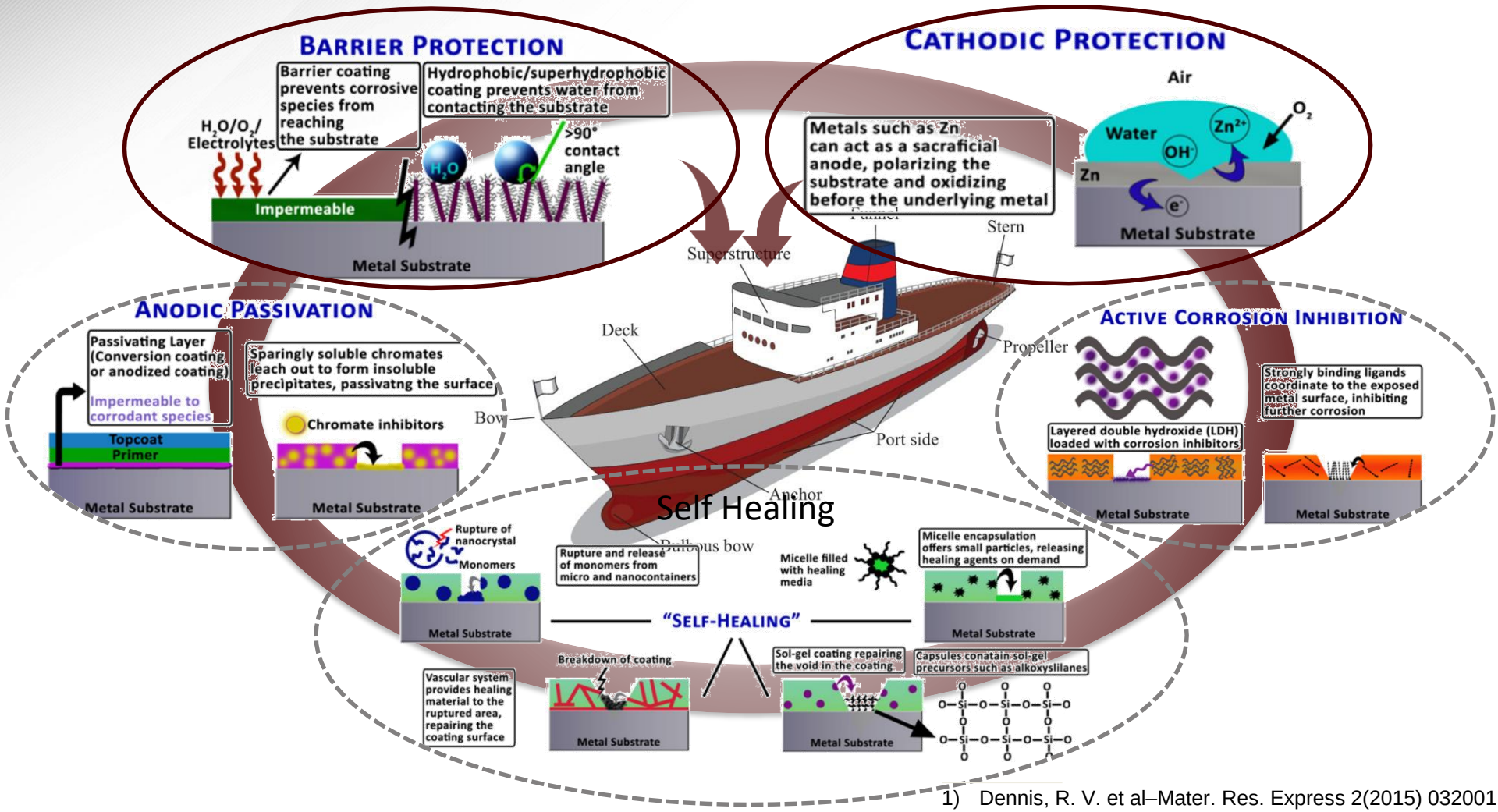

# Marine/Maritime corrosion

**Basic and Applied Research Capabilities for the following topics:**

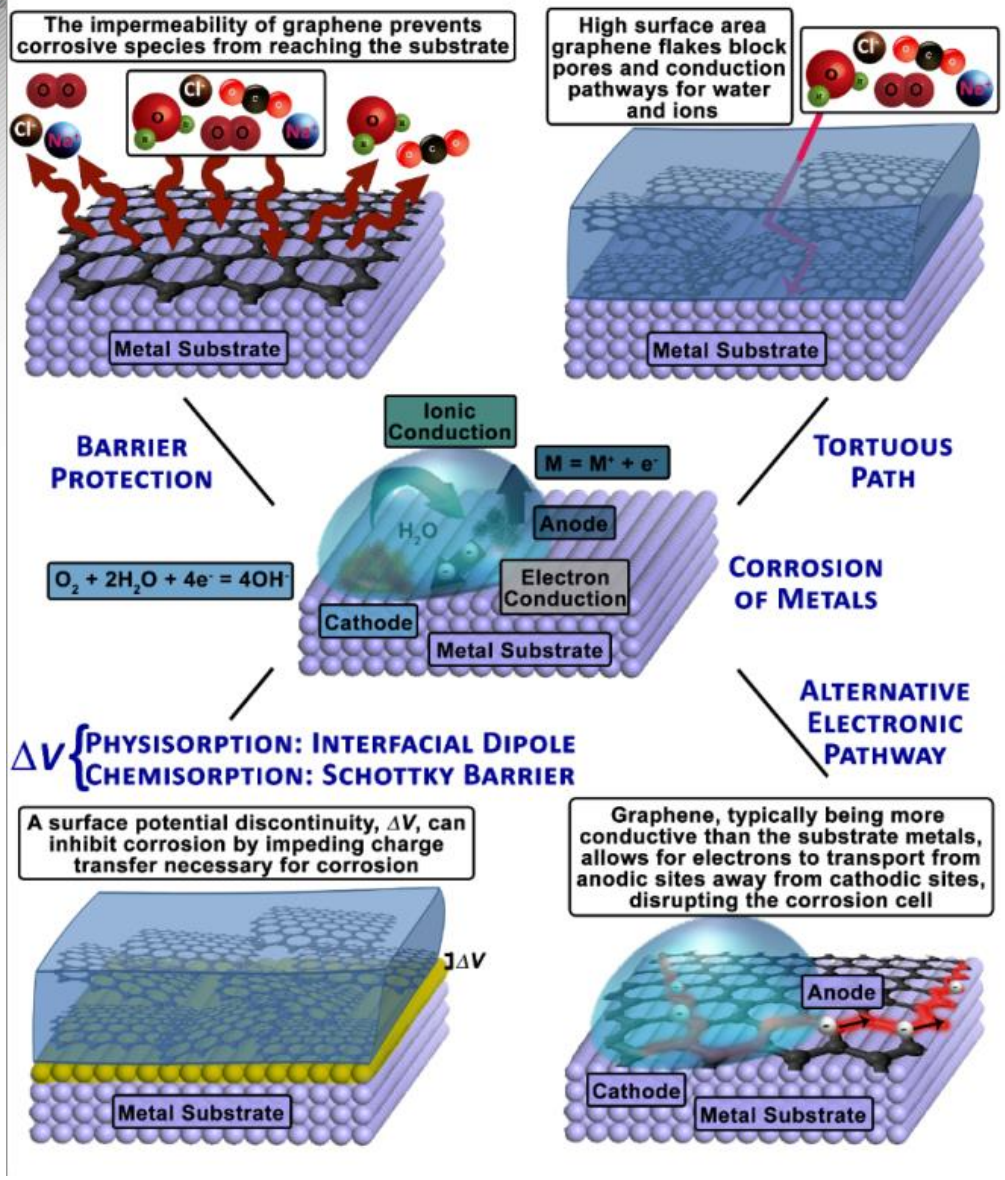
- VOC Reduction for Maritime Coatings (Design of coatings)
- Biofouling Technology in the Marine Industry
- Effect of Ballast Water Treatment on PSPC-compliant Coating in Ballast Water Tanks
- Characterization and quantification in harsh environments
- Reliability, Life time prediction Models based on deterministic-probabilistic approach (Artificial intelligence)- corrosion management
- Sensors use and development for marine applications

# Corrosion control and protection for Maritime coatings

## Design and trends for anti-corrosion-performance of substrates/coatings




1) Dennis, R. V. et al–Mater. Res. Express 2(2015) 032001



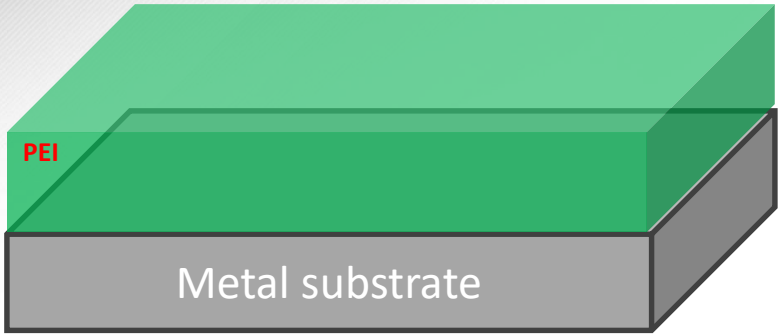

# Graphene at Work Preventing Corrosion

- The four main modes of corrosion inhibition by graphene include:
  - Barrier protection
  - Tortuous path
  - Establishment of a Schottky barrier
  - Providing an alternative electronic pathway
- These modes help to impede or cut-off the electrochemical processes required for corrosion to occur

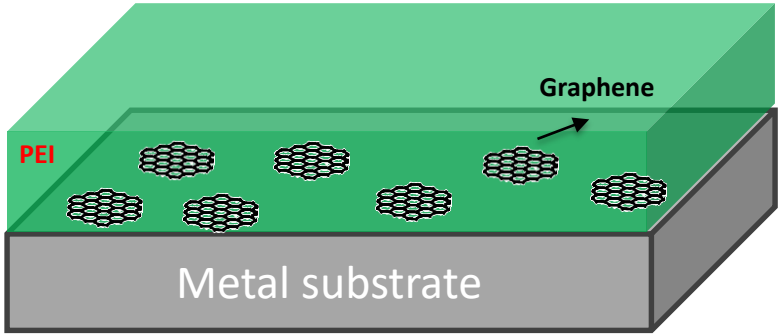
-Dennis, R. V.; *et al.* Graphene Coatings for the Corrosion Protection of Base Metals In *Graphene Technology*. Wiley-VCH, Weinheim, Germany. **2016** (in press).
-Dennis, R. V.; Patil, V.; Andrews, J. L.; Aldinger, J. P.; Yadav, G. D.; Banerjee, S. *Mater. Res. Express* **2015**, 2, 032001.

# Poly(ether imide) (PEI) systems containing nanostructured magnesium and graphene*

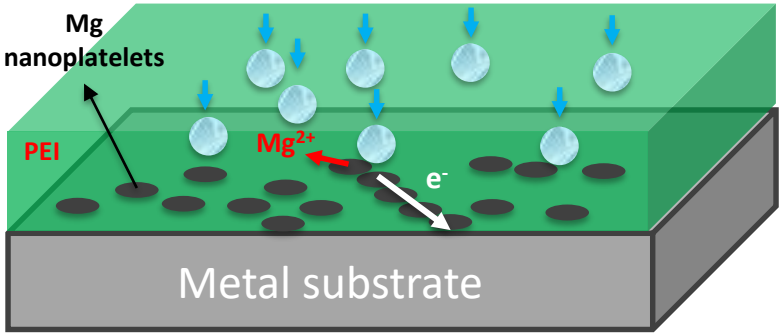
## Barrier Protection



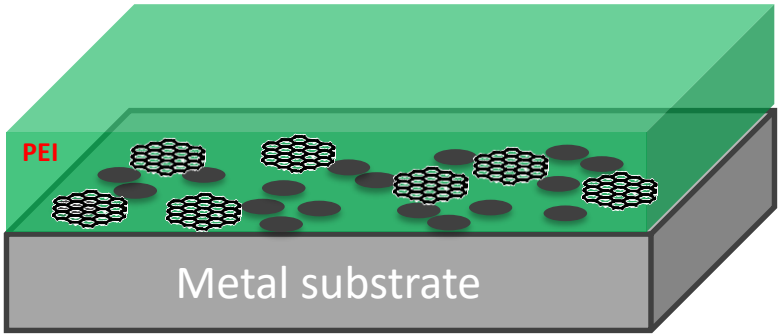

## Barrier Protection + Oxygen inhibition




## Sacrificial Protection




## New Paradigm



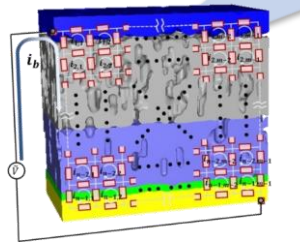

*In collaboration with Dr. Sarbajit Banerjee and Rachel Davidson

# What information can be extracted from 2D impedance model?

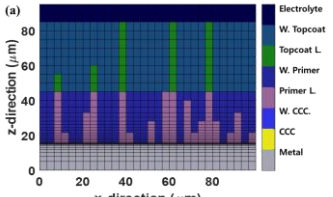
- **Proposed to characterize the degradation mechanism of a multilayered coating/metallic substrate system.**
- **Determined the ratio of penetration/wetness of coating**

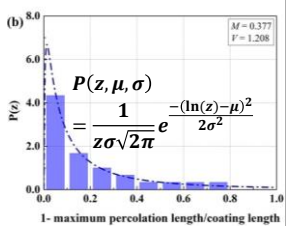
## Physical information

### System description



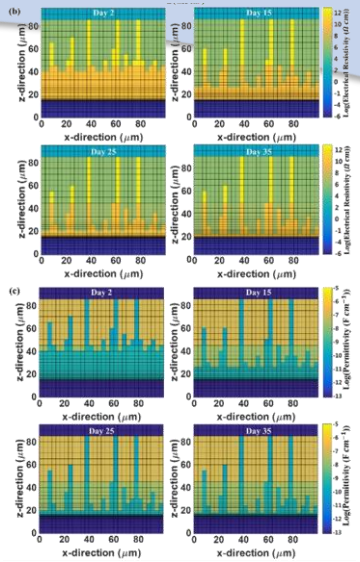

- Randomly structured model
- Distribution of electrolyte percolation length

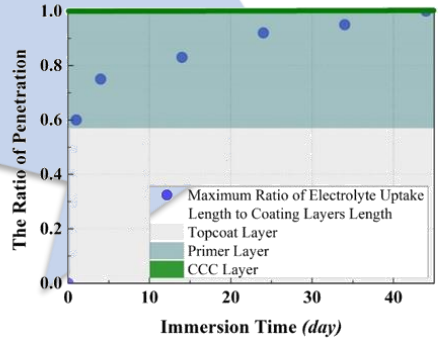


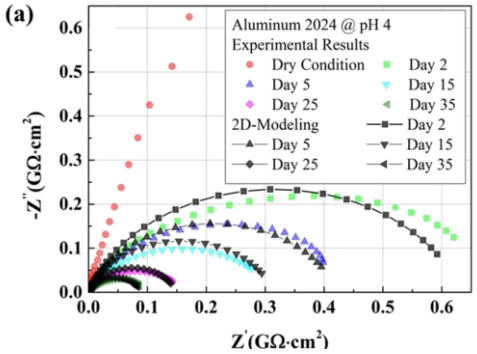




1) Cho et. al., Electrochimica Acta, 236 (2017) 82-96;

## EIS response



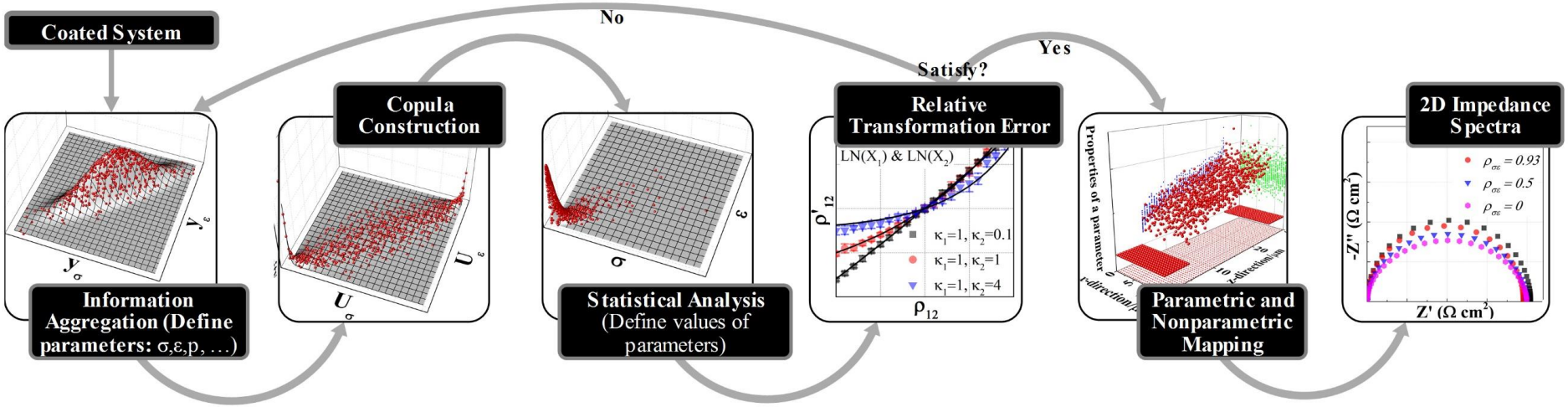



# Design based on material heterogeneous

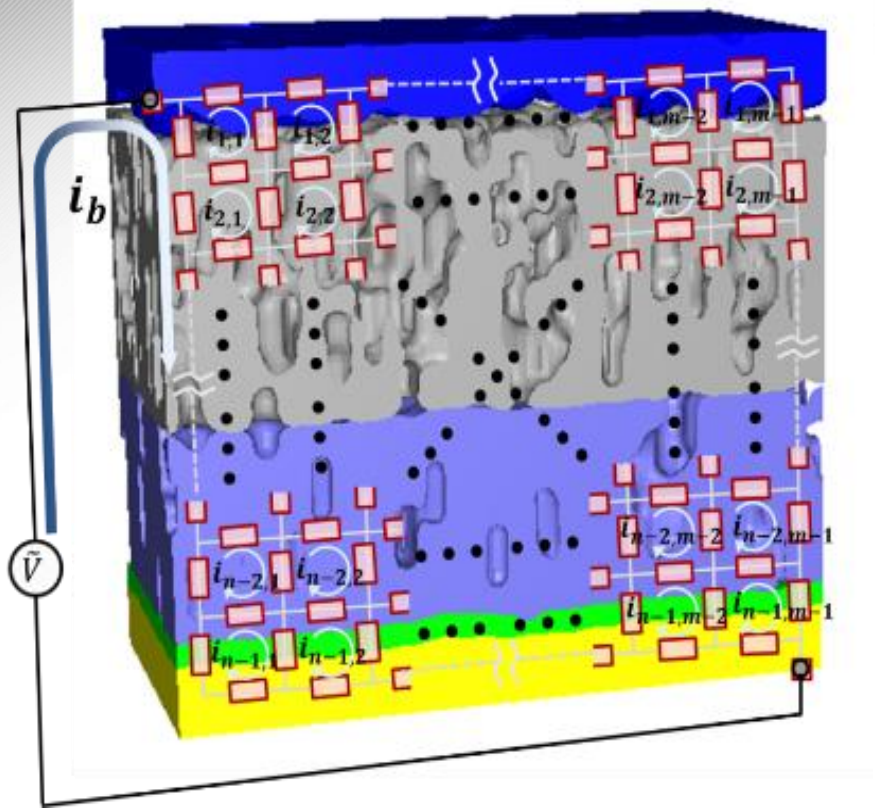
## Multivariate Control Process

- The distribution of physical properties is proposed to understand the non-ideal responses of coatings.
- Understanding methods and techniques response through local physical properties
- **A unique attempt** to apply jointly multivariate physical properties to **the field of research from analytical and electrochemical methods**




1) Cho et. al., in Review, Corrosion Science 2019

# 2D schematic in different harsh environments




- Substrate-characteristics
- Pretreatment characteristics–thickness – material
- Primer characteristics- thickness- material
- Topcoat characteristics– thickness – material
- Additives
- **Pressure**
- **Temperature**
- Electrolyte concentration and conditions (cyclic or full immersion)
- **Environmental parameters (ionic species, Cl, SO4=, HCO3-, H2SO4, etc..)**

The schematic of 2D networks of electrochemical impedance elements for layer-by-layer composite coating system based on charge and energy conservation

# RELLIS CAMPUS/TEES CENTERS

## Offshore technology center

Towing carriage

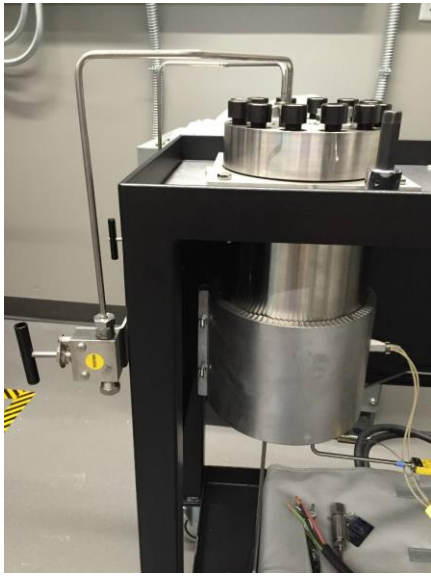
Current Generator

Wave boards

## Extreme Environments

- **Capable of strain rate from $10^{-5}$ to $10^{-7}$ $s^{-1}$**
- **Adapted for use with $H_2S$ containing**
- **Cells available for tests using electrochemical instrumentation**
- **3000 psia and 300°F**

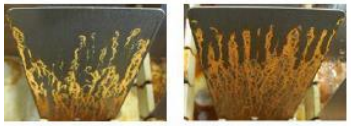
**Cortest Autoclave system**:
A 4-liter autoclave vessel, which is made from Hastelloy© C-276.
This autoclave system is designed for a MAWP of 350 bar (about 5000 psi), and it can withstand a maximum working temperature of 300°C



# Testing and characterization

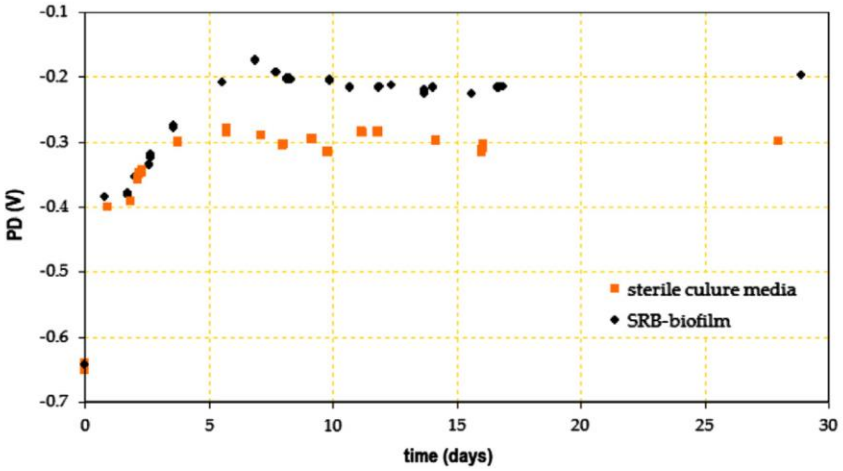

Laboratory testing

Accelerating testing and characterization simulating Marine conditions real time monitoring

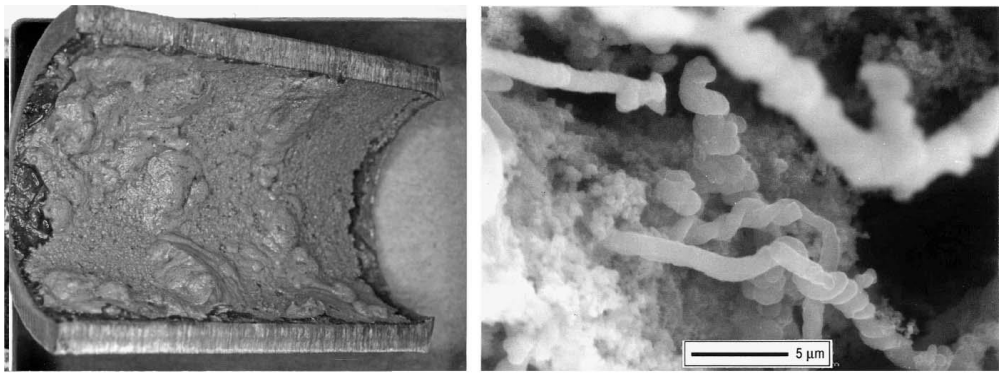
| | At 16 h | At 136 h | At 232 h |
|---|---|---|---|
| OS287296 |  no corrosion indication |  corrosion indication |  corrosion indication |
| OS287297 |  no corrosion indication |  corrosion indication |  corrosion indication |
| OS287299 |  corrosion indication |  corrosion indication |  corrosion indication |

# Antifouling and MIC

MIC testing set-up in an anaerobic chamber




Castaneda et al, Corrosion Science , 2008

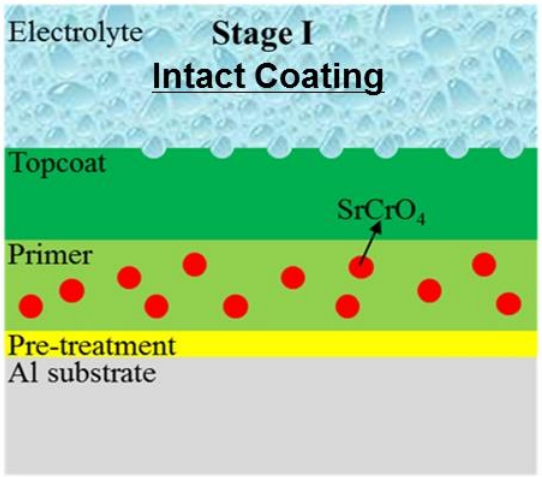


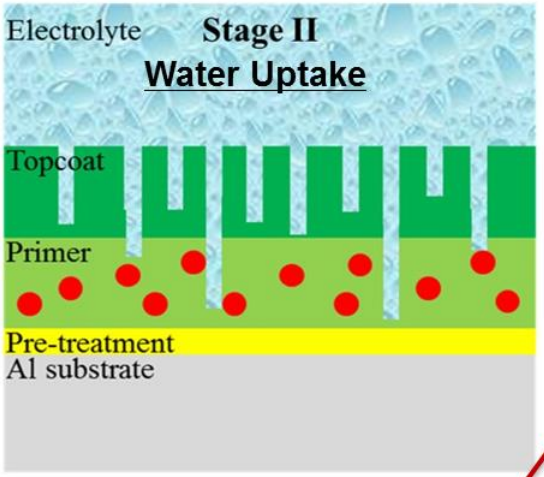

(*a*) (*b*)

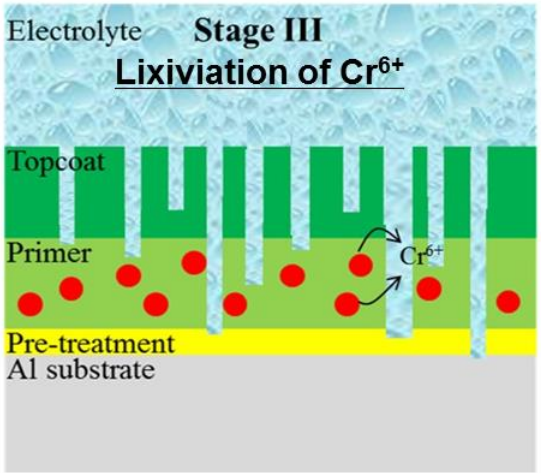
Ref. www

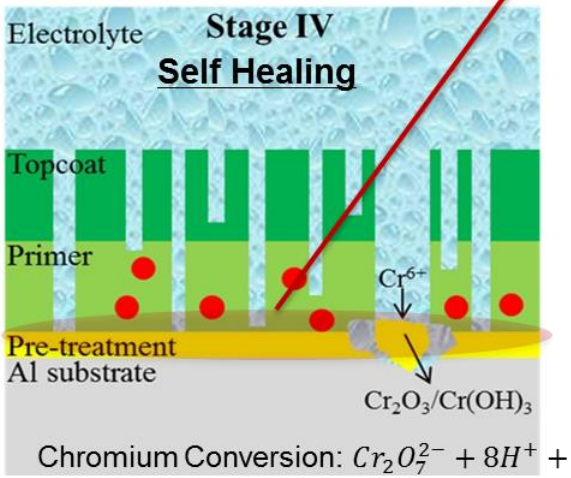
# Quantification of degradation mechanisms

## Cr (VI) coating/aluminum 2024 system

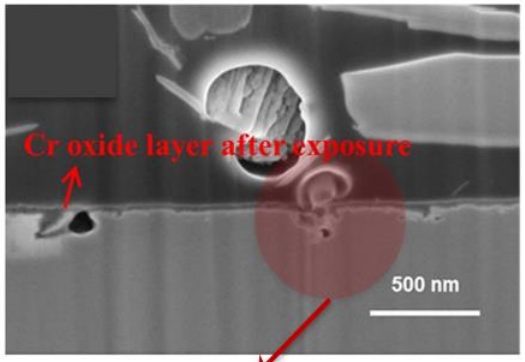


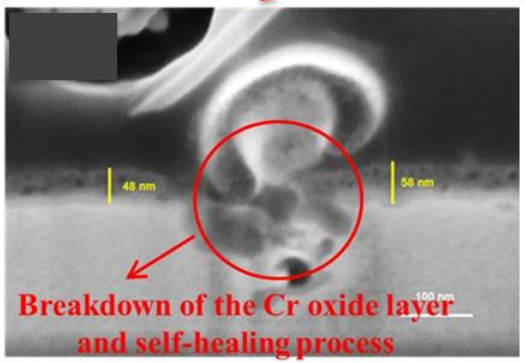




**SEM morphology of CCC in the Interface of primer/substrate after exposure for 260 days**



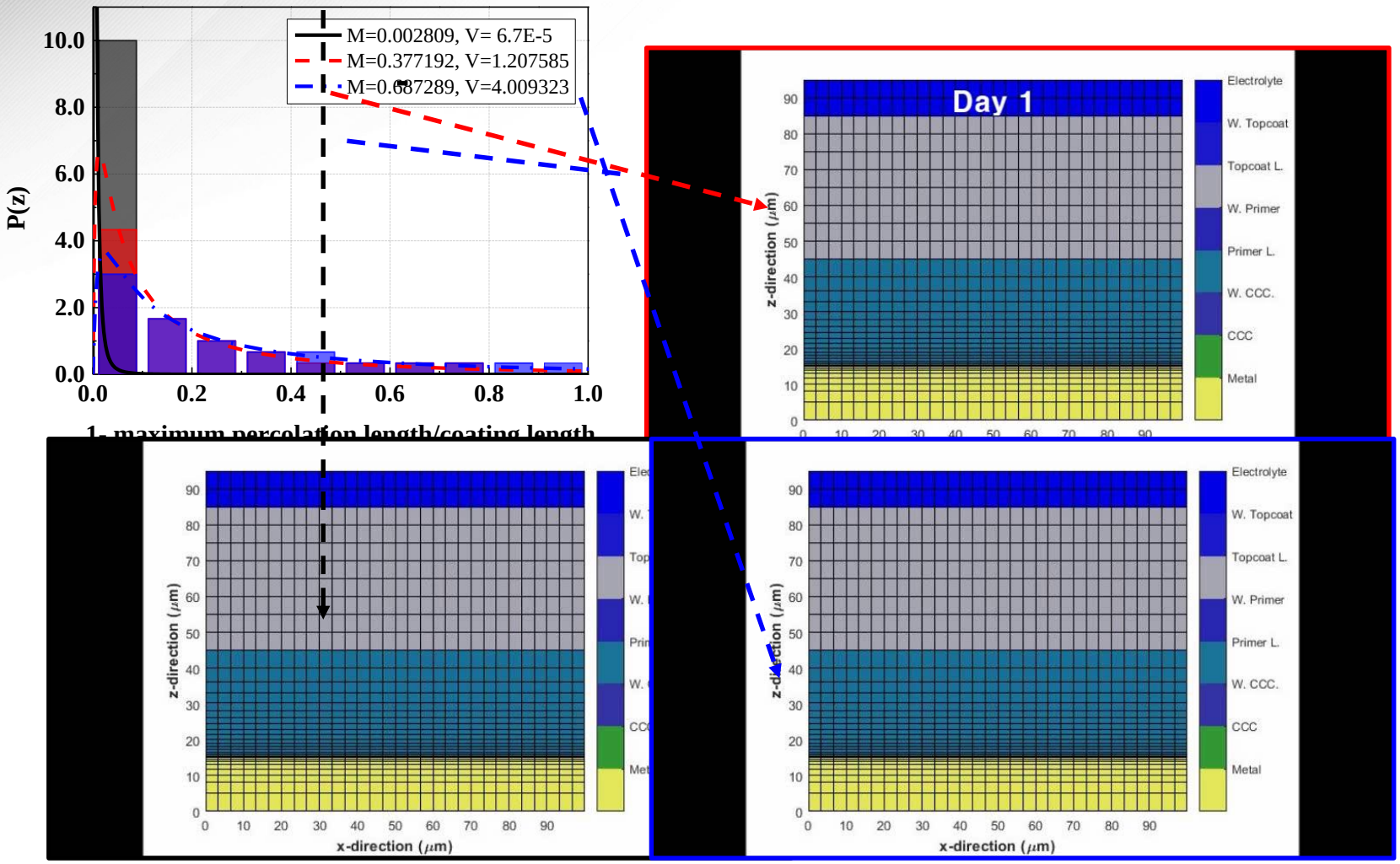




Chromium Conversion: $Cr_2O_7^{2-} + 8H^+ + 6e^- \rightarrow 2Cr(OH)_3 + H_2O$

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

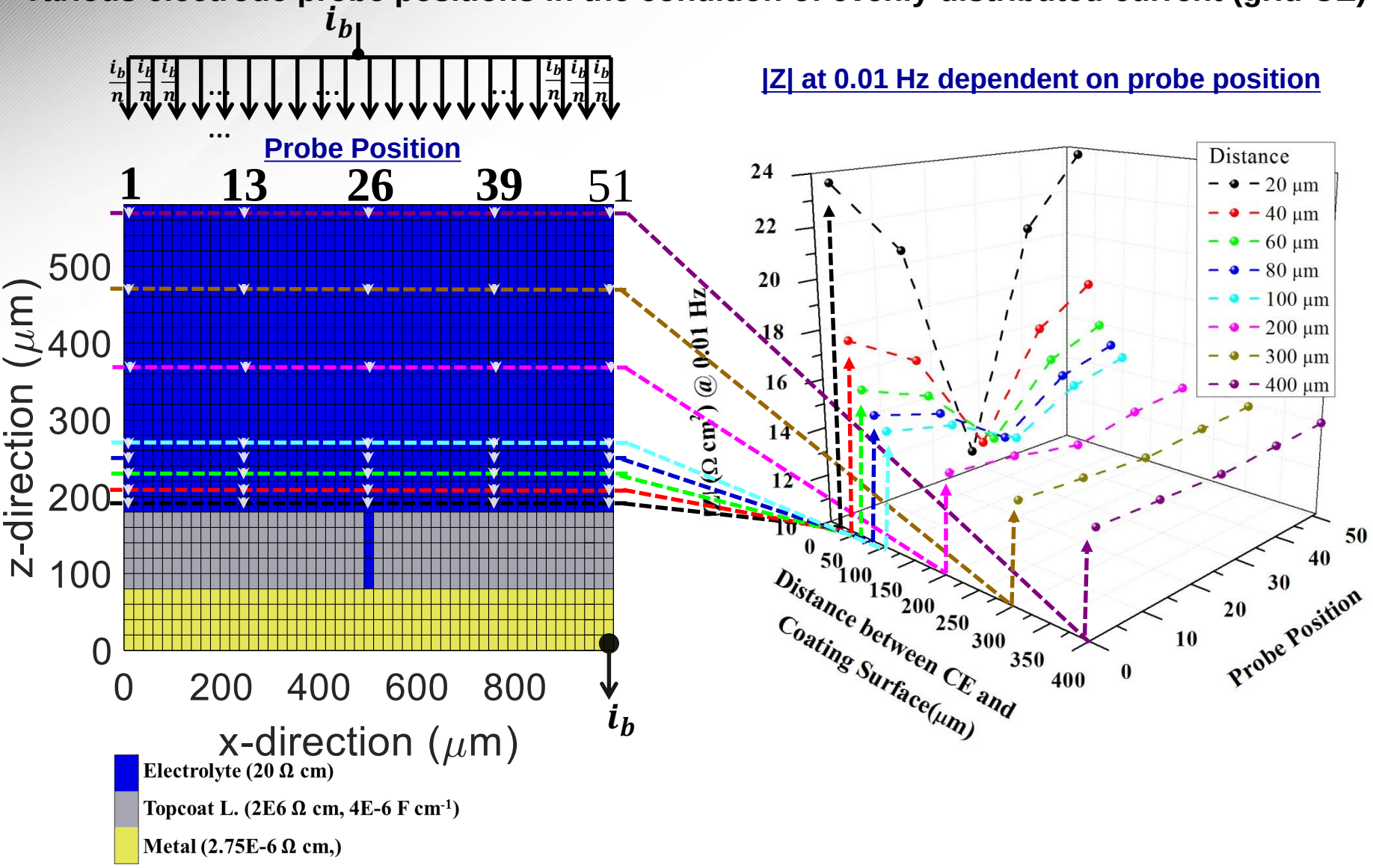
1) S. Cho et al (2017) – Electrochimica Acta

# Simulation and design of Performance



# Electrochemical Impedance Modeling Based on Nodal Analysis

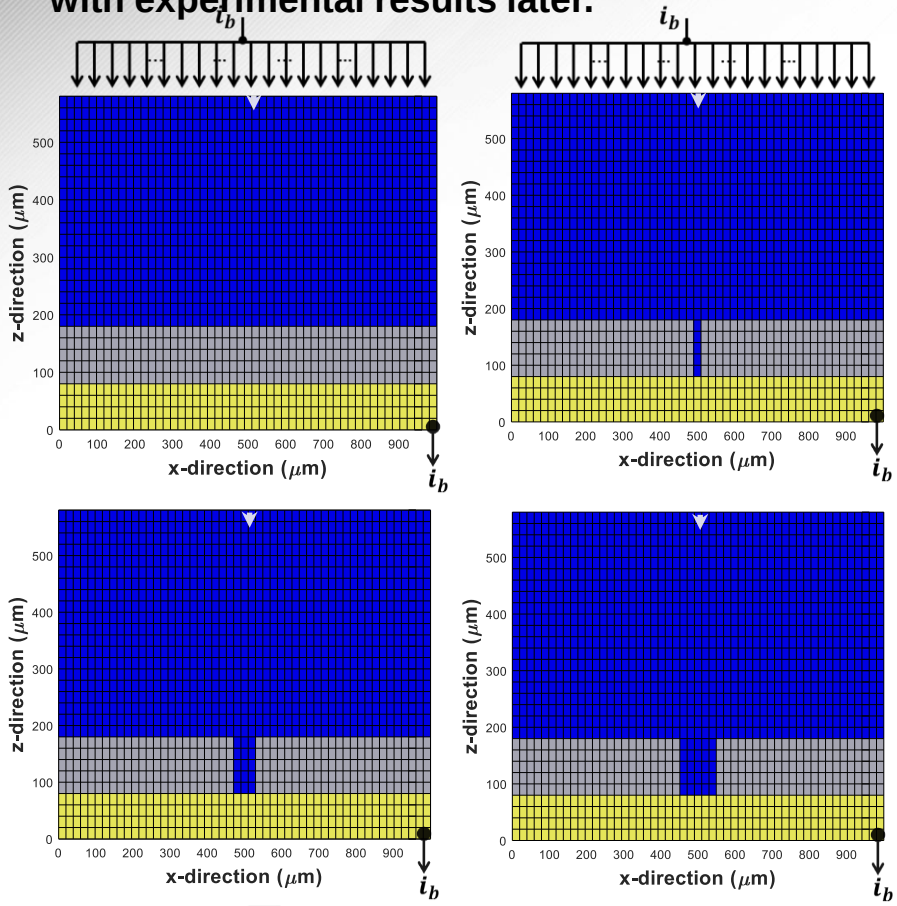
## Various electrode probe positions in the condition of evenly distributed current (grid CE)



# Electrochemical Impedance Modeling Based on Nodal Analysis

## Effect of defect size

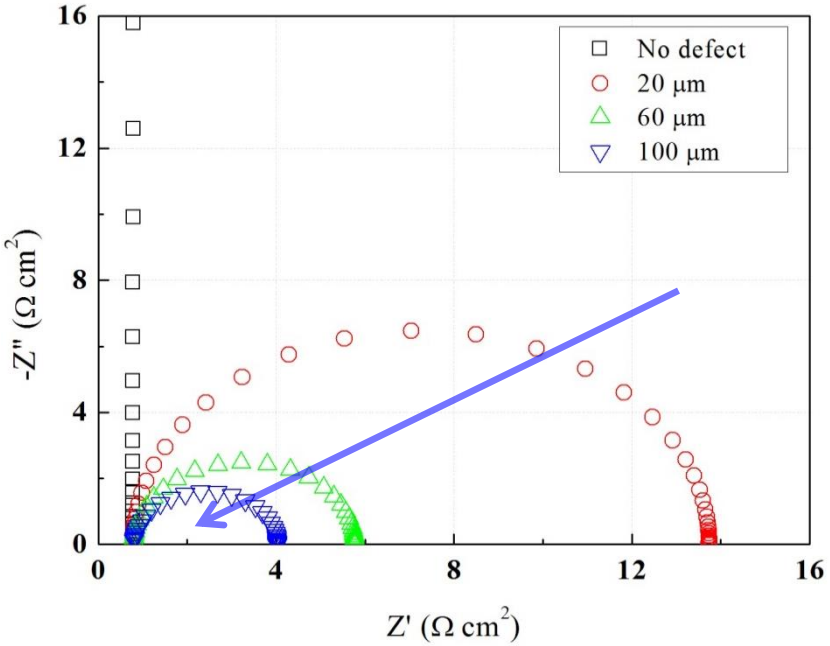
- This calculation does not consider interfacial electrochemical process which will be considered with experimental results later.




Electrolyte (20 Ω cm)

Topcoat L. (2E6 Ω cm, 4E-6 F cm$^{-1}$)

Metal (2.75E-6 Ω cm,)



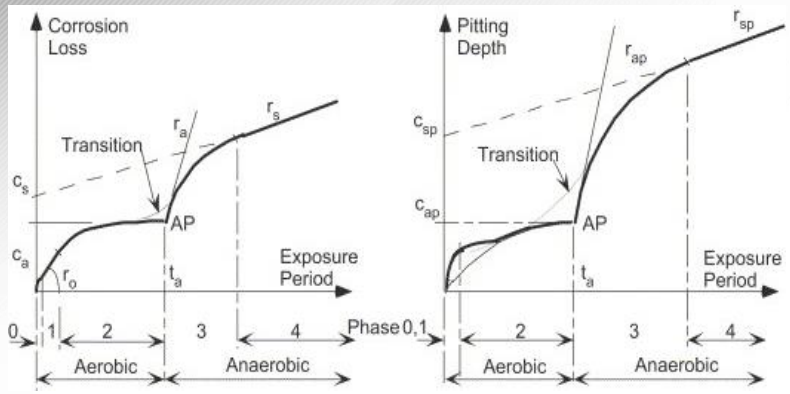
# Reliability Models

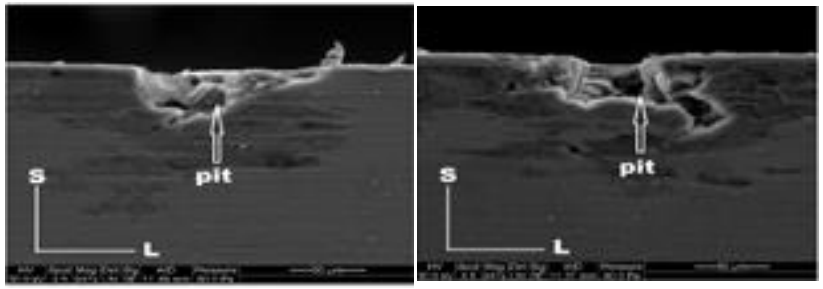
We have proposed a rational characterization and quantification concept of damage/performance evolution that incorporate modular elements corresponding to deterministic and probabilistic modeling approach.

Distinctive modes of corrosion inhibition, self-healing, and mass transfer blocking based on different properties of the coatings. The presentation includes a versatile library of multifunctional coatings that each bring about a distinctive mode of corrosion control and deploy an experimental-theoretical-driven approach to rapidly leading to the performance of the systems in different corrosive-harsh environments.

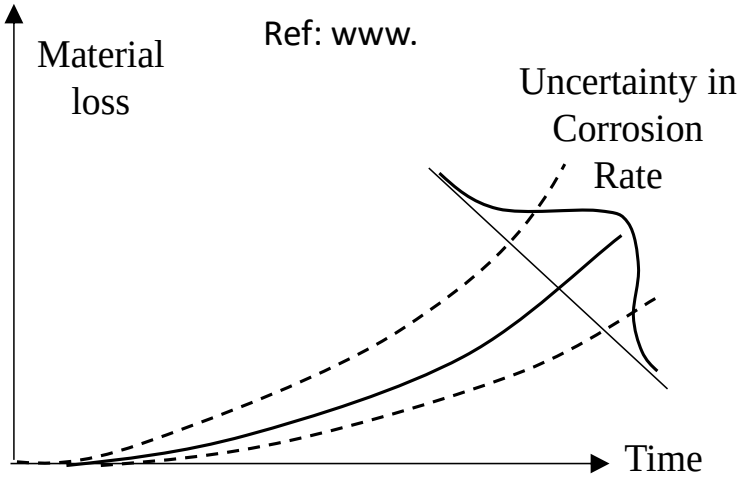
***The effort seeks to combine distinctive aspects of coating design with deterministic and probablilistic damage/performance modeling in extreme environments and predicting operational lifetime for the design coatings/substrate system.***

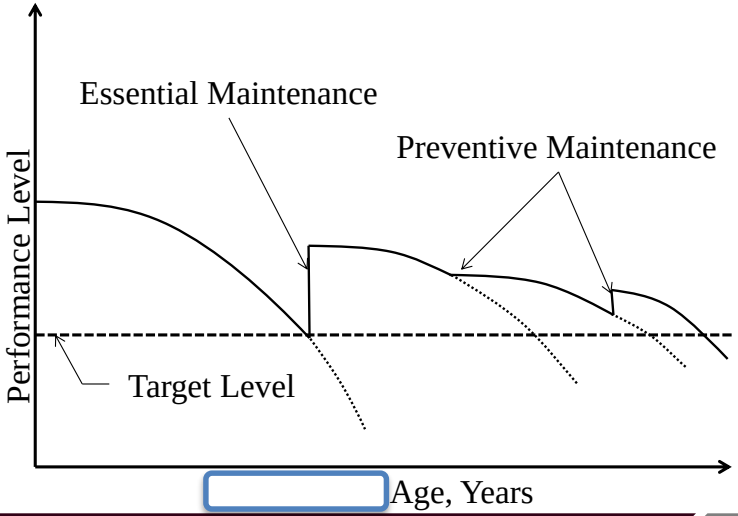
# Reliability Modeling




Ivan Karayan et al, Journal of Alloys and compounds, 2016



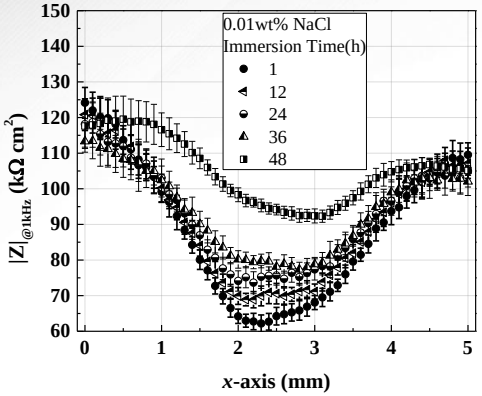



# Validation for Modeling

## The effect of electrolyte conductivity in the condition of concentrated current probe

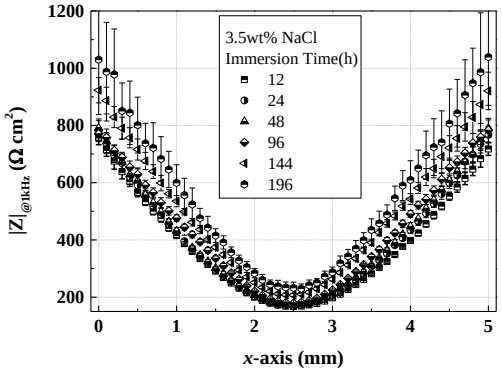
### Experimental Result

#### Low Electrolyte Conductivity (220uS/cm)



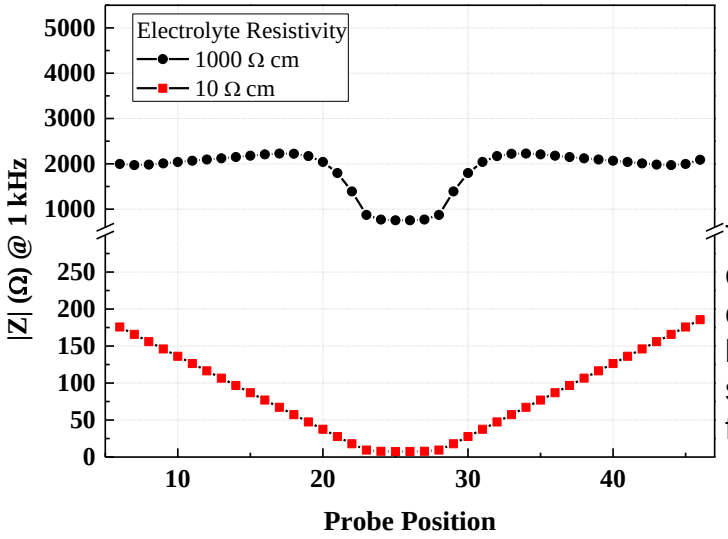

Localized effect in coated system -Water uptake inside of coating -formation of corrosion product on defect

#### High Electrolyte Conductivity (59.7mS/cm)

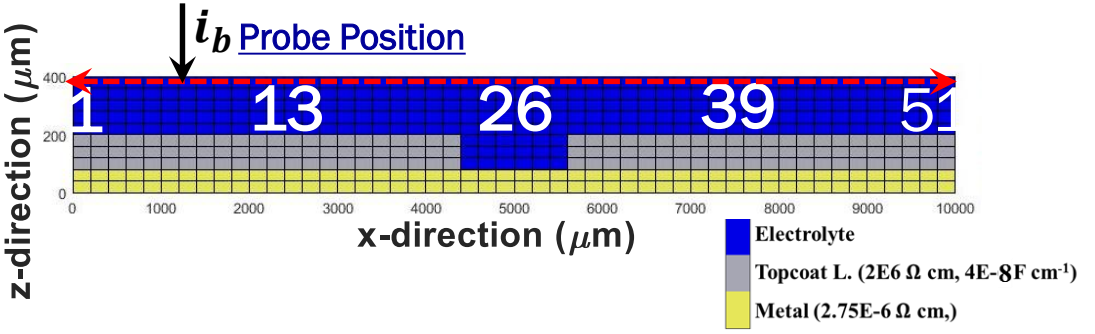



Formation of corrosion product on defect with the effect of tip prove distance

### Computational Result



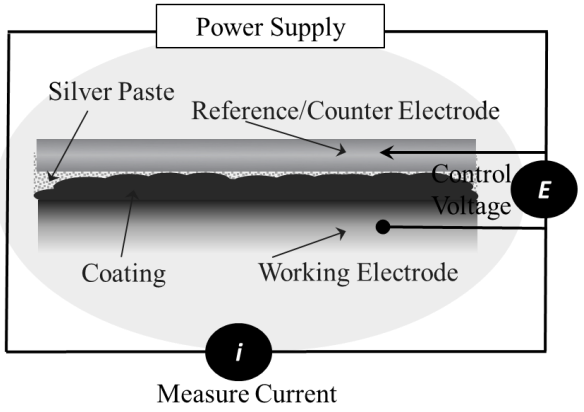

The results qualitatively explain well for effect of electrolyte conductivity on localized impedance spectroscopy at high frequency

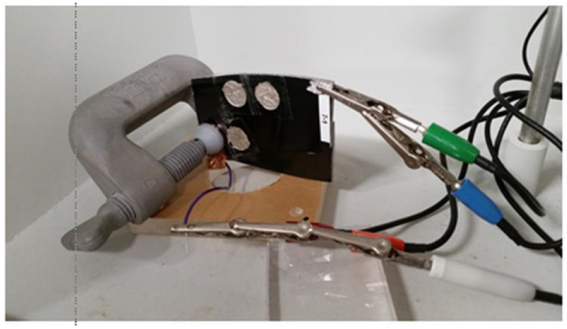


# Sensors for Marine conditions

## Experimental test for various curved structures of marine applications

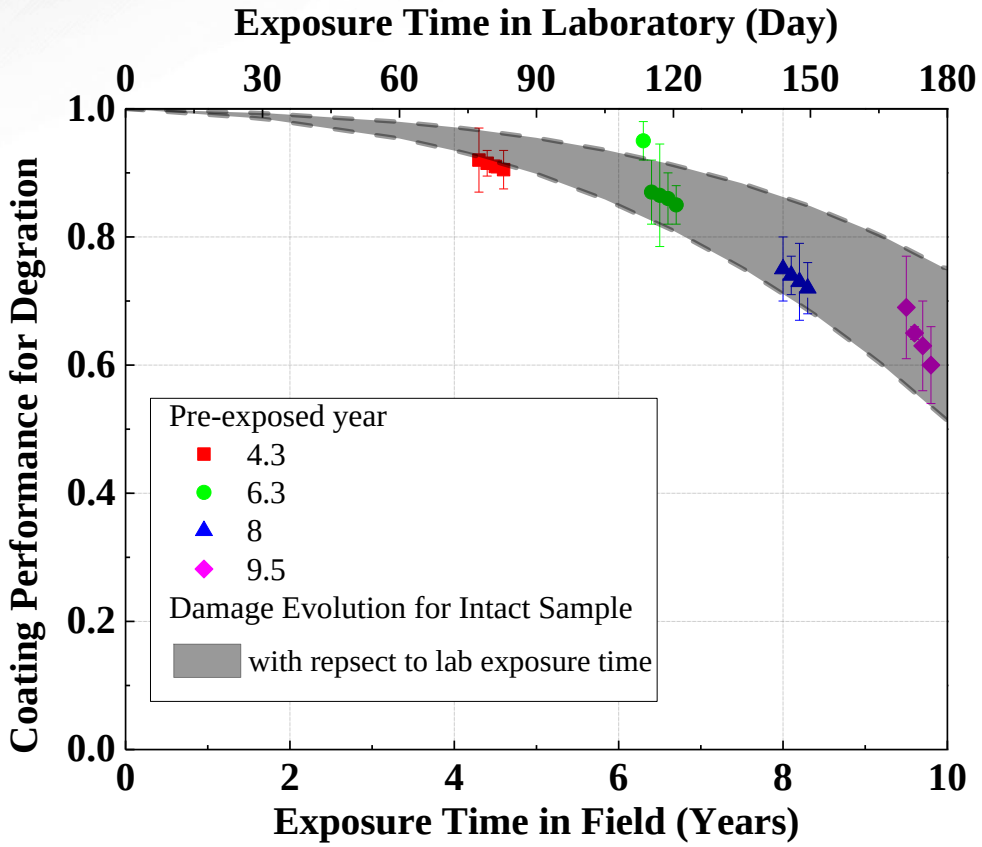
- ***Two-electrode system in the dry condition***
  - ✓ A symmetrical two-electrode sandwich-like cell (area of 2.25 $cm^2$ )
  - ✓ Metal substrates (WE) and a stainless-steel panel with silver paste (CE/RE)
  - ✓ Test sequences
    - Potential difference between two electrodes: 5 min
    - EIS range of $10^5$ Hz to 10 Hz and an amplitude of 50 mV rms



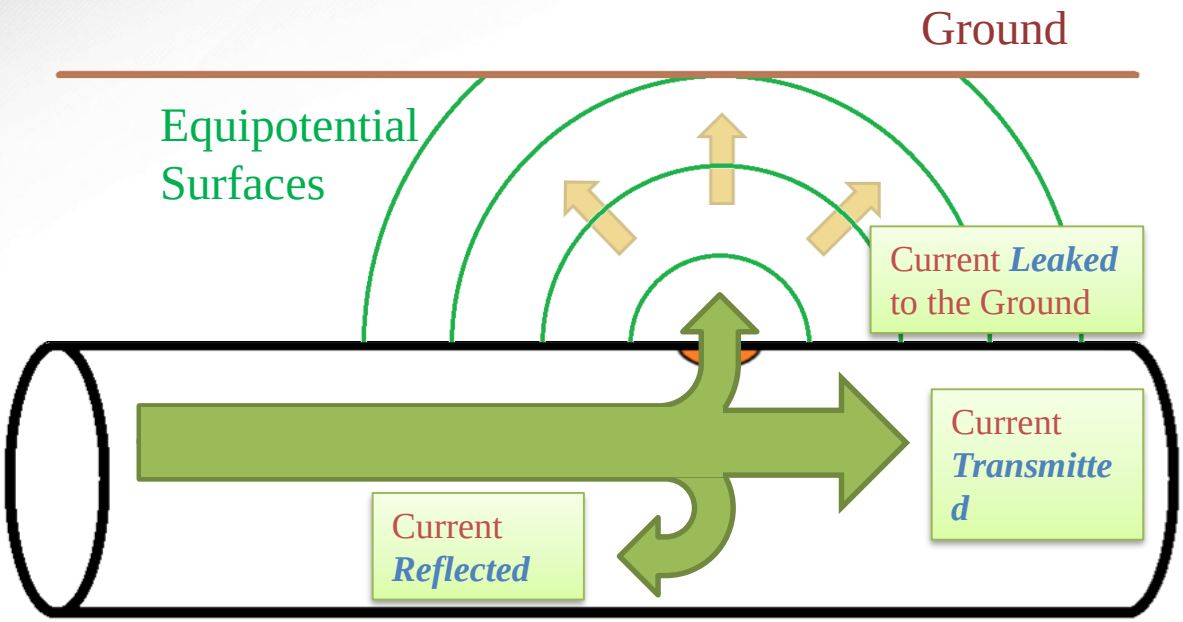
# Probabilistic life prediction model

- The probabilistic approach considers the laboratory and field exposure samples correlation.




**The image of an anticipated final outcome for probabilistic life prediction**

# Detection and Location of Early Corrosion Substrate/Coating with Electromagnetic Reflectometry

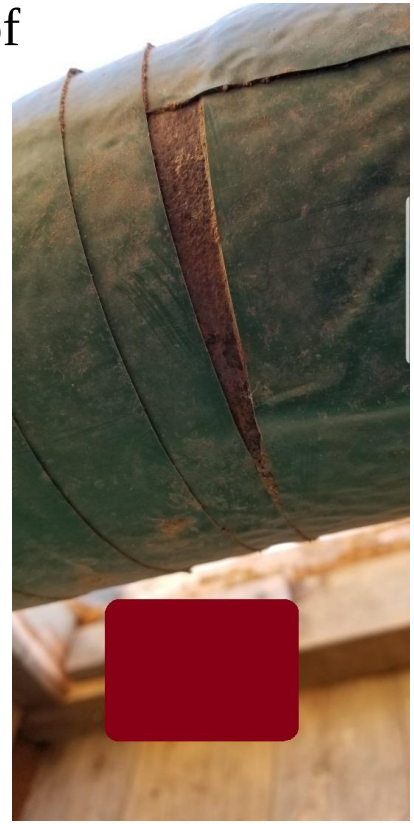



**Paradigm Shift**

**Current-based approach**

# Detection and Location of Early Corrosion Substrate/Coating with Electromagnetic Reflectometry

Defects have been successfully detected, located and excavated with EM reflectometry on different kind of pipeline coating (coal tar, somastic, tape coating...)



# Thanks to our corrosion group

# Sponsors for the NCMRL