CENTER FOR ELECTROCHEMICAL SCIENCE AND ENGINEERING
Department of Materials Science and Engineering

University of Virginia Engineering

SAND2020-9448C

Sensor Design, Construction and Validation for in-situ Water Layer Thickness Determination during Accelerated Corrosion Testing

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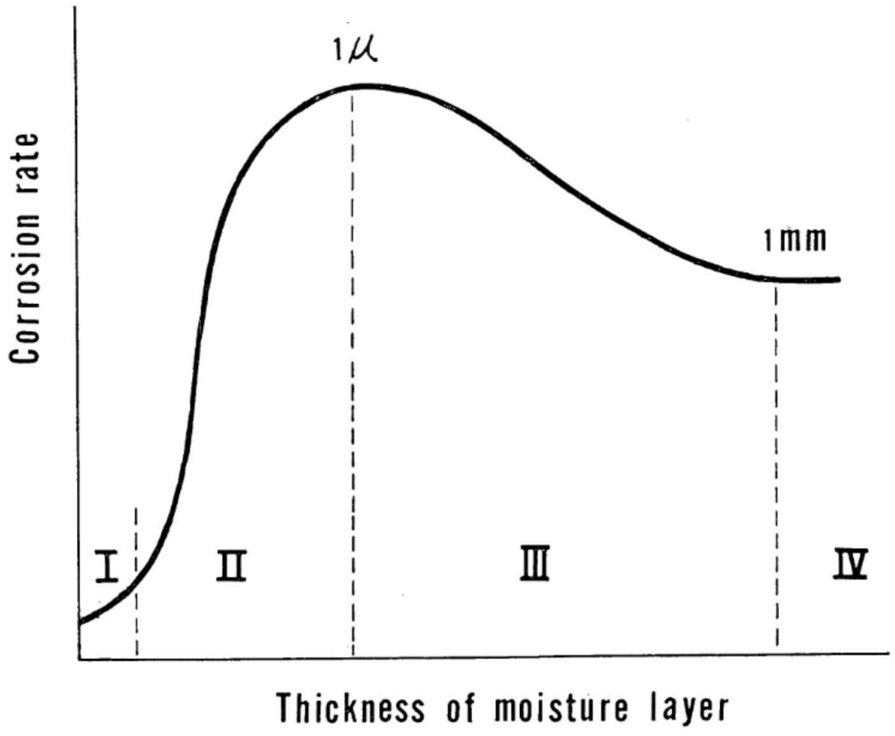
Overview

- Motivation and Background
- Objective
- Modeling approach and Results
- Results and Discussion
- Implications and future work

Motivation

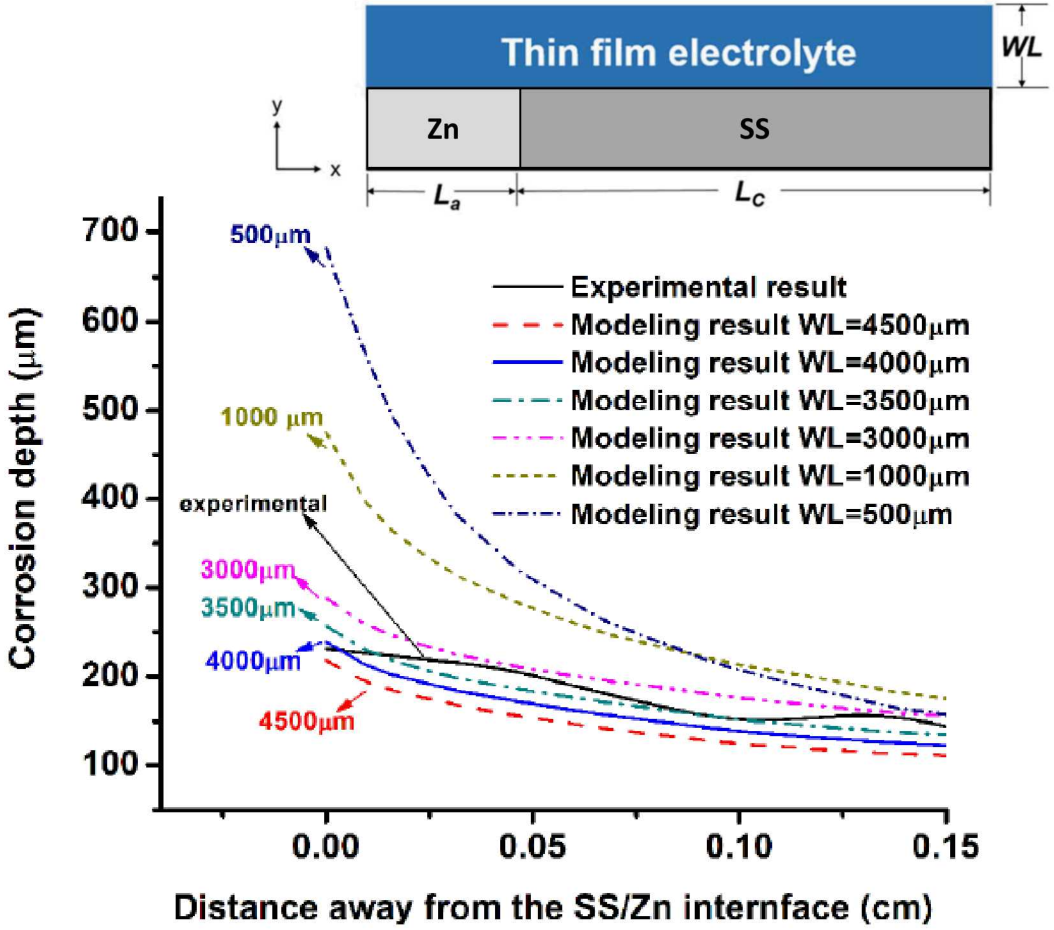
- The importance of the WL in corrosion testing has been long recognized



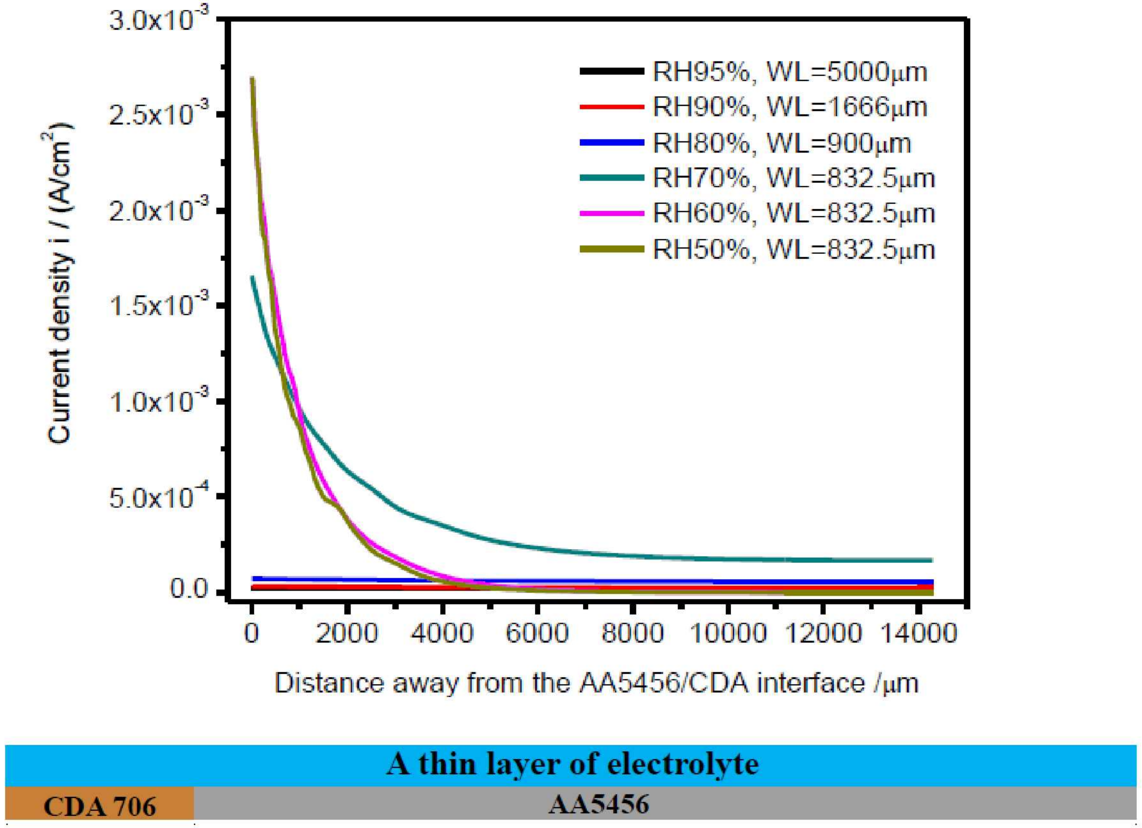
N.D. Tomashov,, CORROSION. 20 (1964) 7t-14t.

Motivation

- In galvanic couples, WL defines current distribution



Liu, C., PhD Thesis, UVA



Blohm, L. Masters Thesis, UVA

Motivation

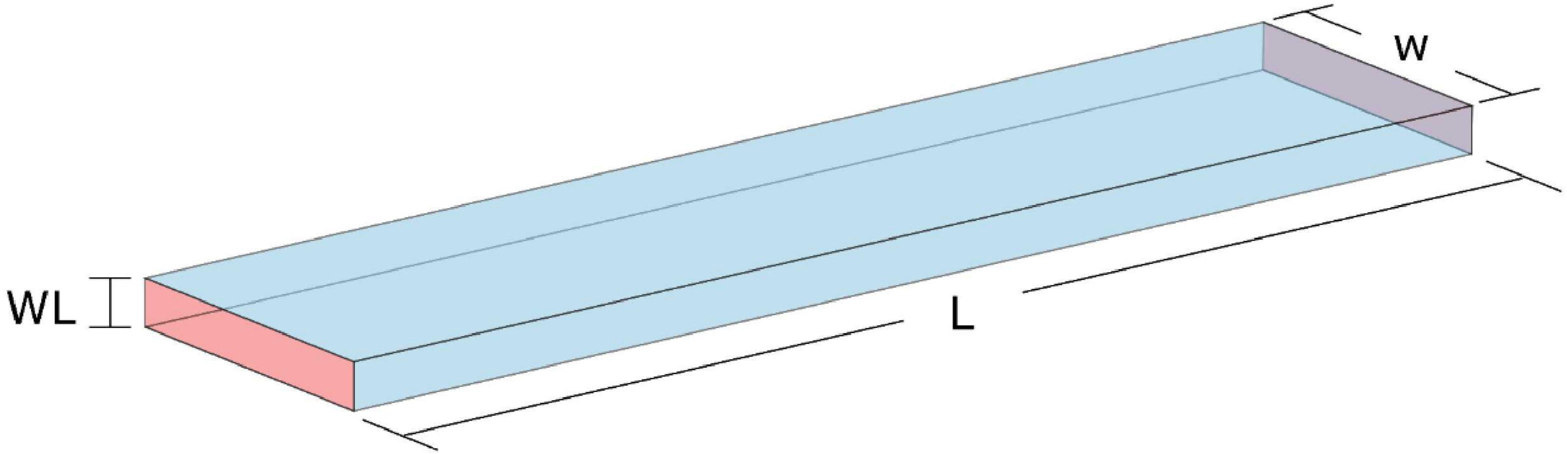
- Ability to measure WL in accelerated testing needed to understand corrosion damage distribution and improve test-to-test and chamber-to-chamber variability
- Thus a resistance based sensor will be created in which WL can be measured in a salt spray environment

The presented work is based on recently published paper:

- Katona, R.M.; Tokuda, S.; Perry, J.; Kelly, R.G., Design, "Construction, and Validation for in-situ Water Layer Thickness Determination during Accelerated Corrosion Testing," *Corros. Sci.* 175 (2020) 108849. https://doi.org/10.1016/j.corsci.2020.108849.

Governing Aspects of the Sensor

- For a parallelepiped WL, we know that WL is related to the solution resistance (R_s), length (L), width (W), and conductivity (κ) of the solution

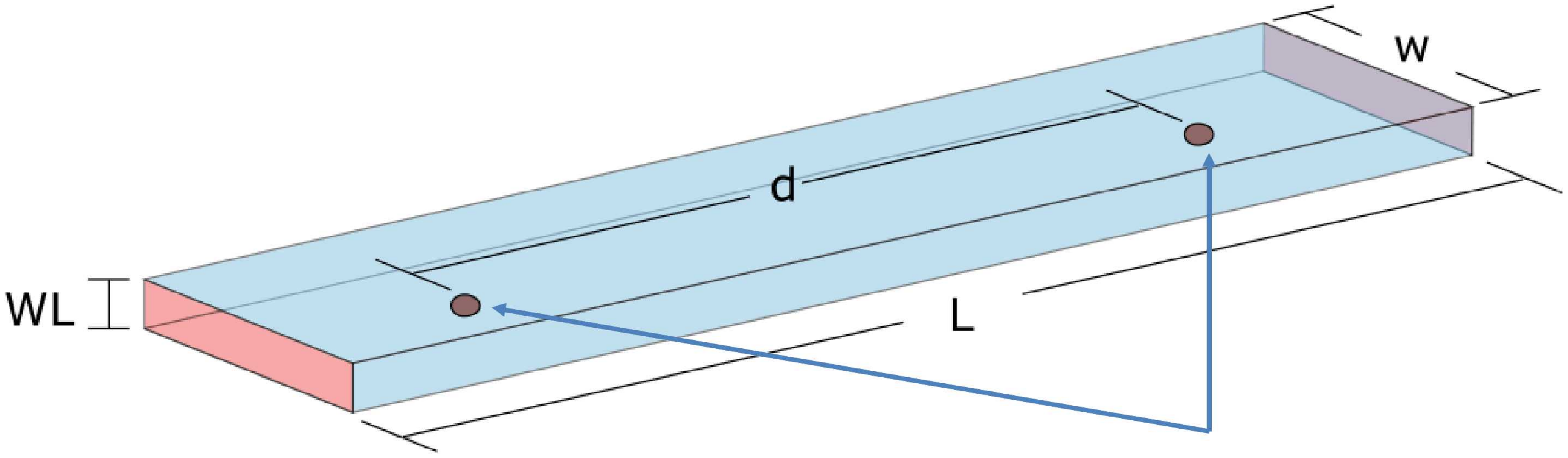


$$WL = \frac{L}{R_s * w} * \frac{1}{\kappa}$$

- Applies to measurement from end-to-end
- WL formation would be influenced by the walled sides

Governing Aspects of the Sensor

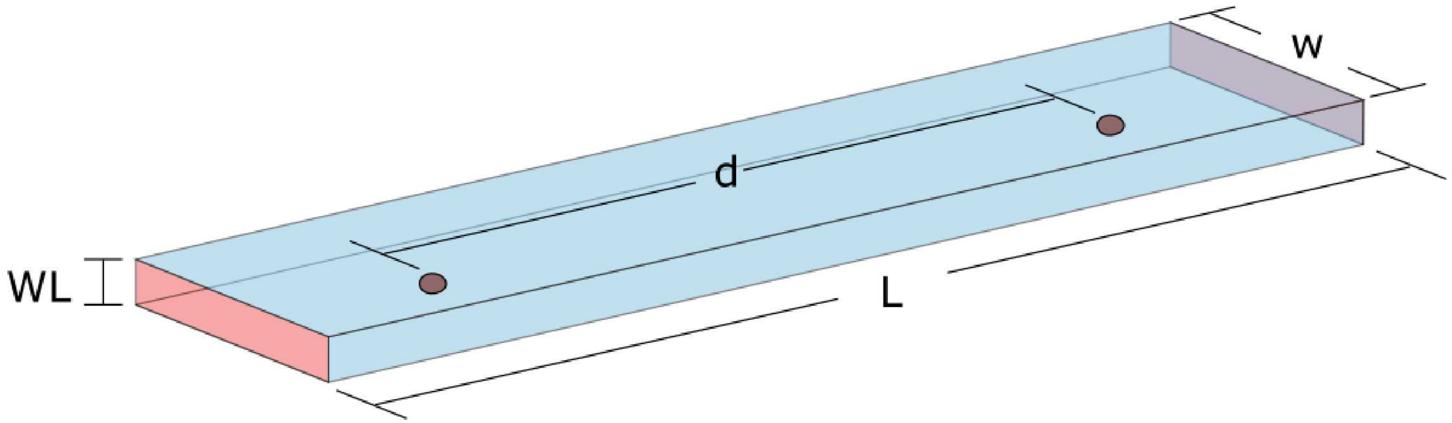
- A geometry that would avoid influencing the WL formation would involve mounting electrodes flush with the surface upon which the WL was being formed

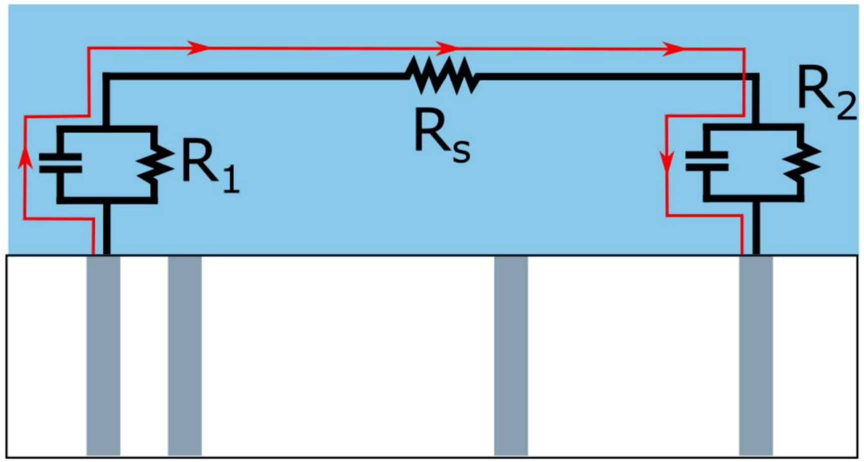


Mounted electrodes with spacing d

Governing Aspects of the Sensor

- EIS at high frequencies would measure the solution resistance

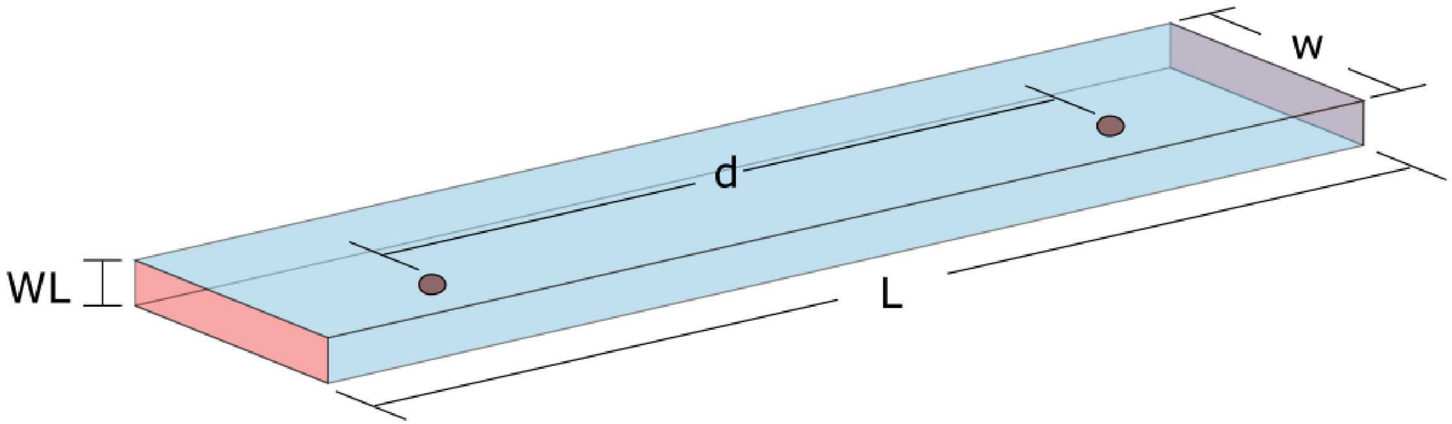




- No direct solution for the resistance as a function of WL which is a function of voltage (V) and current (I)
- FEM can be used to evaluate the expression

$$R_s = \frac{\Delta V}{\int I}$$

Goal

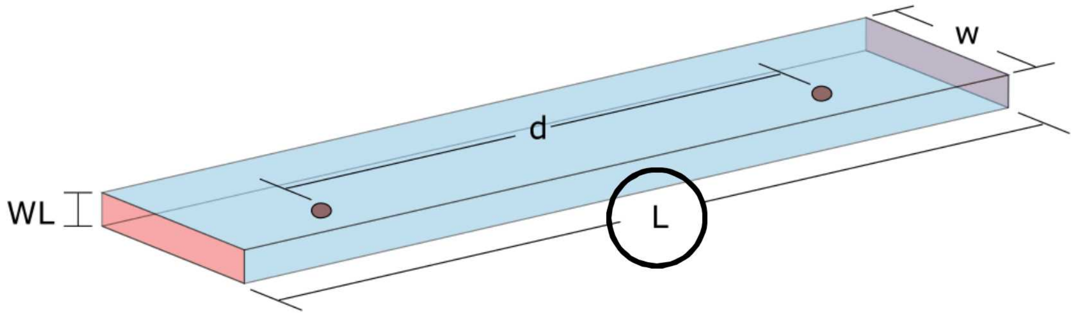


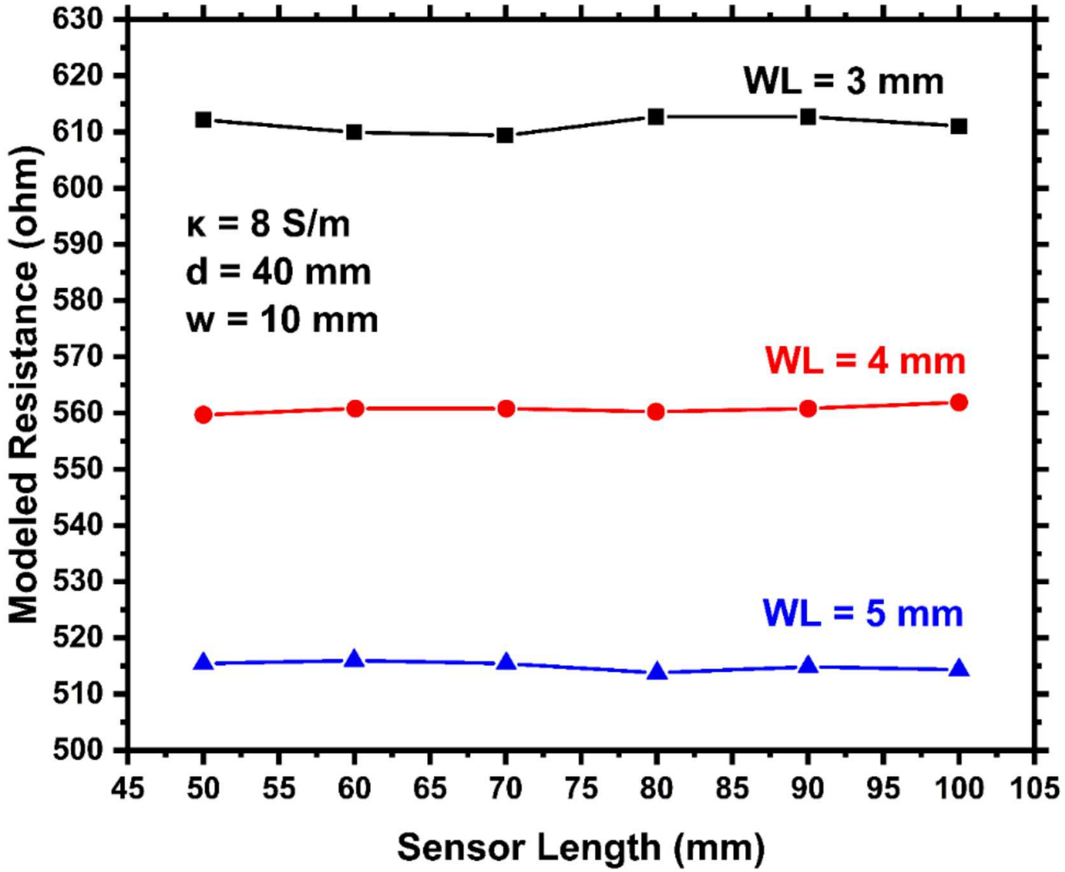
- Create a resistance-based sensor to measure WL thickness in continuous salt spray environments that is sensitive in the range of 0-5 mm

- Approach
  – Utilize FEM to create the sensor and explore various sensitivities (d, w, L, κ)
  – Construct sensor and utilize in accelerating testing scenarios

Sensor length does not influence calculated resistances

- Sensor length does not have an influence on the modeled resistance
- **However, continuous WL needed**

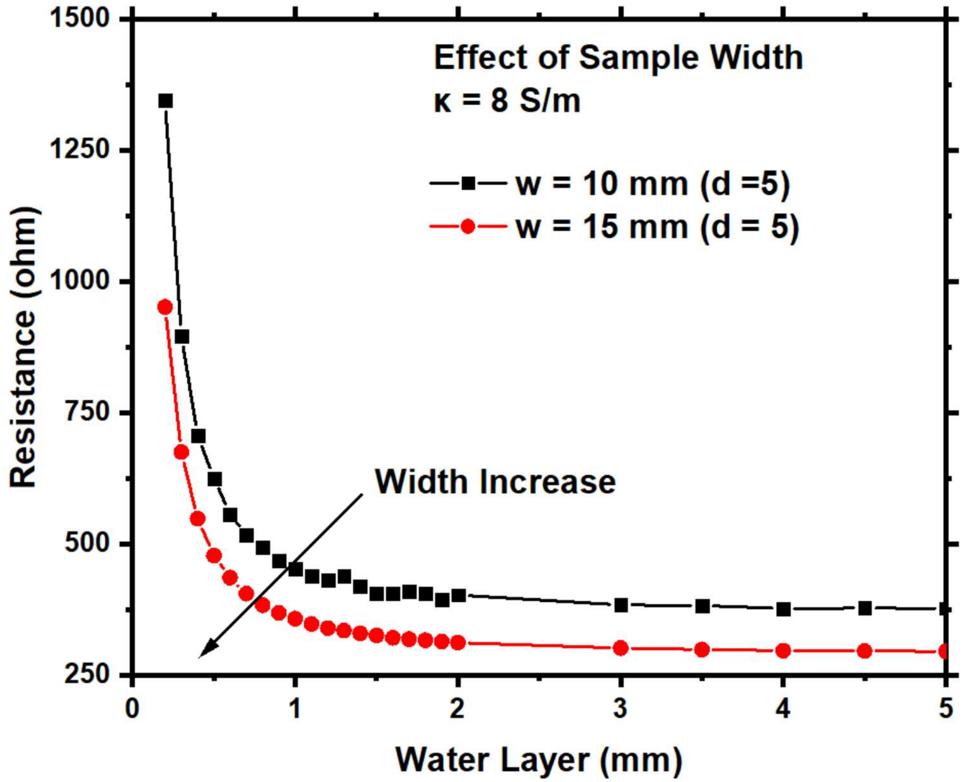


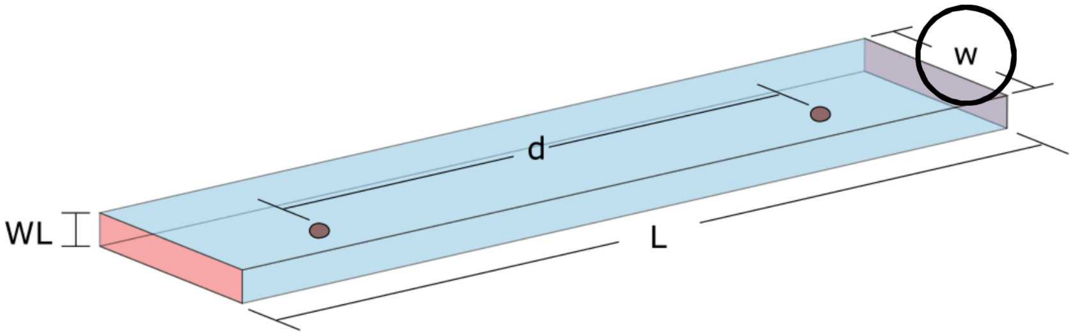


Model results

Smaller sensor widths increase sensitivity

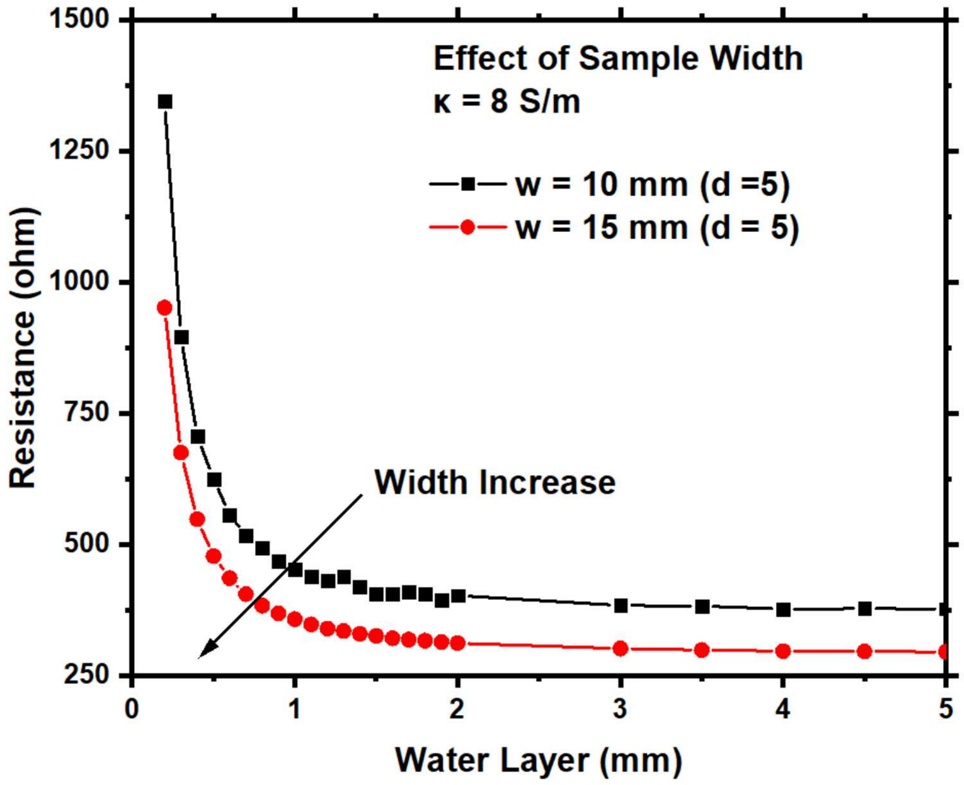
- Increase in width decreases the calculated resistances
- Can determine sensitivity by taking slope of resistance vs. WL (ohm/mm)

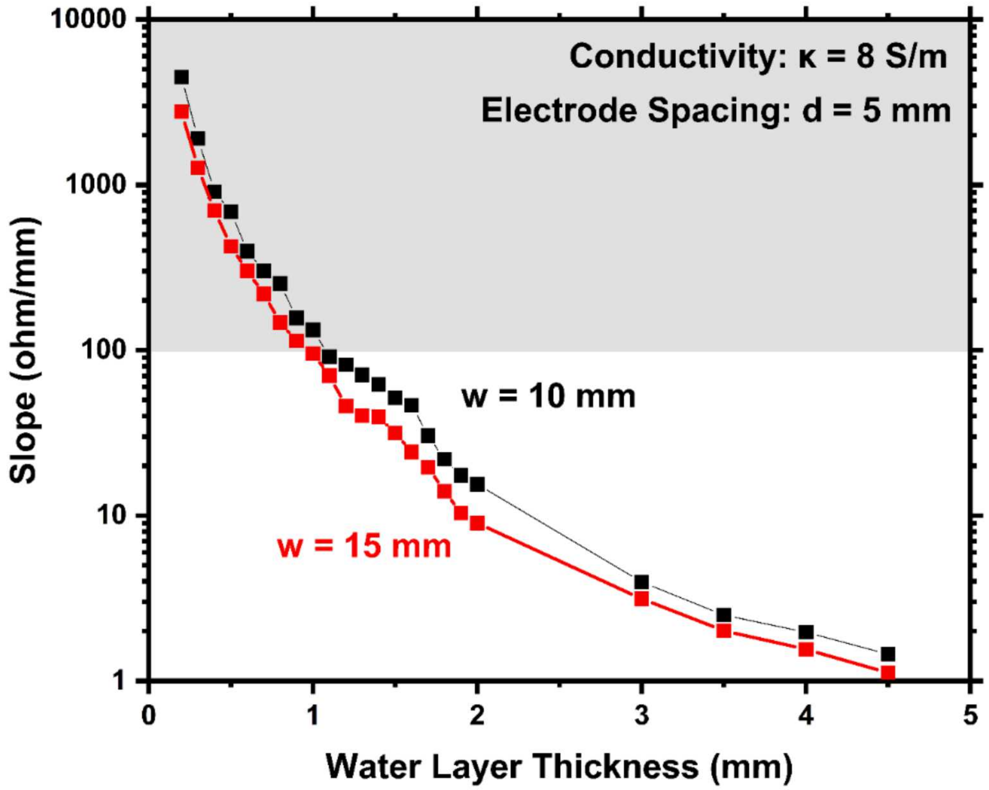




Model results

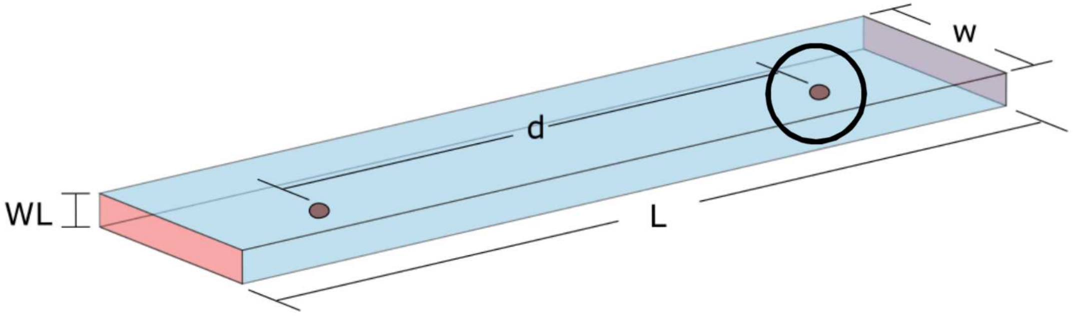
Smaller sensor widths increase sensitivity

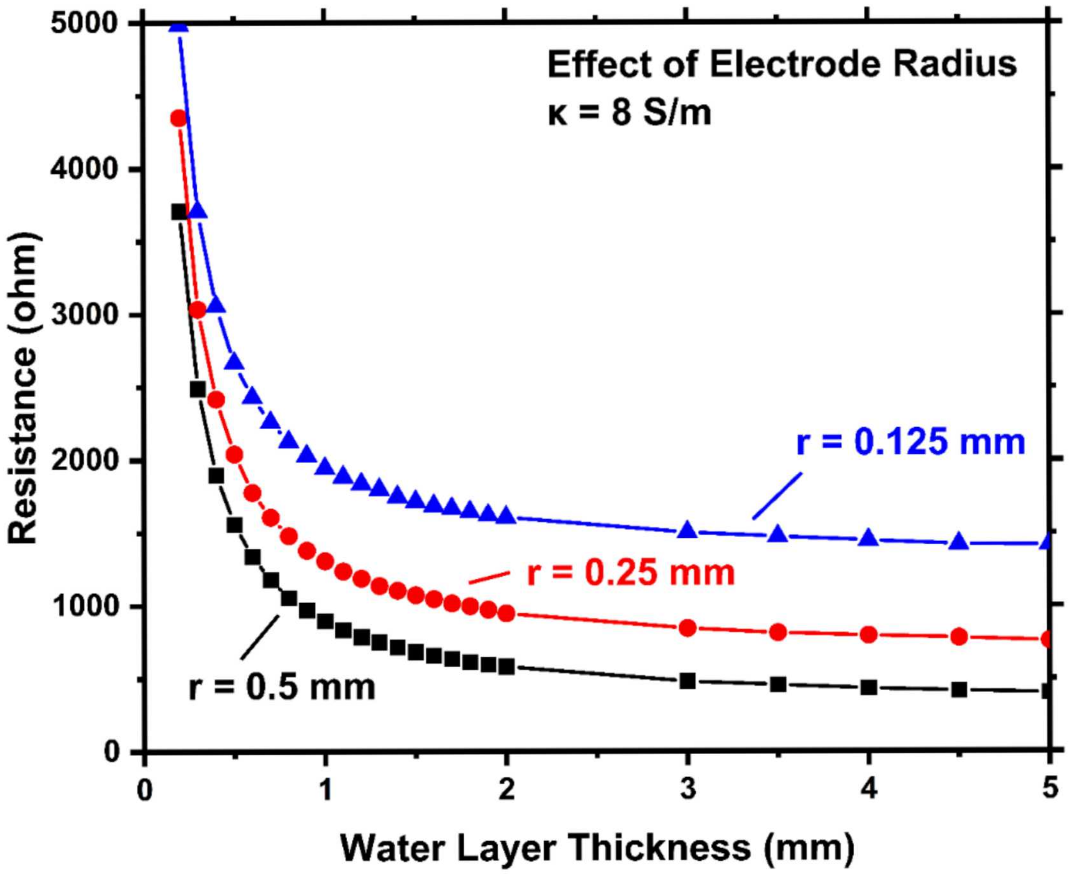




Resistances not sensitive to wire radius

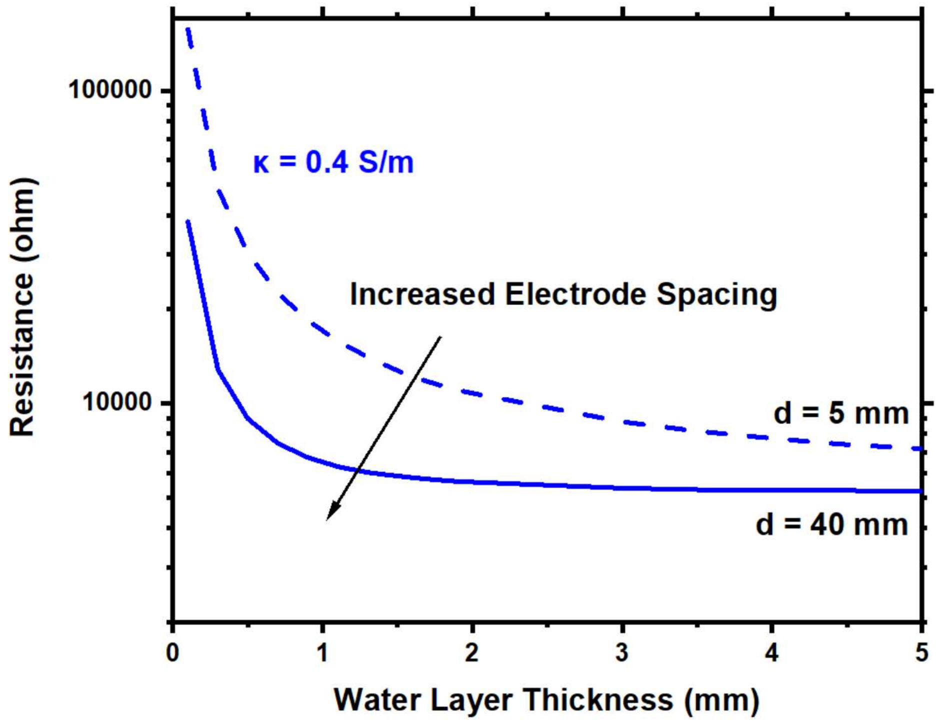
- Increasing embedded wire radius, decreases modeled resistances
- But there is no change in the sensitivity (ohm/mm) due to the radius of the wire

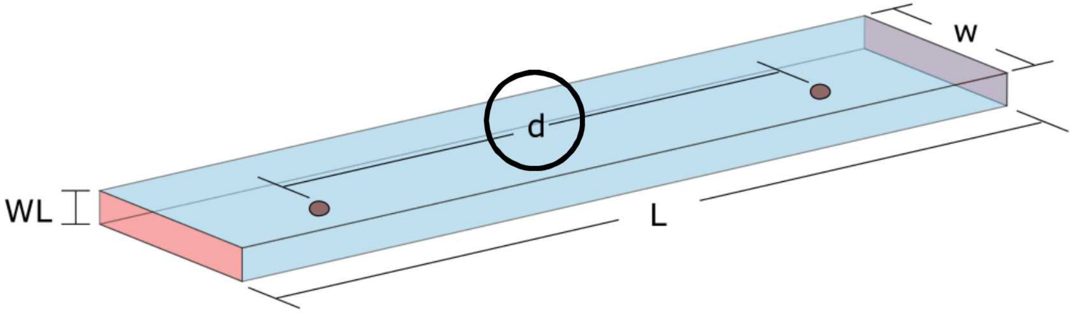




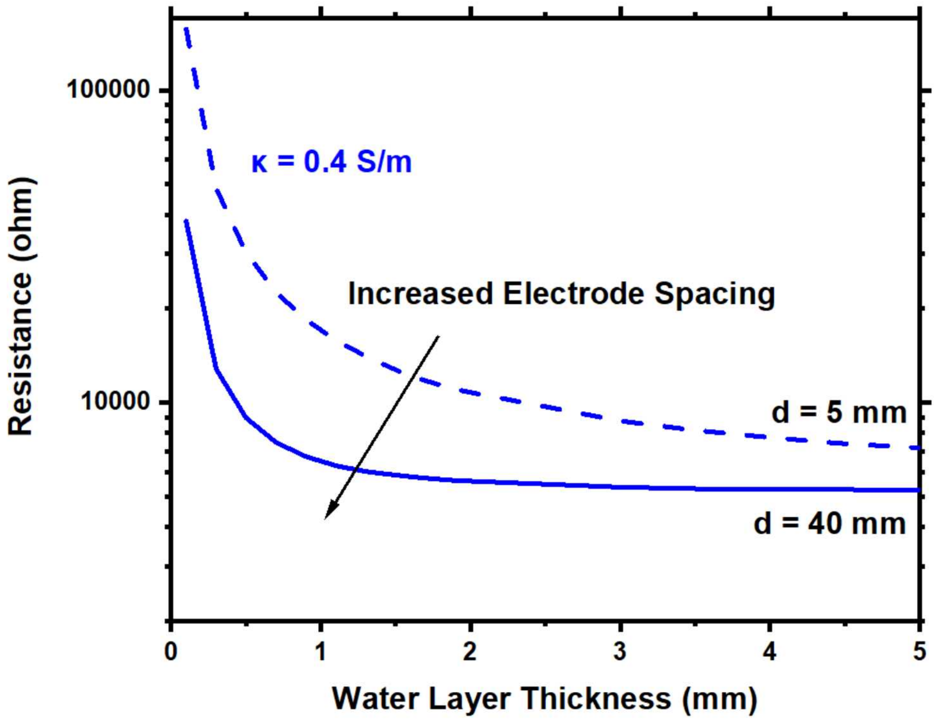
Wide electrode spacing provides highest sensitivity

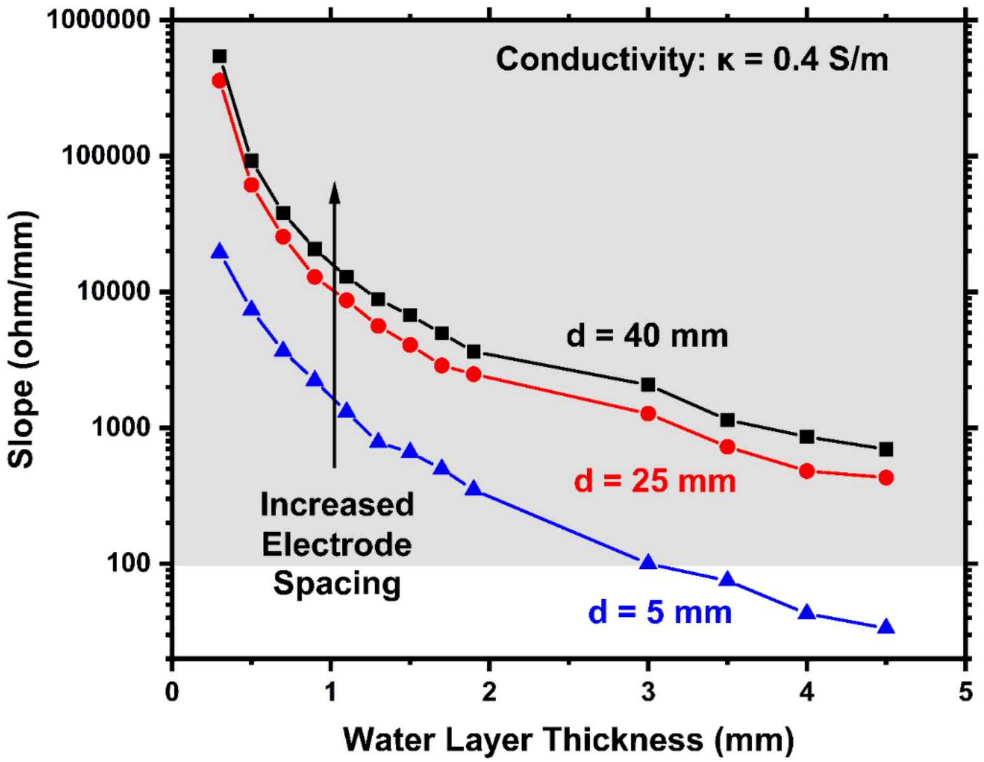
- Increasing the distance between electrode decreases the measured resistances





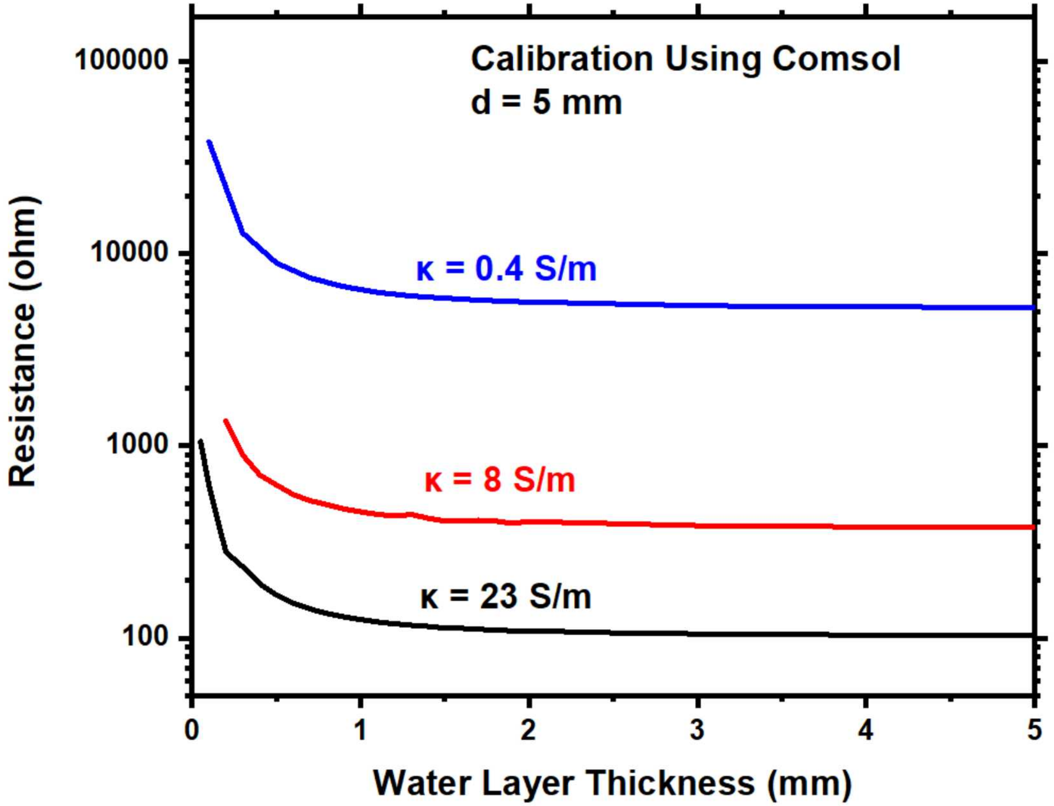
Wide electrode spacing provides highest sensitivity

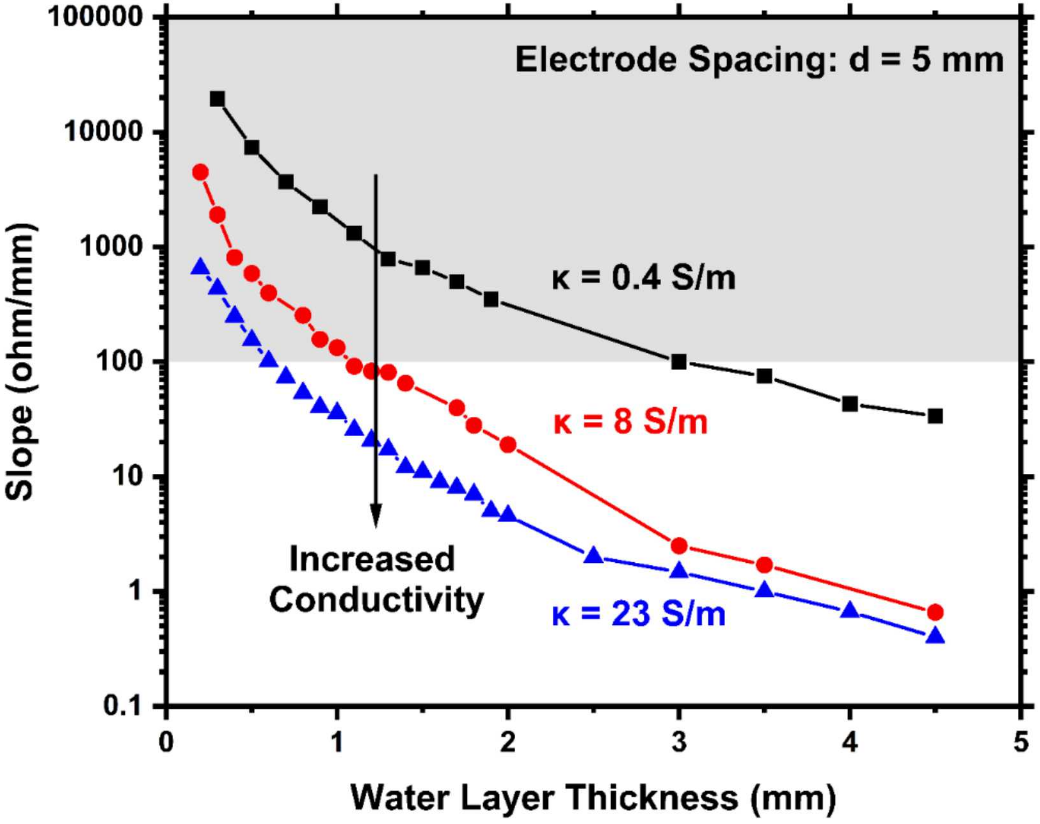




Dilute solutions provide highest sensitivity

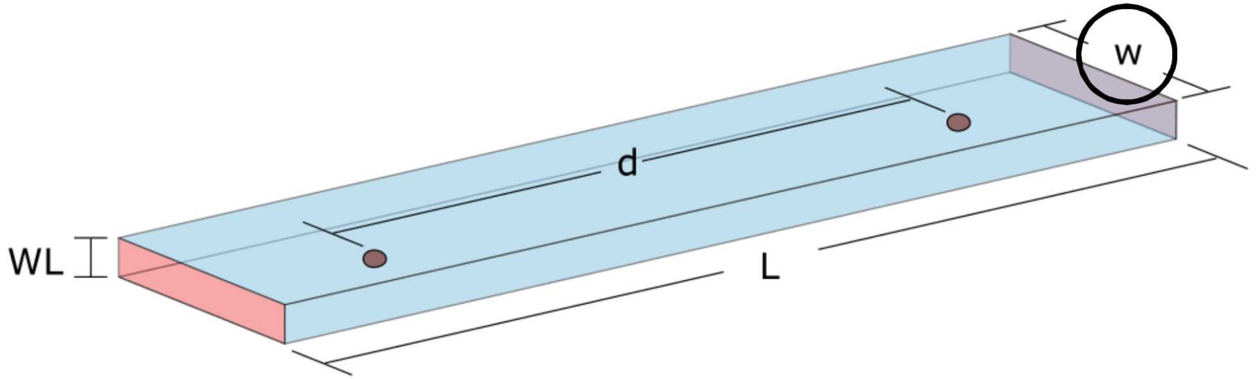
- Decreasing solution conductivity increases modeled resistances
- **Sensitivity is increased for dilute solutions**





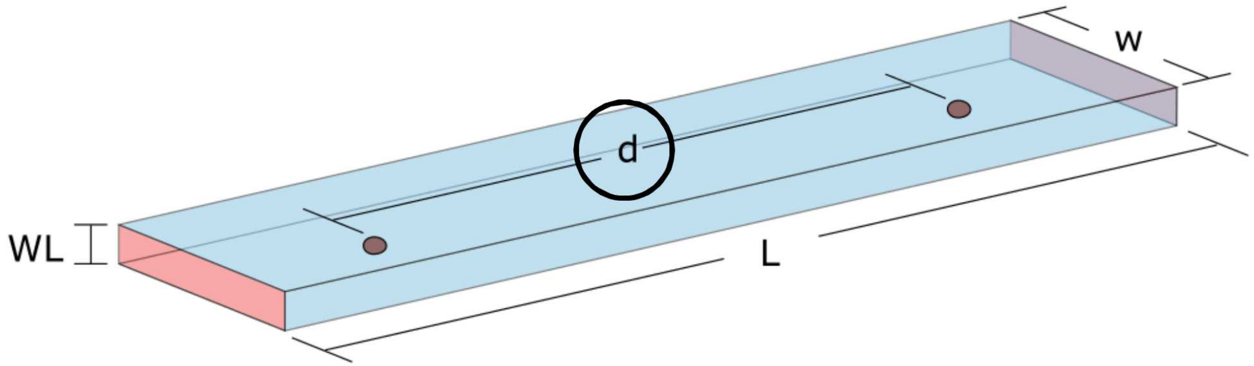
Best sensor qualities

- Small sensor width



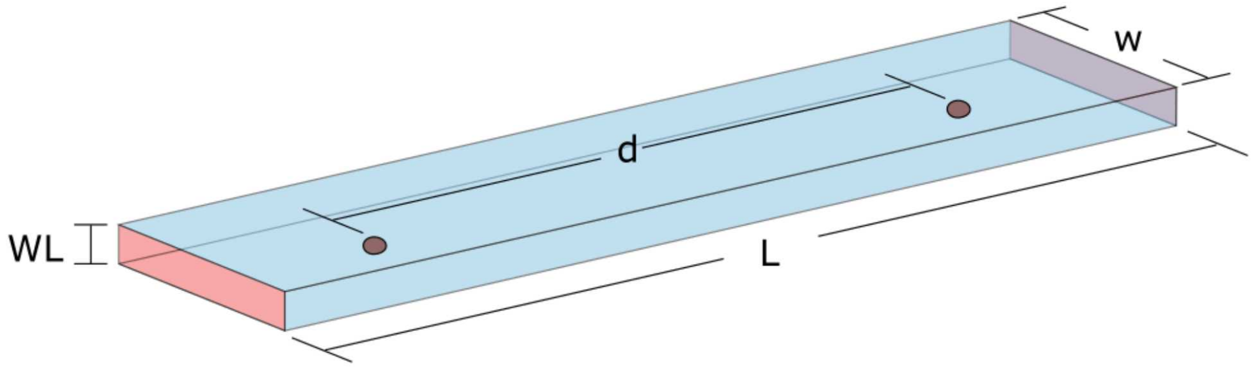
Best sensor qualities

- Small sensor width
- Large electrode spacing



Best sensor qualities

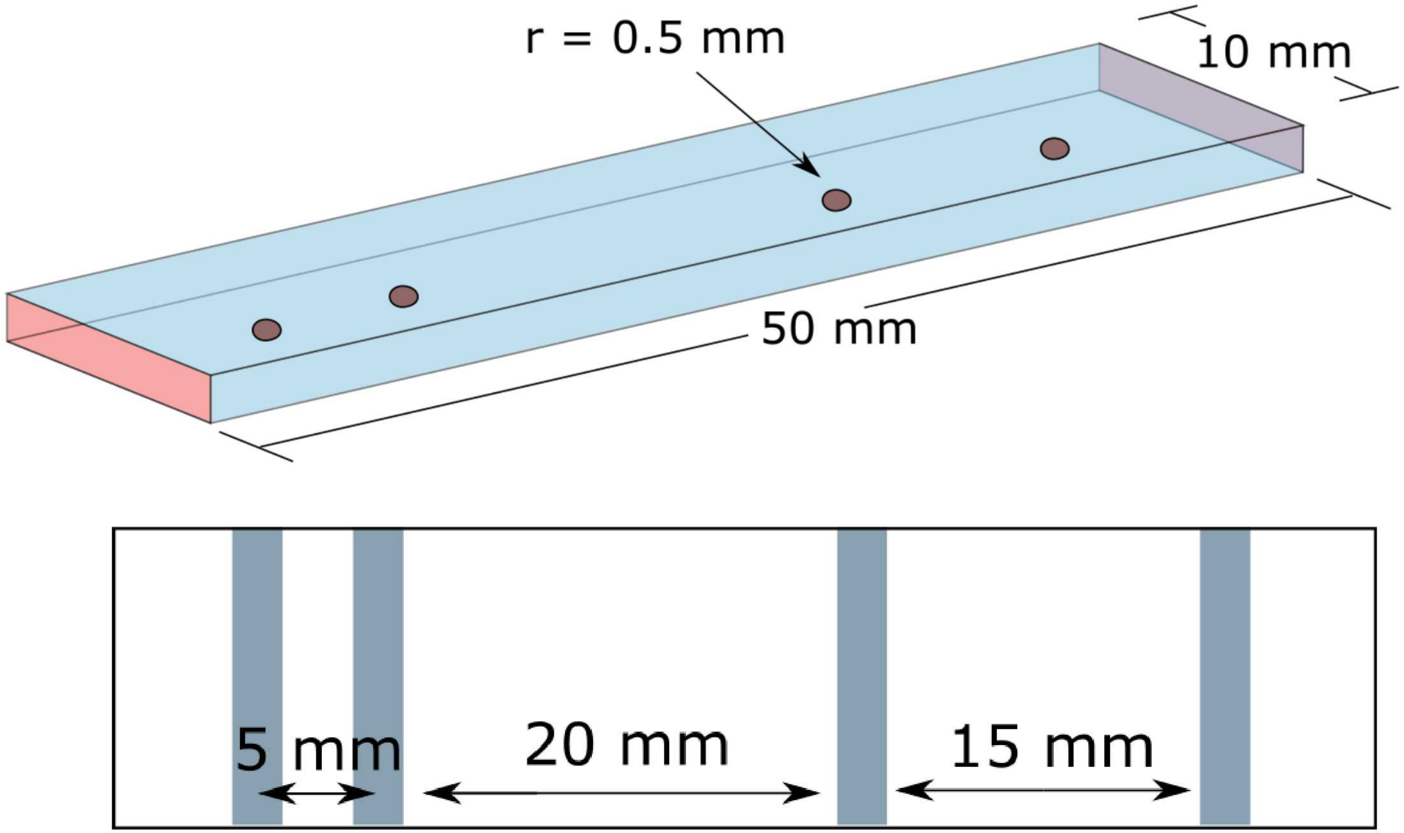
- Small sensor width
- Large electrode spacing
- Low conductivity solutions



- Several concerns related to the creation of a sensor:
  - Continuous WL formation
  - Influence of edge effects on WL formation (high angled meniscus)

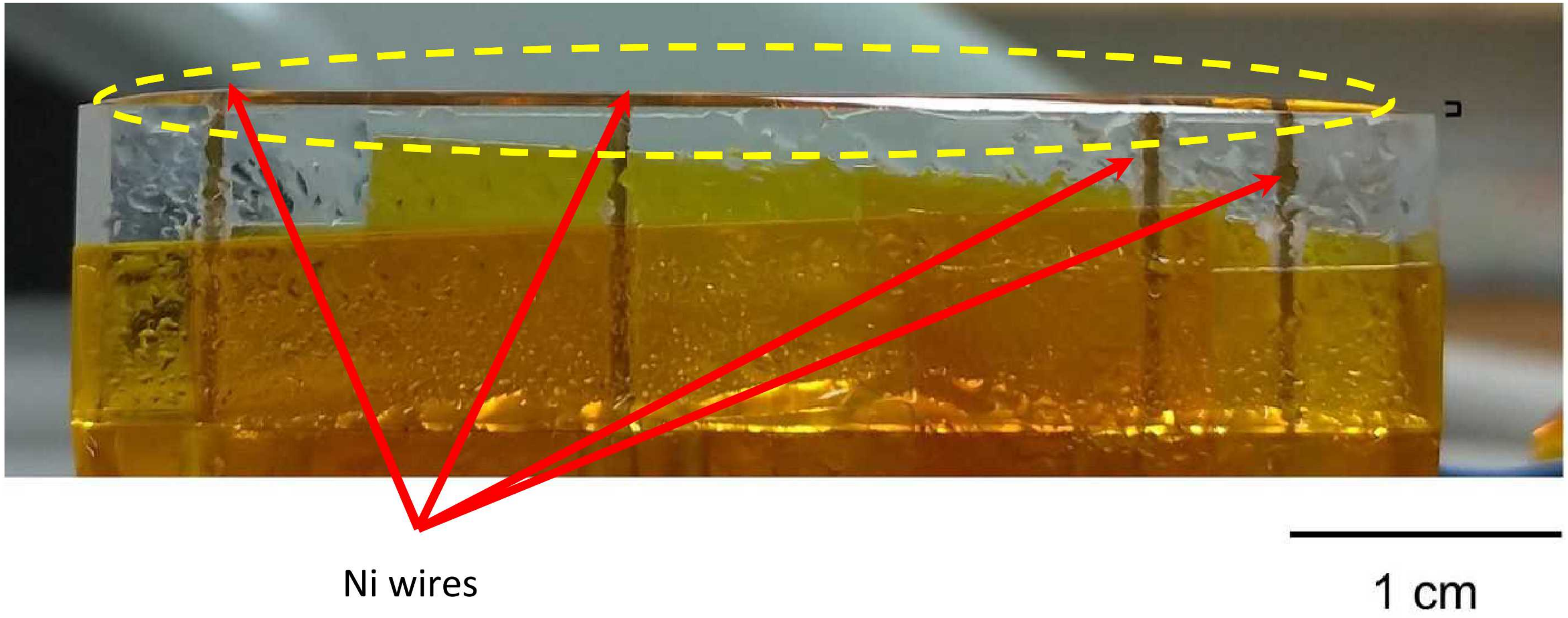
Final sensor dimensions

- Based on the FEM modeling, the sensor was created with the shown dimensions
- A variety of electrode spacings was created



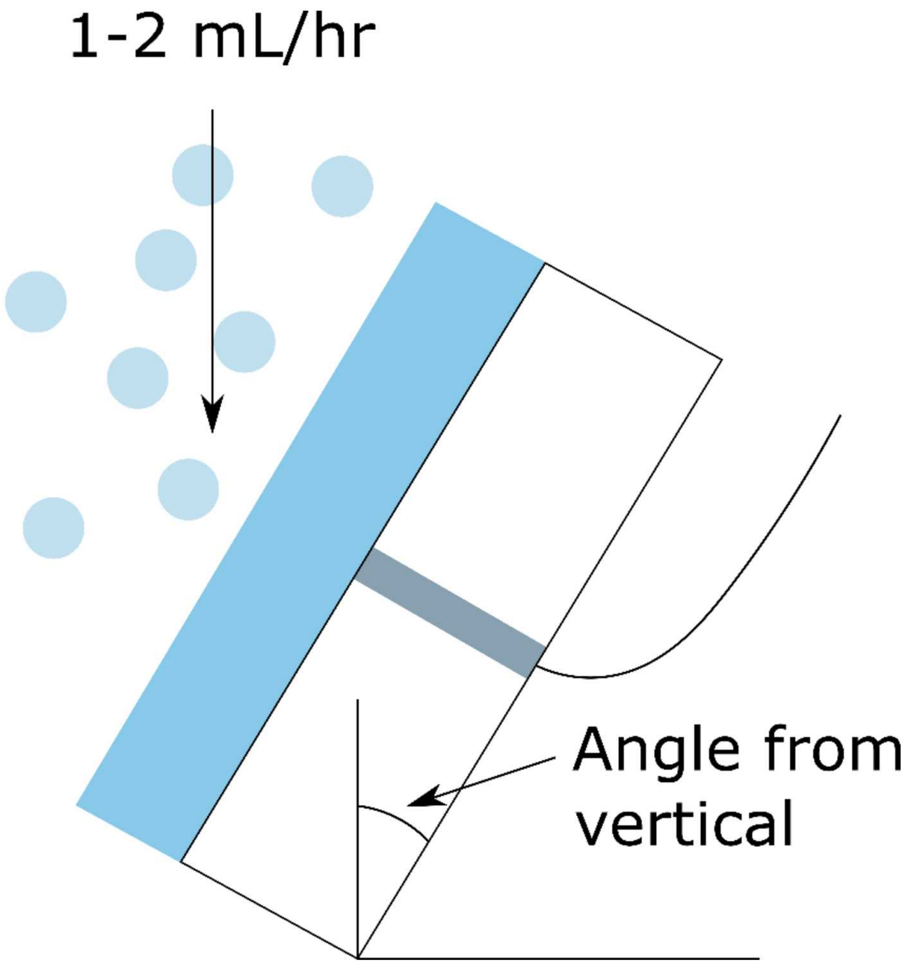
Created sensor

- To create the sensor, nickel wires were mounted in plexiglass
  - High conductivity nickel wires decreases influences to resistance measurements
- Wires electrically insulated to connect to external potentiostat



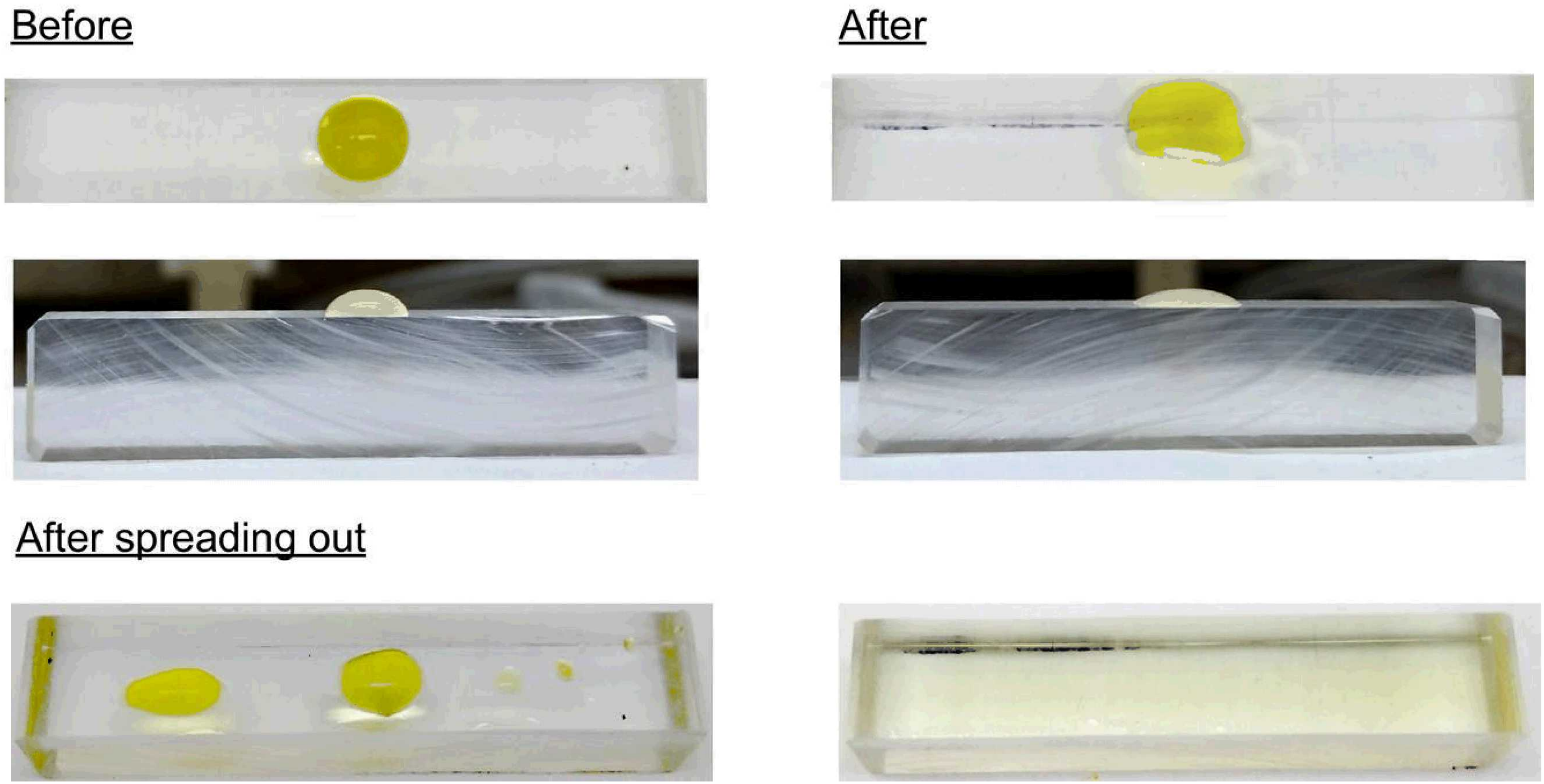
Experimental Approach

- Calibrations with known volume of liquid
  - Walled structure
  - Thin AAO membrane
- Continuous salt spray environment utilized
  - Various solution conductivities
- Extent of accelerated corrosion standards were explored
  - Deposition rate (ranging from 1-2 mL/hr)
  - Test interruptions
  - Angle of exposure



Experimental Approach

- In all experiments, the sensor was cleaned in a plasma cleaner for 1 hour, under 100 Watts in an oxygen-only environment

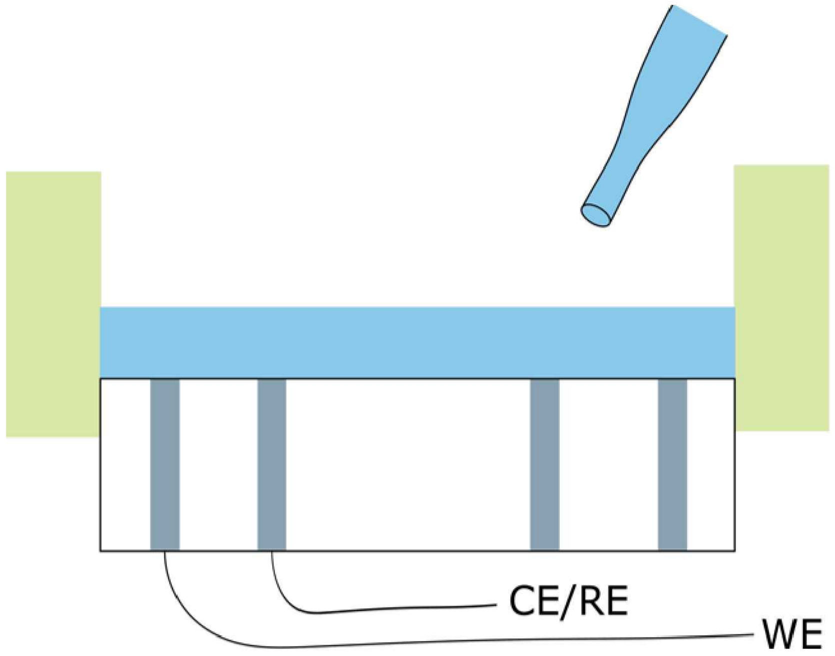


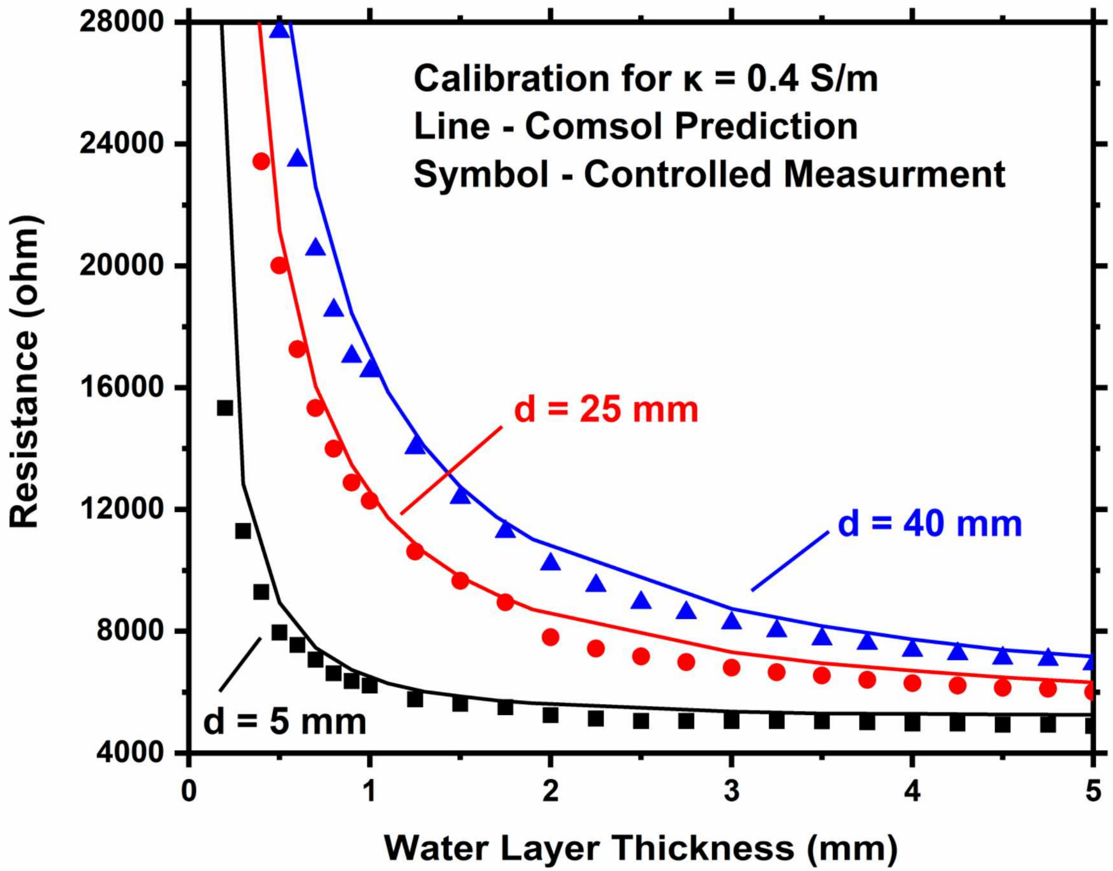
Experimental Approach

- High frequency EIS was utilized to determine WL thickness
- Frequency was scanned from 7MHz to 1kHz with six points per decade
- Sine waves of amplitude of 10 mV were applied about open circuit
- Each point was an average of 10 measurements

Calibration of Sensor

- Known volumes of solution were placed on top of the sensor
  - WL thickness calculated through known densities and exposure area

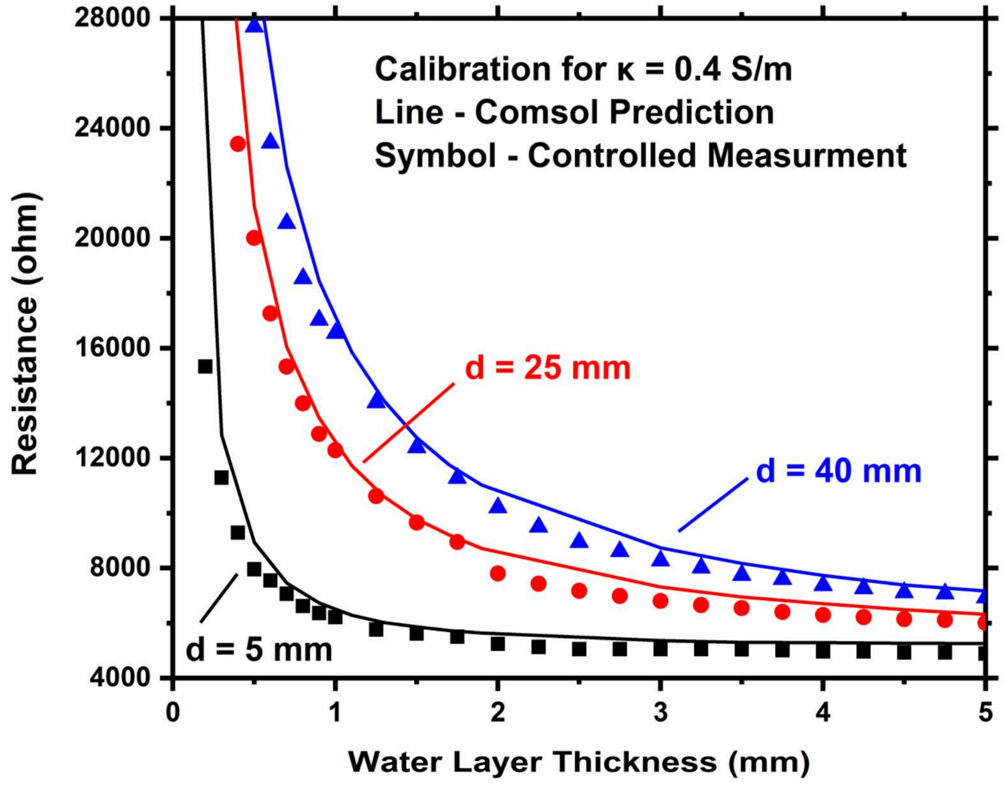


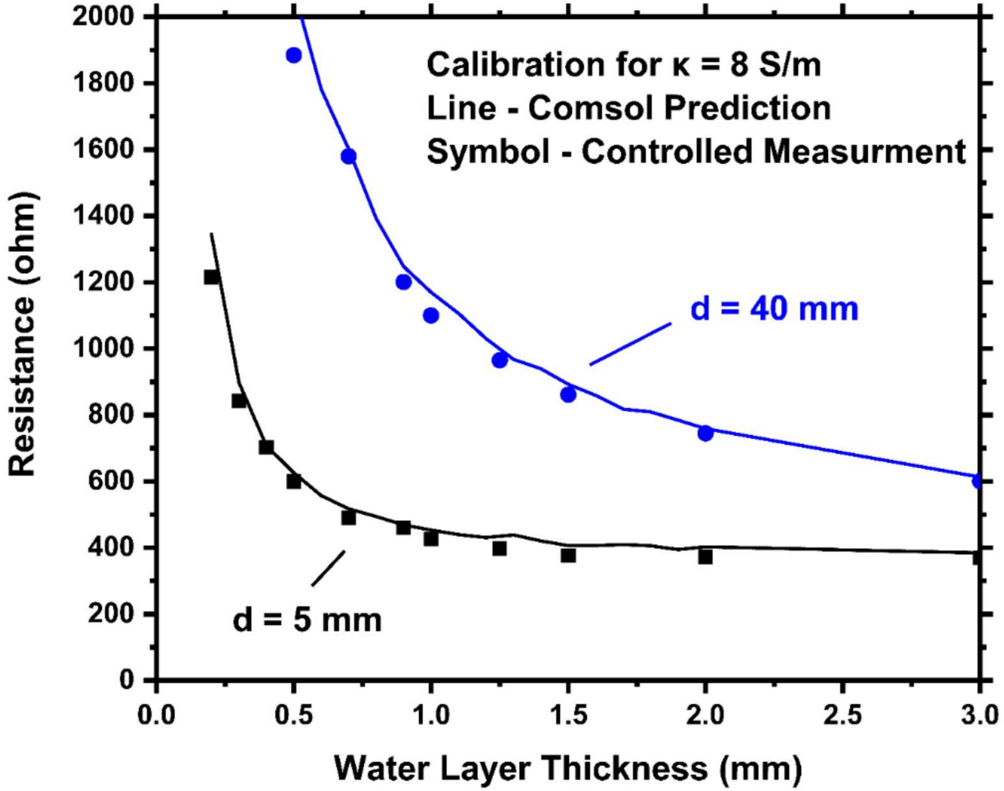


- Measured resistances match well with modeled resistances

Calibration of Sensor

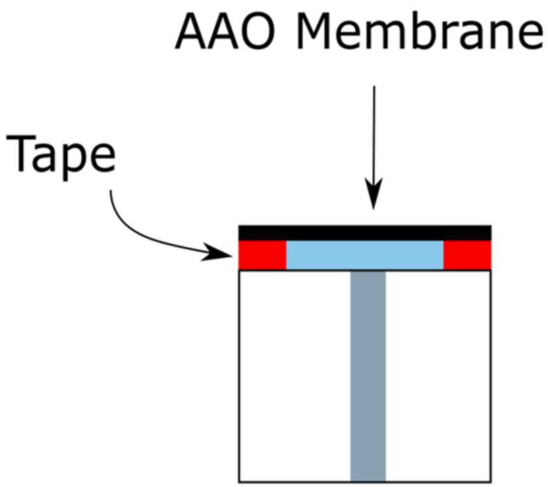
- Sensor efficacy shown across multiple solution conductivities and electrode spacings

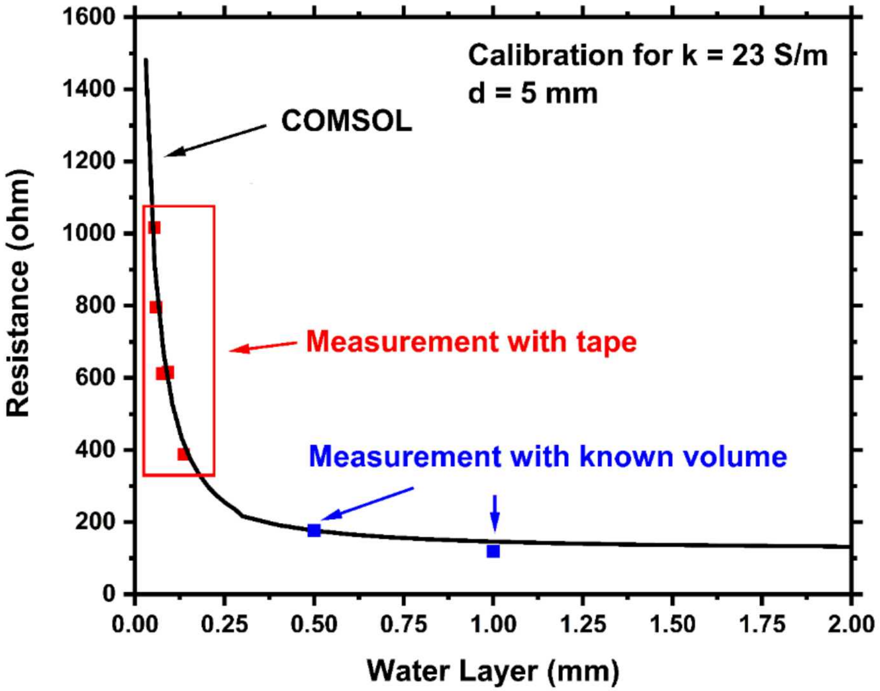


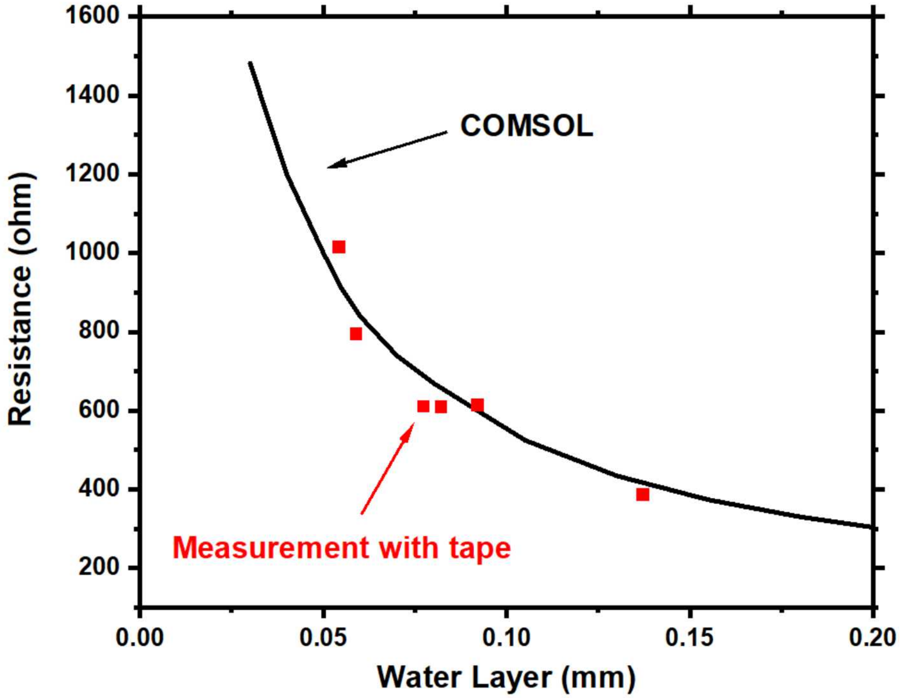


Calibration of Sensor

- Known tape thicknesses placed around edge of the sensor and an anodic aluminum oxide (AAO) placed on top
  - AAO was treated with trimethoxy(octyl)silane to increase the hydrophobic behavior



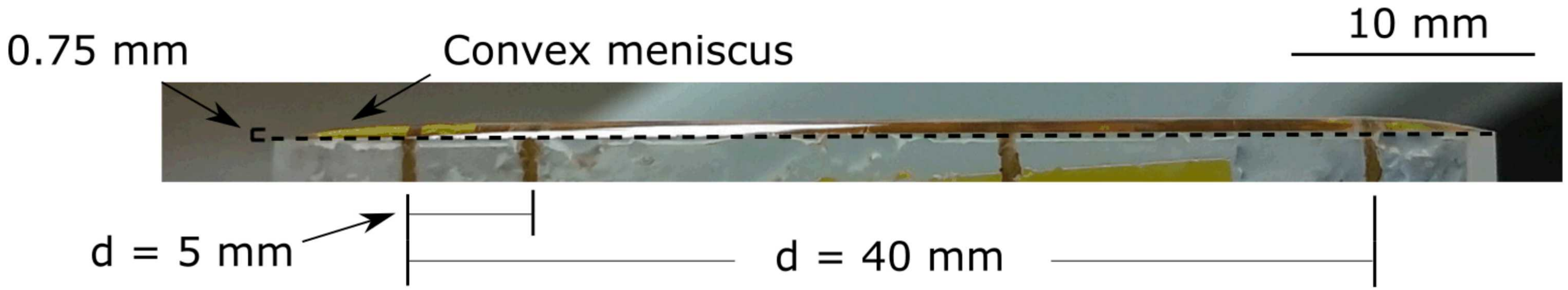




- Small water layer thicknesses also match well with modeled results
- Smaller error in resistances

Increased accuracy with membrane due to no meniscus

- Increased accuracy shown when using AAO membrane in comparison to known volume of liquid on surface
- Small convex meniscus seen when water layer present on the top of plexiglass

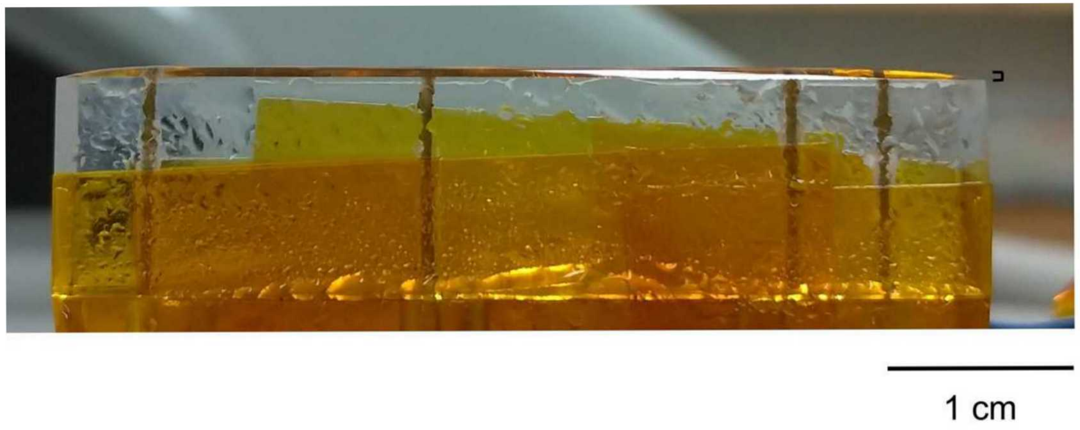


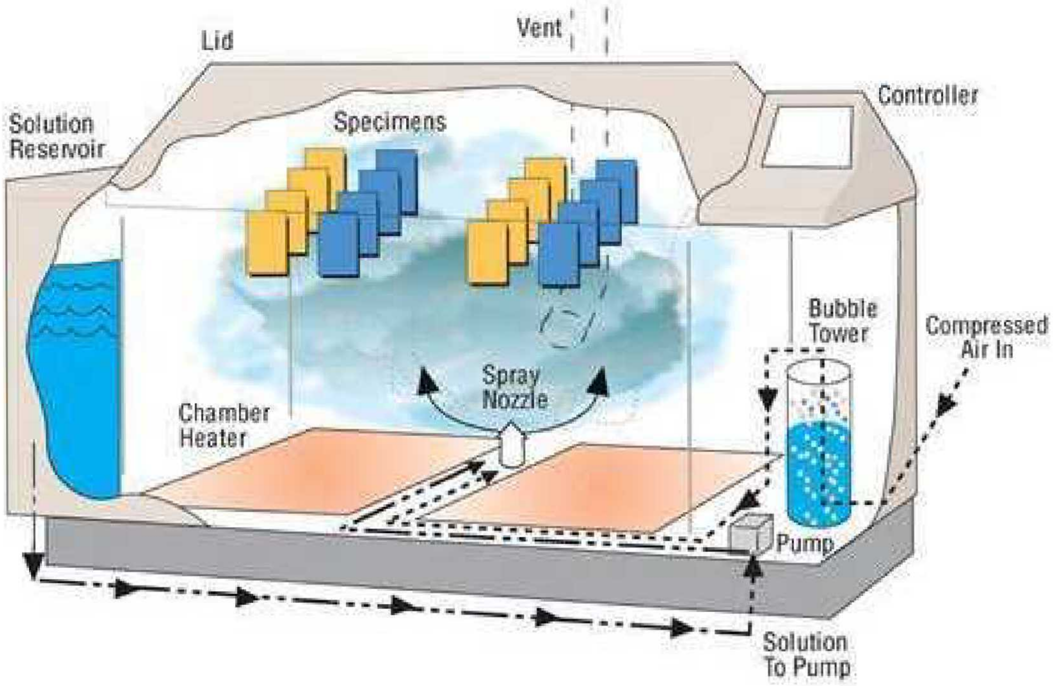
- Considering a simple parallelepiped, increased WL decreases R_s

$$R_s = \frac{L}{WL * w} * \frac{1}{\kappa}$$

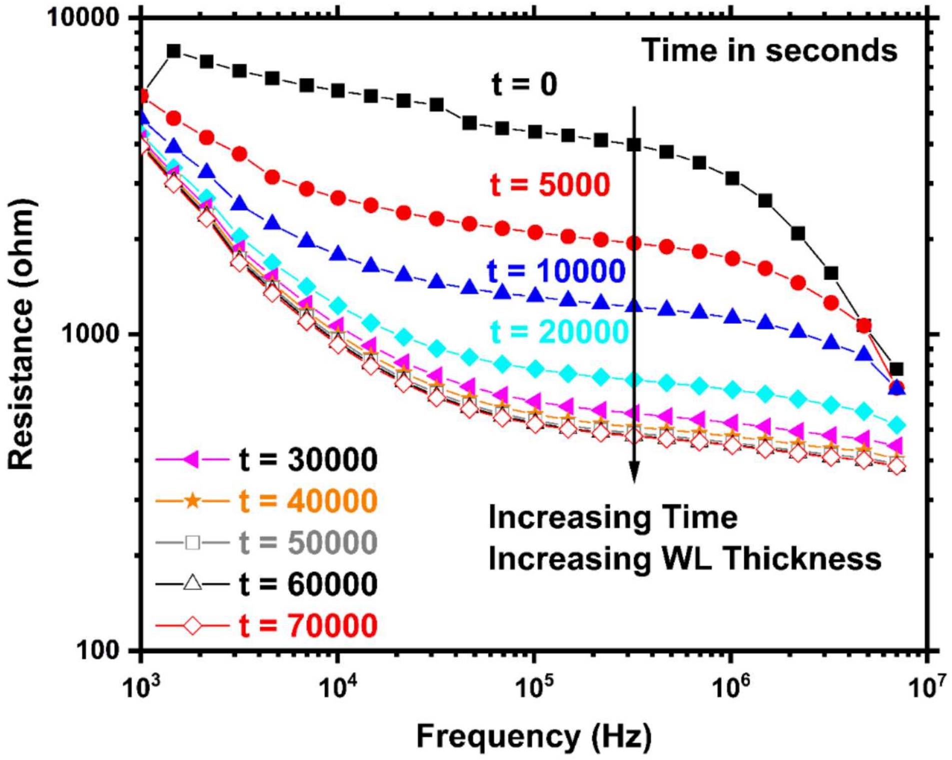
Application of sensor to salt spray test

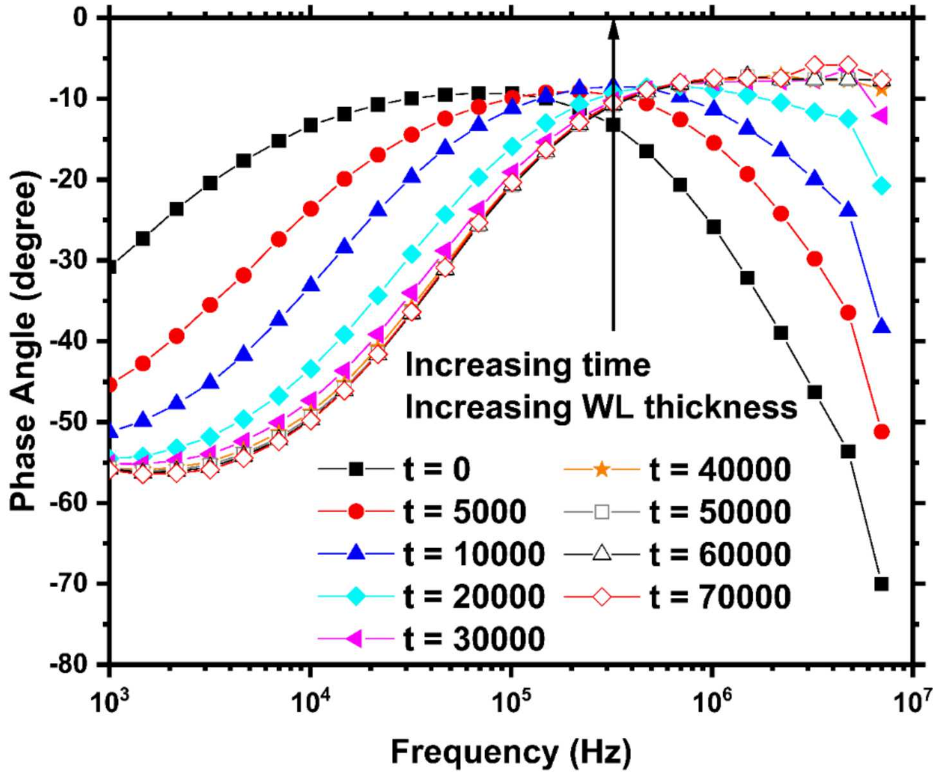
- Sensor placed in constant salt spray chamber to measure WL as a function of test parameters





Decreased in resistance with increased exposure time



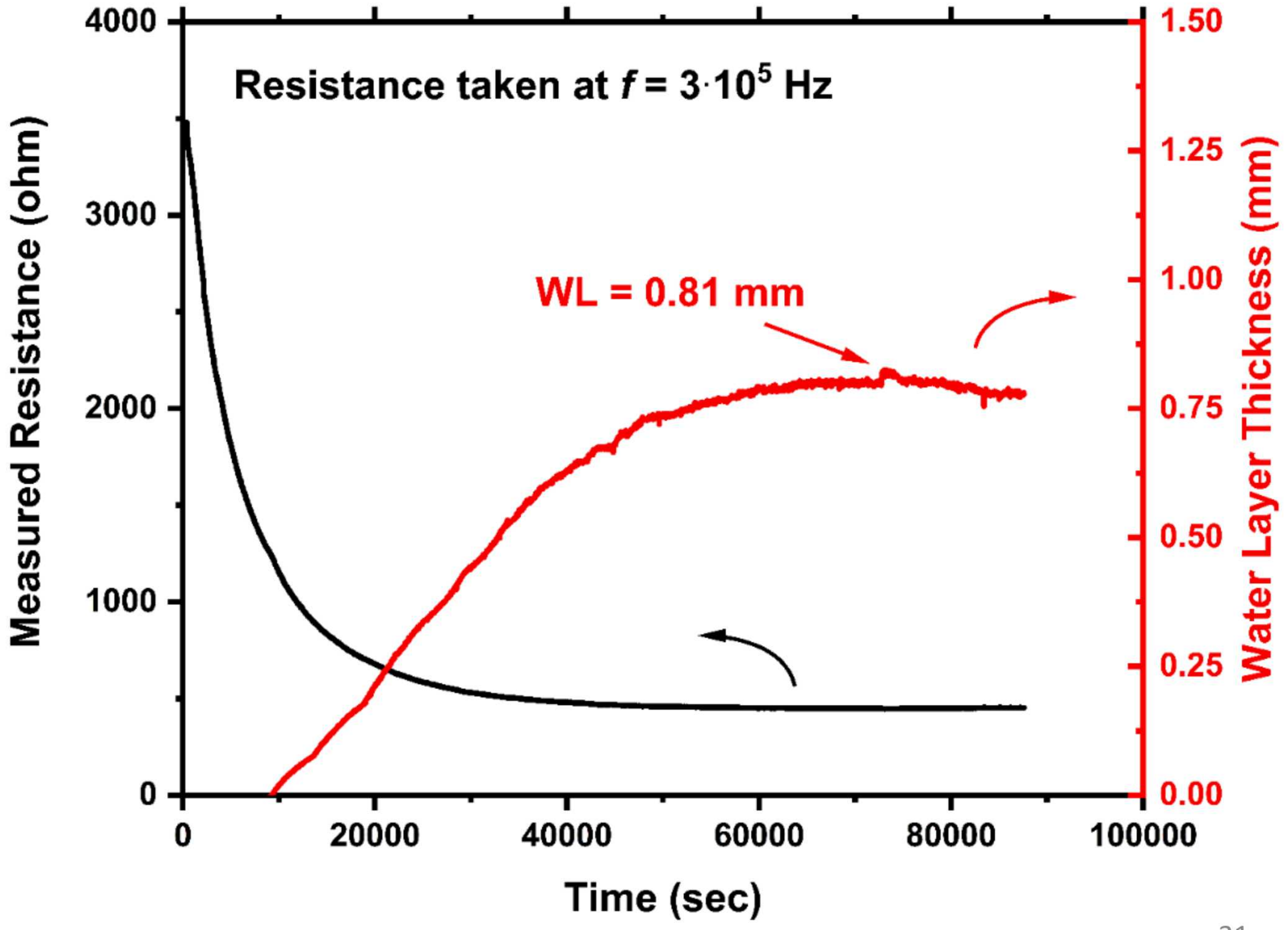


- Resistances were compiled at a relatively constant phase angle with time
- Initial rewetting of sensor took ~17 hr

Plateau in WL thickness at long exposure time

- EIS measurements taken at 0.6 M NaCl (κ = 8 S/m), 25 ˚C, and **angle of 20˚**

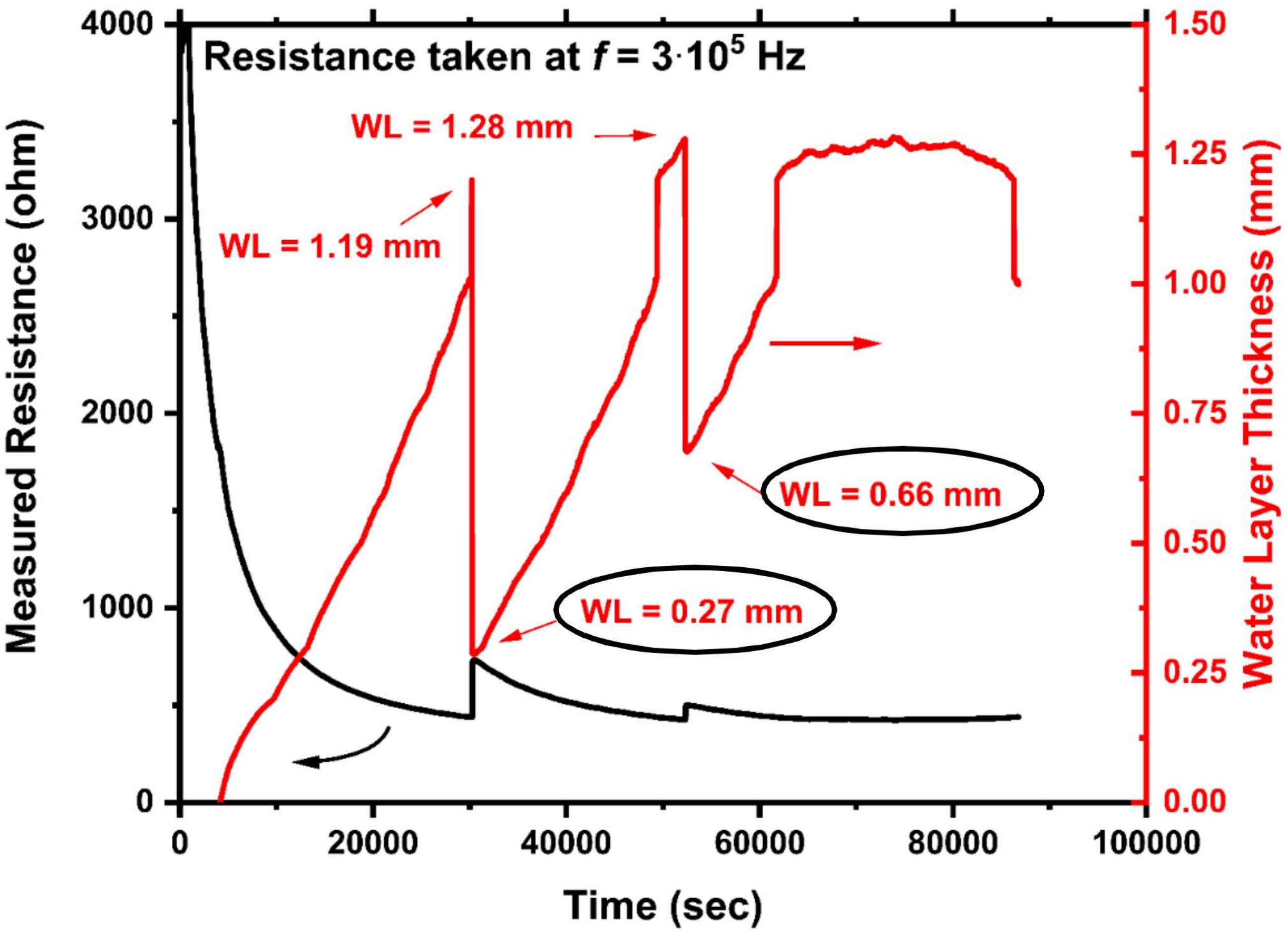
- Resistances evaluated as a function of time at a constant frequency showing a plateau
- WL thicknesses calculated based on calibration curve
- Roughly 17 hours needed to achieve steady state
- All measurements taken for at least 24 hours in chamber



Increased exposure angles cause semi-periodic run-off

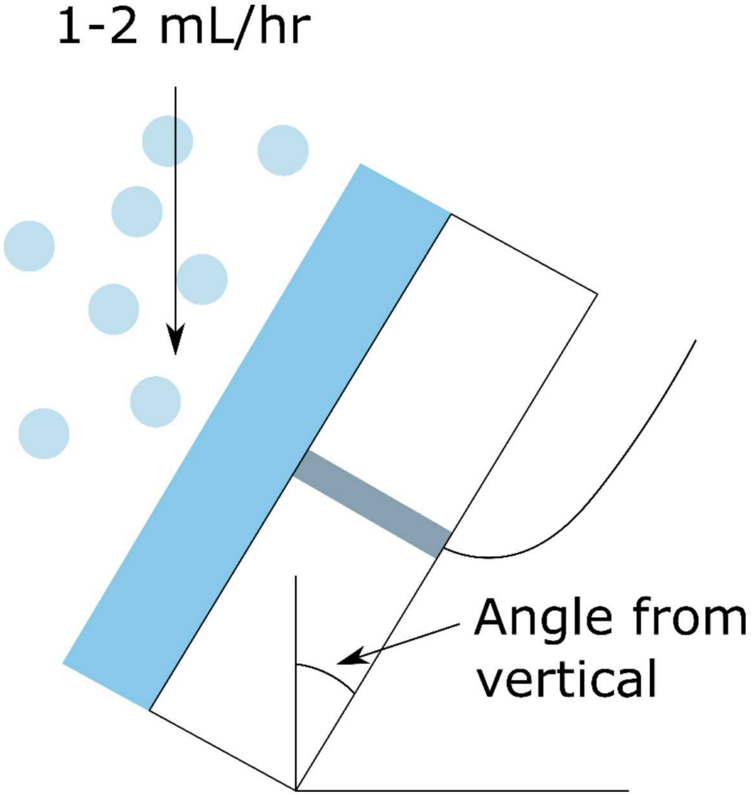
- EIS measurements taken at 0.6 M NaCl (κ = 8 S/m), 25 ˚C, and **angle of 30˚**

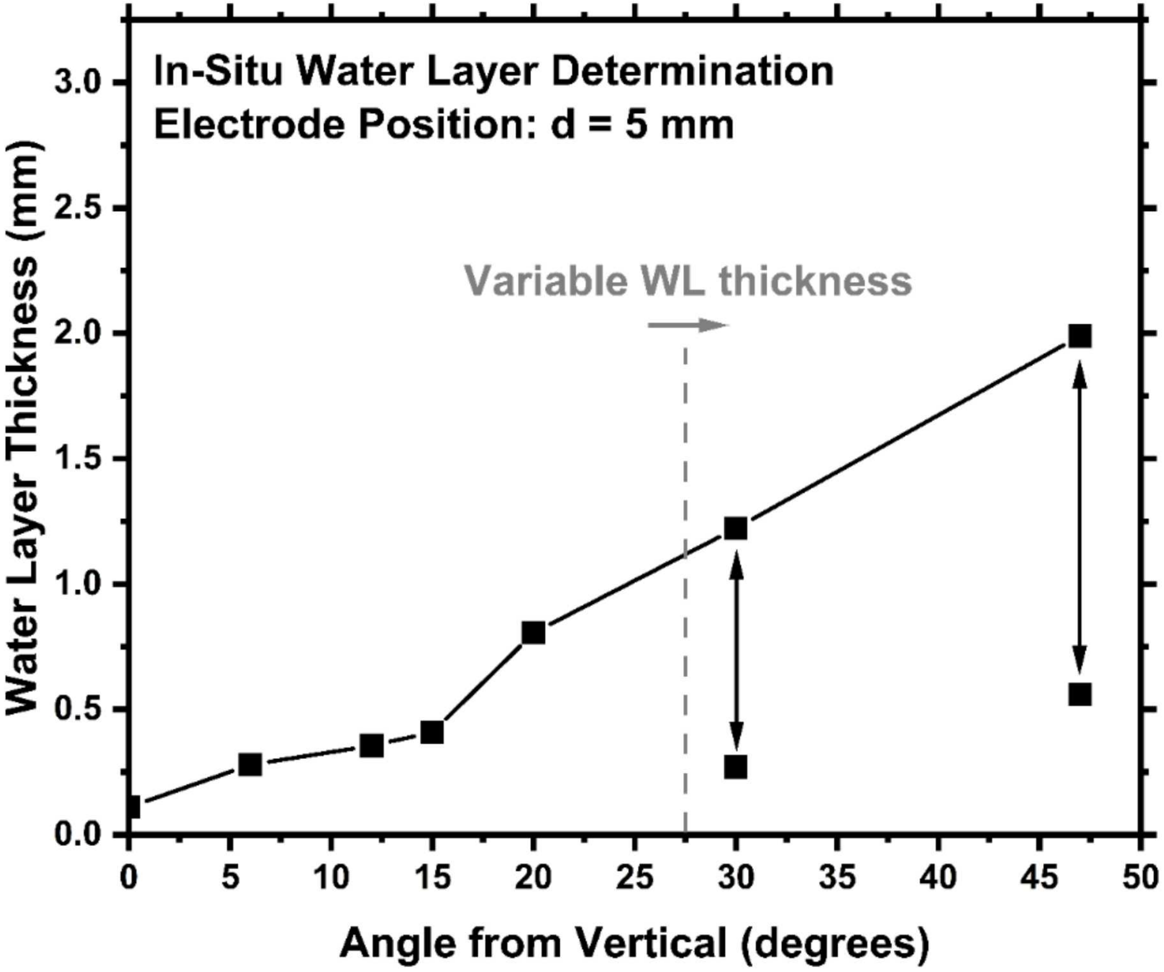
- Variable WL at increased angles of exposure
- Semi-periodic in nature
- Seen at angles larger than 20˚
  - Independent of κ or deposition rate
- Variable final WL thickness



Angle of exposure varies WL thickness significantly

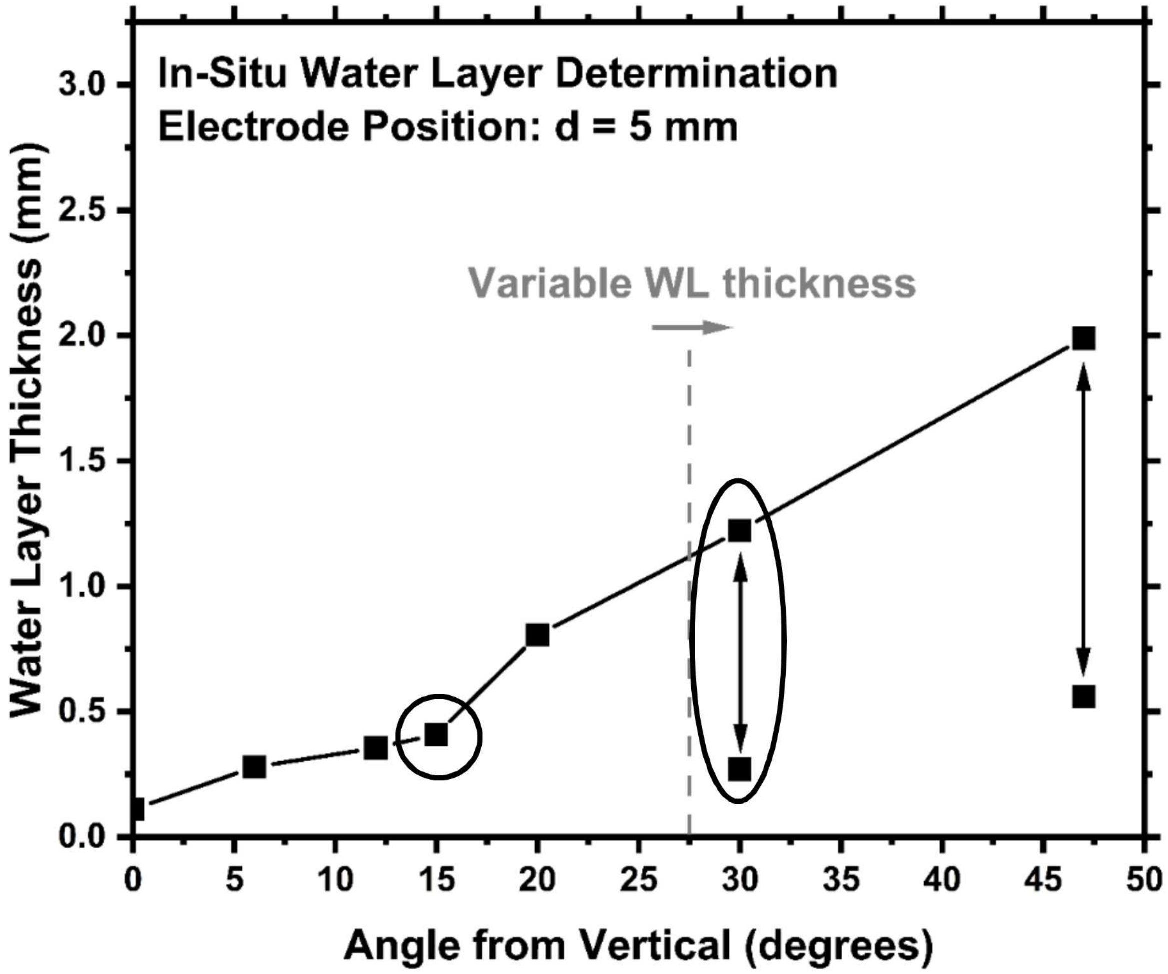
- Increasing angle of exposure increases WL thickness





Angle of exposure varies WL thickness significantly

- Increasing angle of exposure increases WL thickness
- Semi-periodic run-off above an angle of 20˚
- Within the realms of ASTM B117:
  - 15˚ = 0.4 mm
  - 30˚ = 1.25 mm (but variable)



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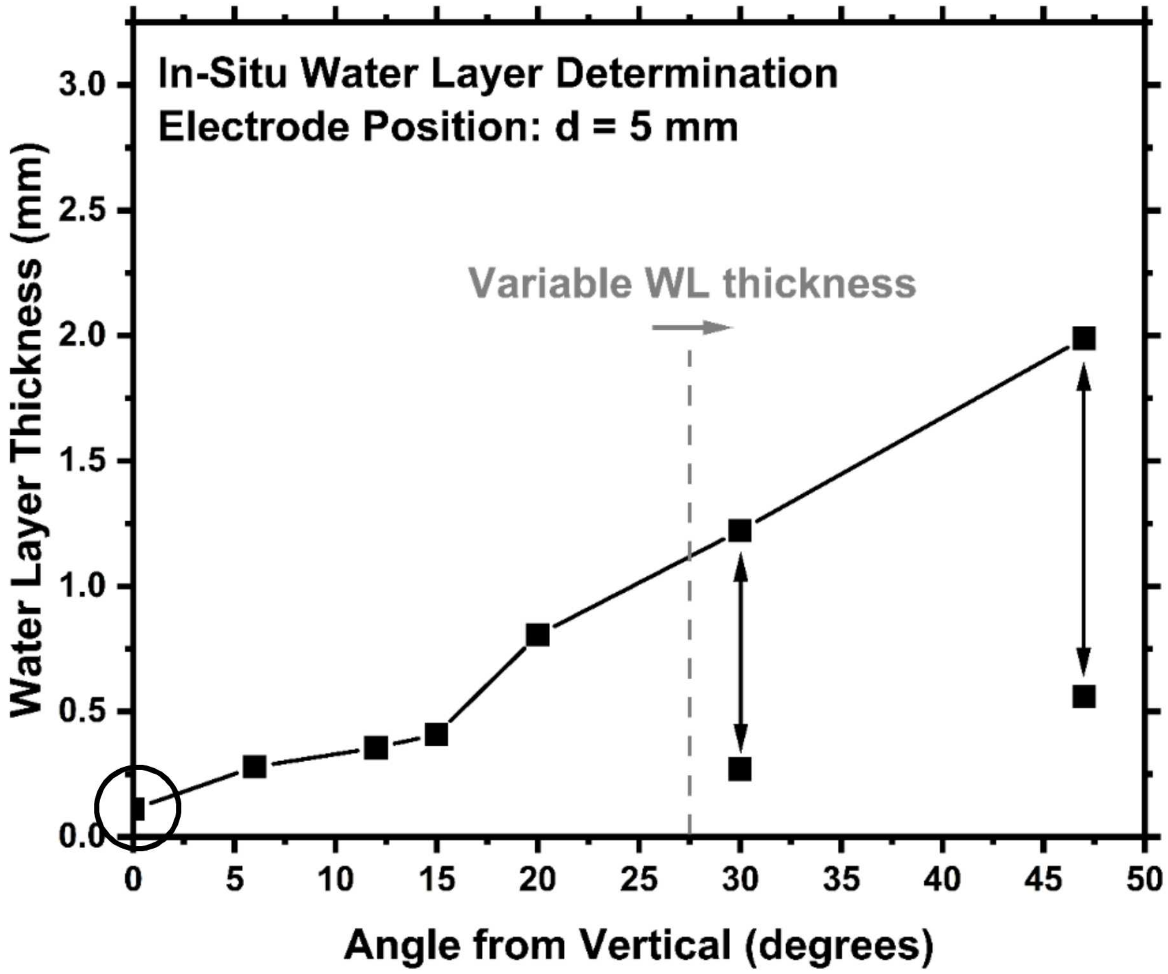
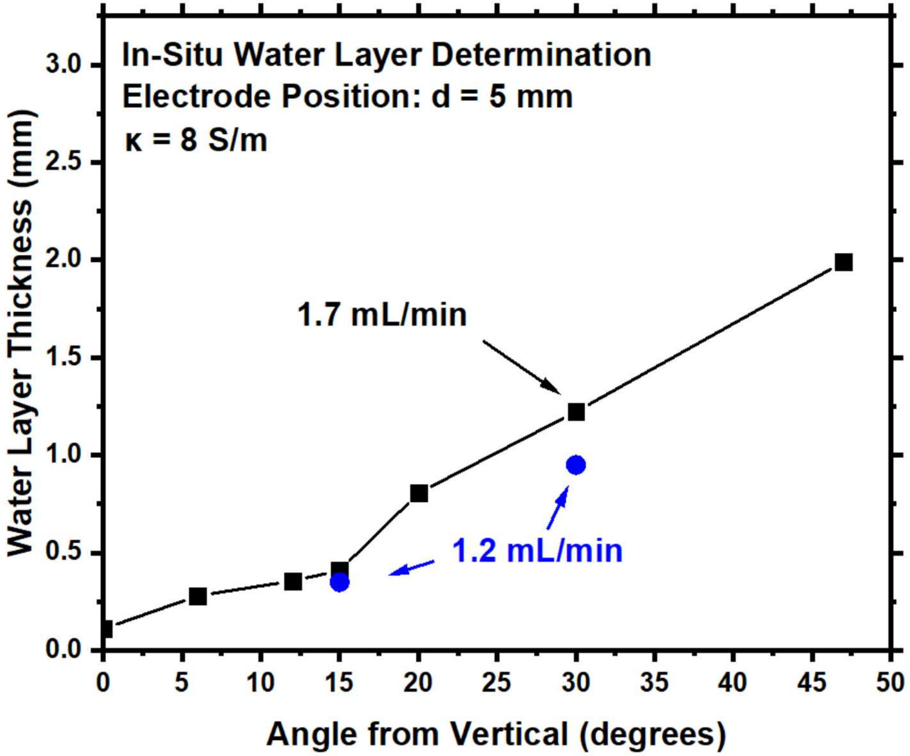
- Semi-periodic run-off about an angle of 20˚
- Within the realms of ASTM B117:
  - 15˚ = 0.4 mm
  - 30˚ = 1.25 mm (but variable)
- When completely vertical, a WL of 0.11 mm was detected



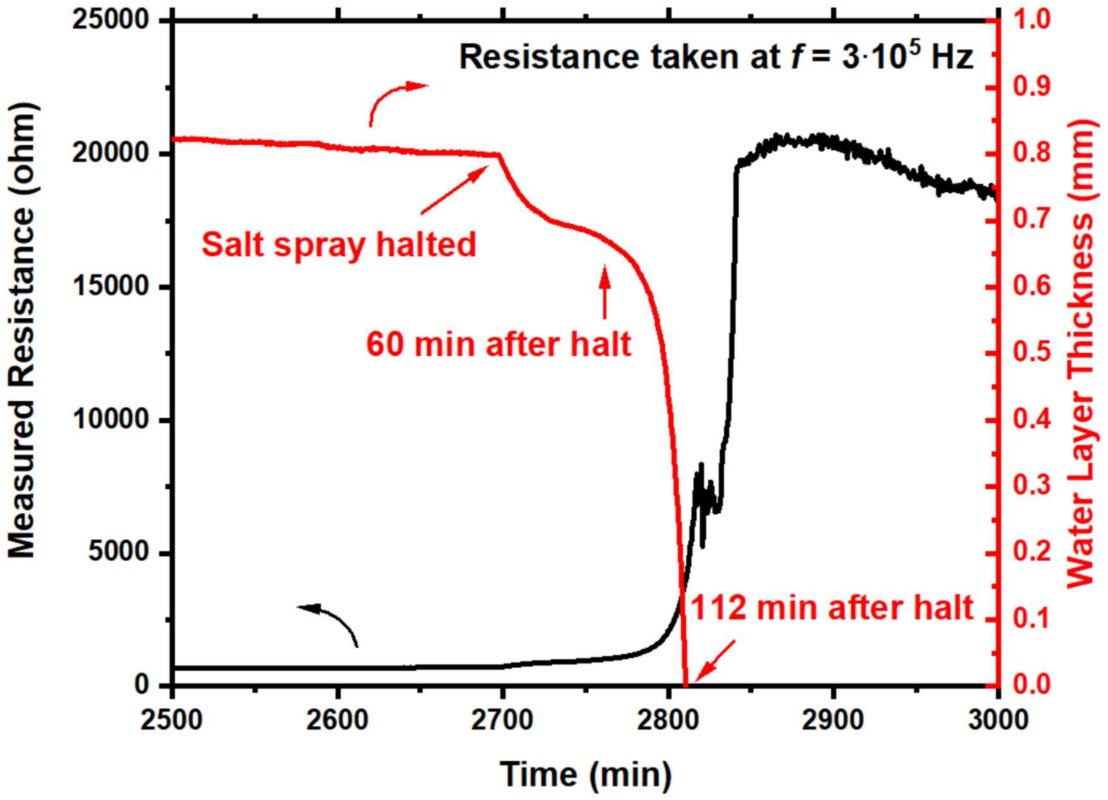
Deposition rate does not play a significant role in WL thickness



- Deposition rate does not appear to influence the WL significantly within ASTM standards

Evaporation occurs during shut-off periods

- Salt spray was stopped after roughly 45 hours of exposure and measurements were continuously taken
- Lid of chamber was left shut but fan started
- Within 1 hour of the shut-off, the WL thickness decreased 0.15 mm (18.5%)
- No WL after 112 min



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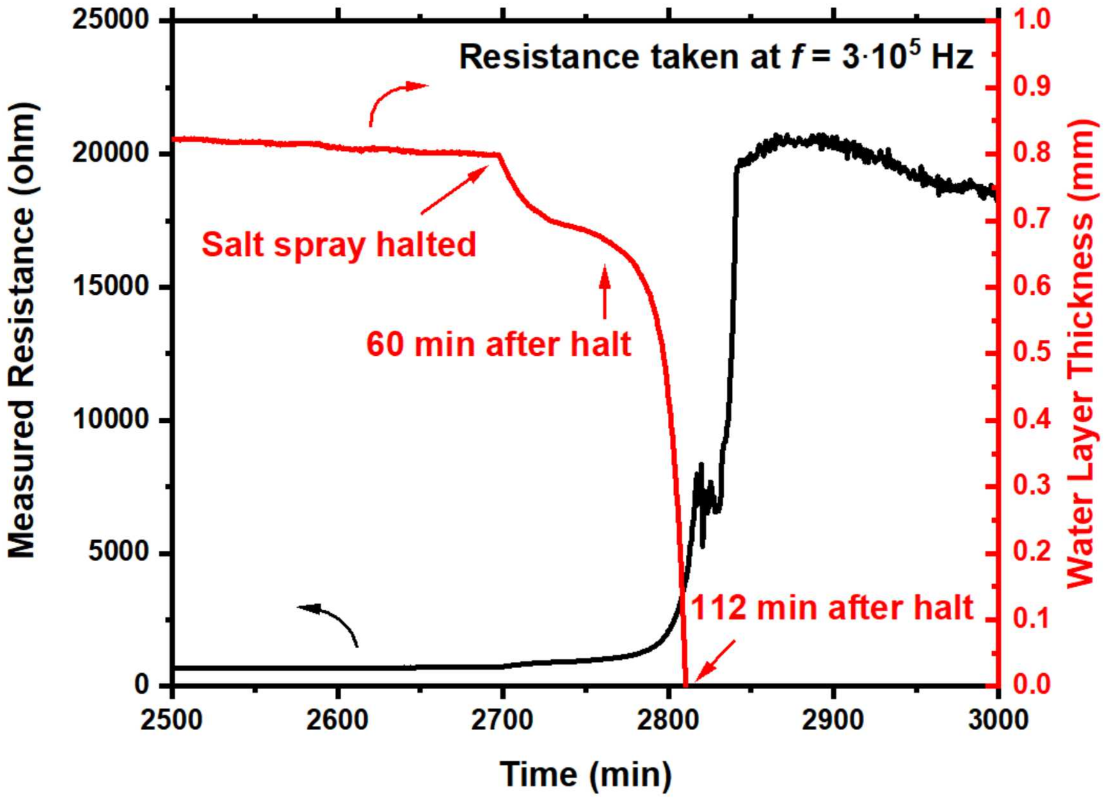
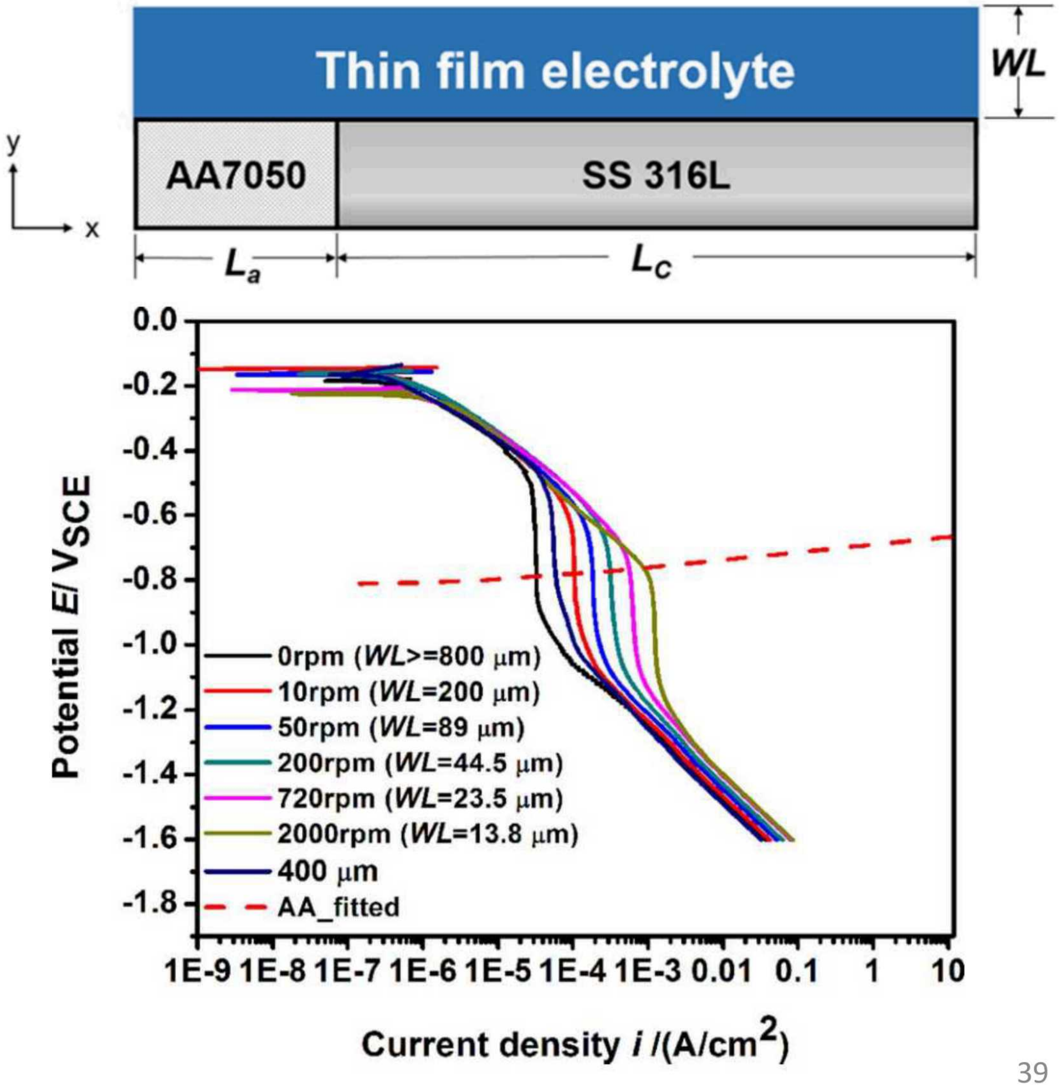


Angle of sample and test interruptions are allowable within ASTM standards can drastically influence WL thickness and corrosion rate

Water layer and cathode length impact cathodic current in a galvanic couple

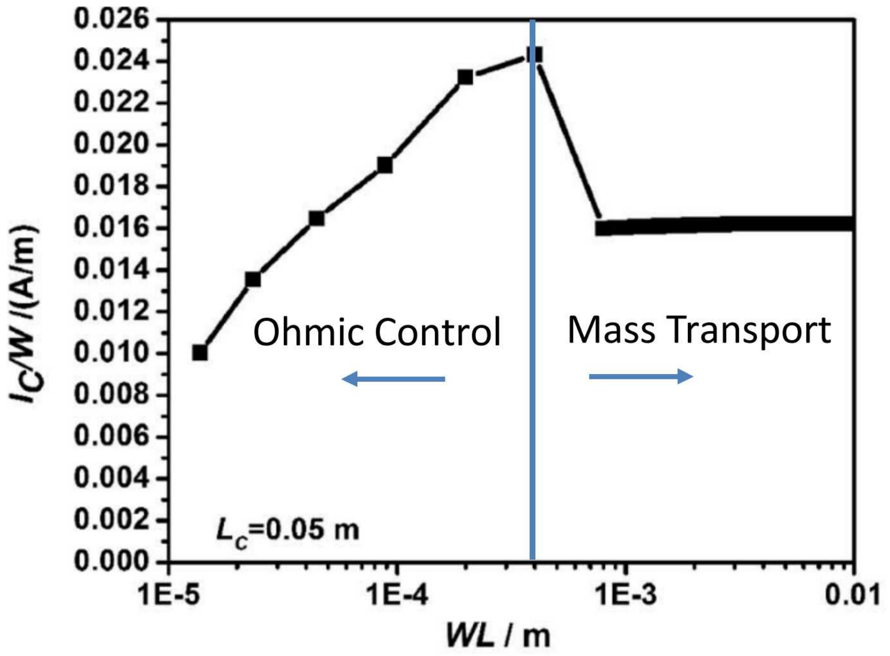
- Liu et al. determined current in a galvanic couple as a function of cathode length and WL thickness
- Determined cathodic kinetics using rotating disk electrode
- Determined anodic kinetics using CPP
- Used FEM to model currents
  - 0.6 M NaCl
  - 25 ˚C

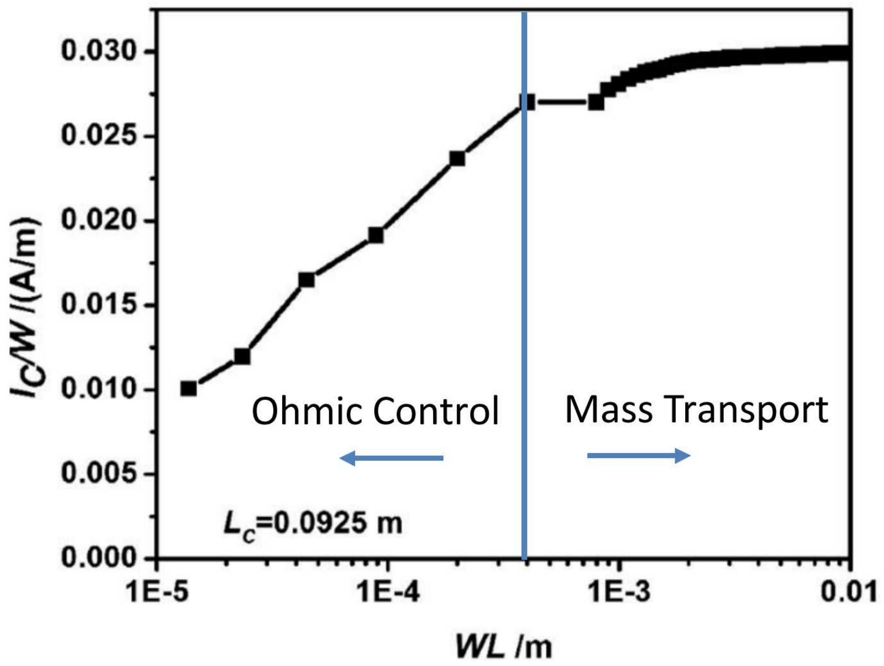


C. Liu et al., J. Electrochem. Soc. 164 (2017) C845–C855.

Water layer and cathode length impact cathodic current in a galvanic couple

- Both cathode size and WL influenced current available for dissolution
- Broadly, two regimes were found: (i) ohmic controlled region and (ii) mass transport regime

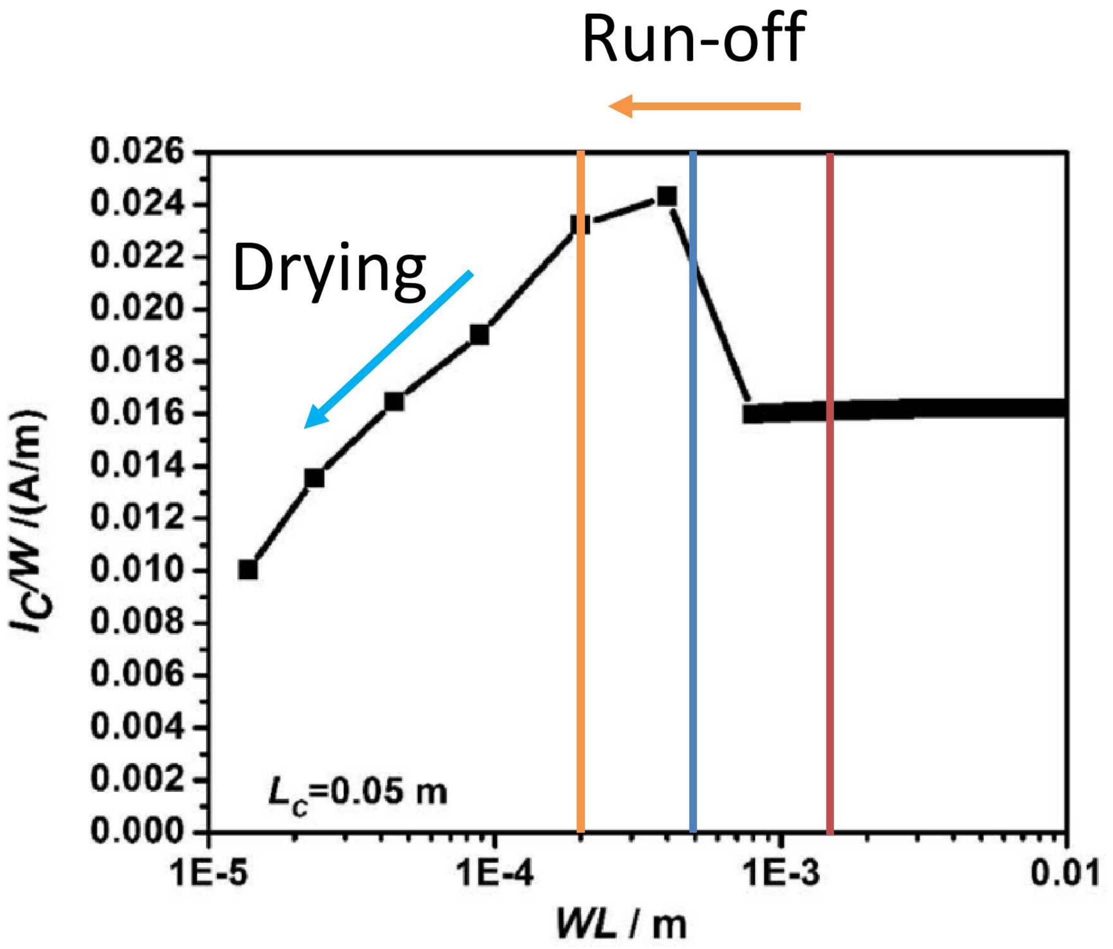




C. Liu et al., J. Electrochem. Soc. 164 (2017) C845–C855.

Water layer and cathode length impact cathodic current in a galvanic couple

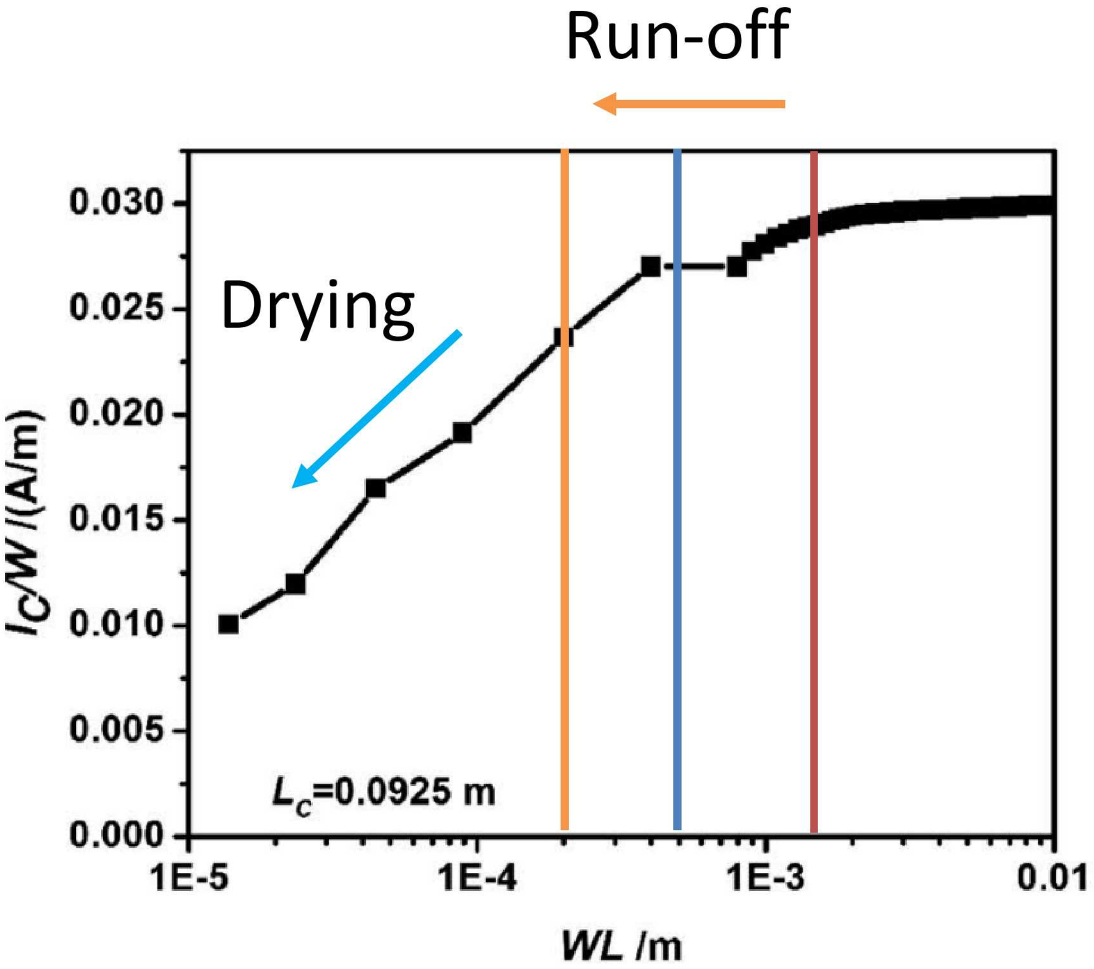
- Increased current seen at 15˚
- Mass transport limitations on current calculated at a WL corresponding to an angle of exposure of 30˚
- But remember, there is run-off at high angles of exposure
- Drying will further decrease WL and current



C. Liu et al., J. Electrochem. Soc. 164 (2017) C845–C855.

Water layer and cathode length impact cathodic current in a galvanic couple

- Highest current seen at an angle of exposure of 30˚
- Decreasing angle to 15˚ decreases current
- Run-off and drying further decrease current



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Water layer and cathode length impact cathodic current in a galvanic couple

- Highest current seen at an angle of exposure of 30˚
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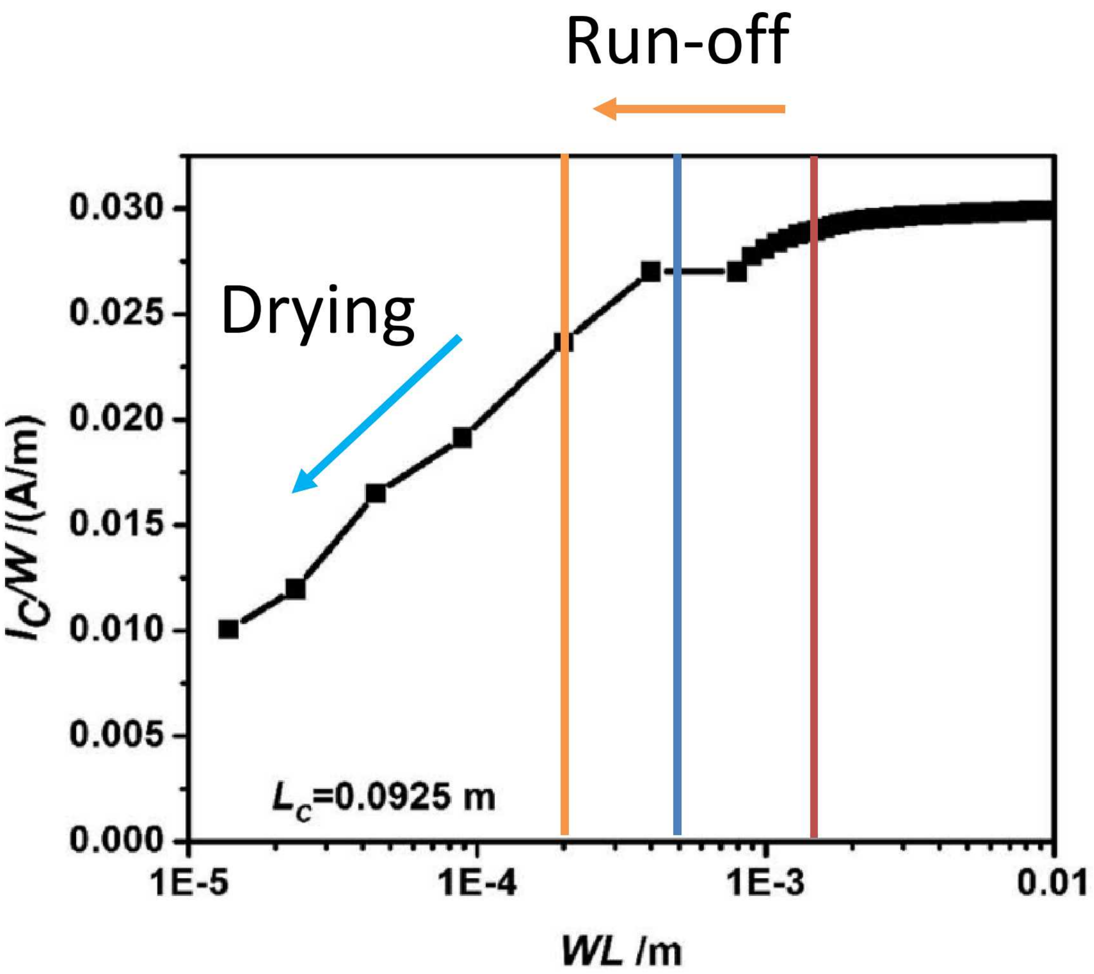
- Variations within ASTM accelerated standards can provide for varying currents, influencing extent of corrosion



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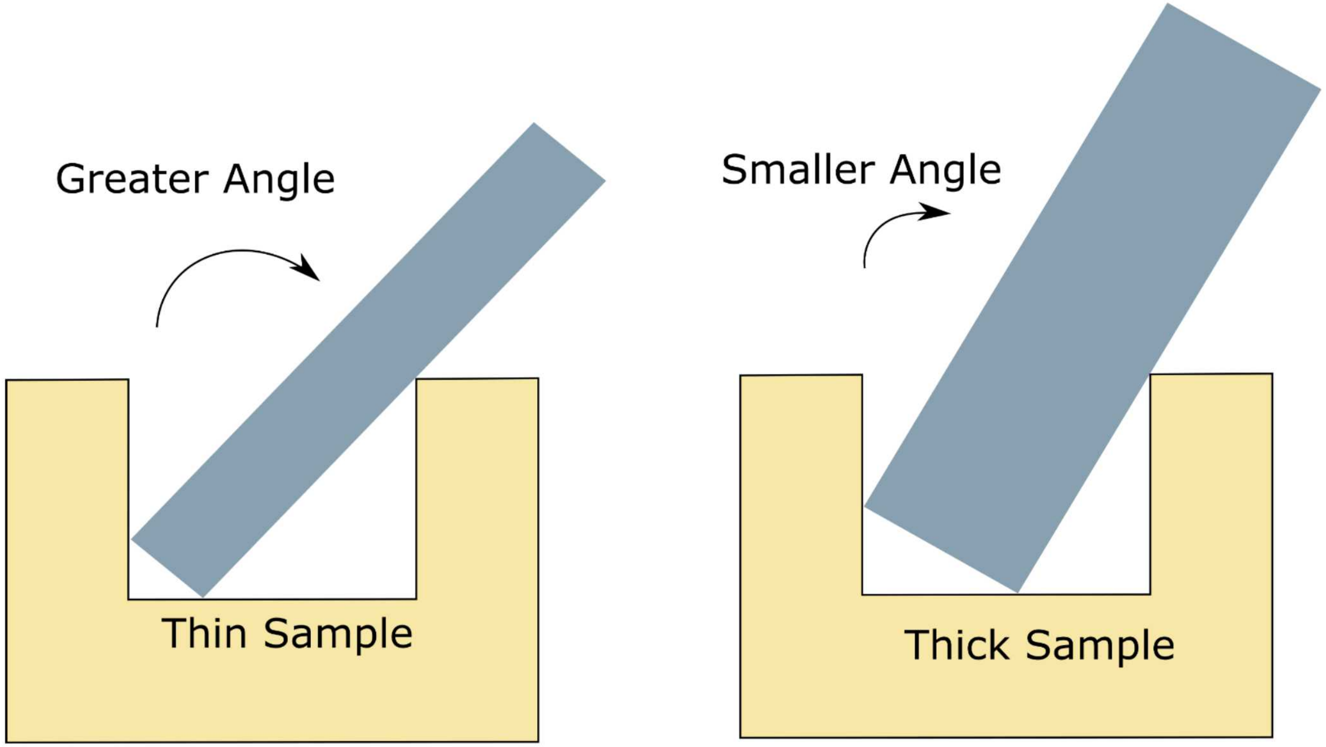
Influence on accelerated testing

- Within standards no guidelines or restriction on the slot width for the samples which will have an impact on the sample angle



- Need for consistency in standards to avoid test-to-test and chamber-to-chamber variability

Conclusions

- Design, construction, validation, and application of a sensor to determine WL thickness in the range of 0 to 5 mm in salt spray testing was presented
- Ideal dimensions for sensor were established with FEM
- Utility of the sensor was shown by measuring WL thickness in a continuous salt spray test similar to ASTM B117
  - Angle of exposure plays the largest role in WL thickness
  - Semi-periodic solution run-off experienced at angles > 20˚
- Angle of sample exposure in salt spray environments determines if thin film conditions are achieved
- Need for tighter standards in accelerated testing

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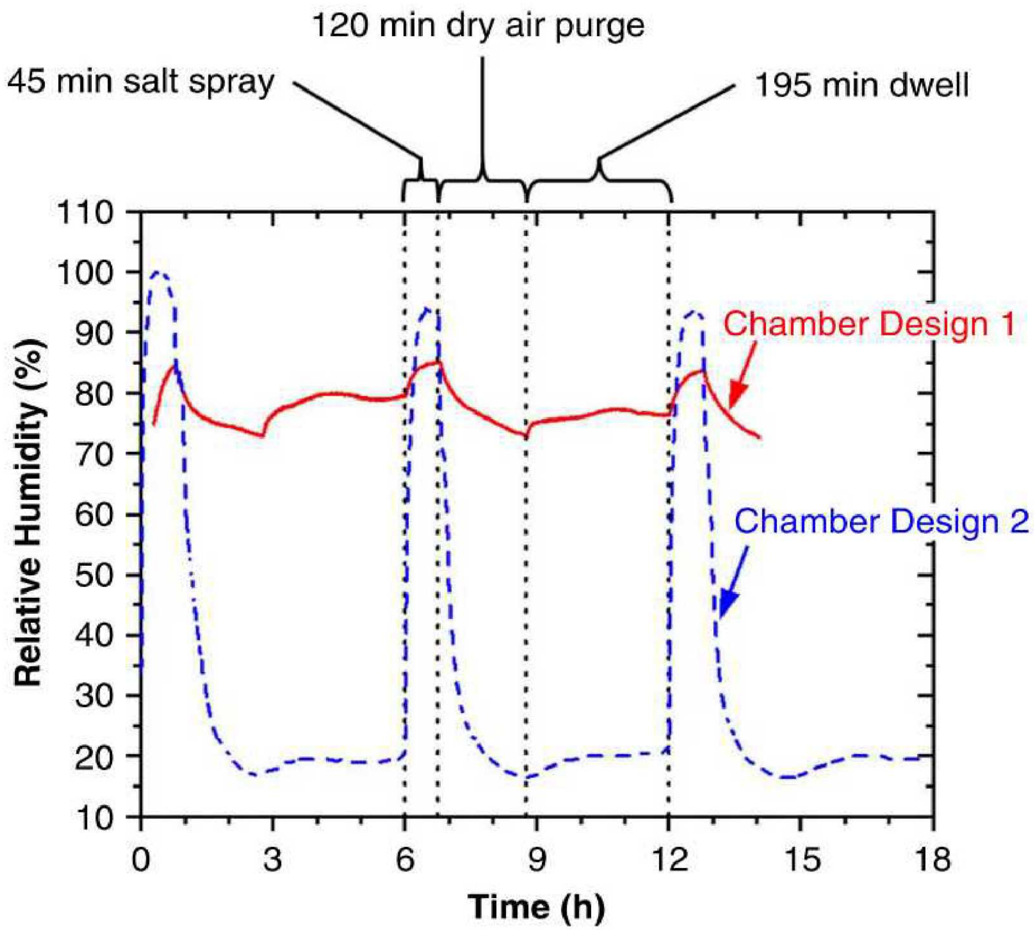
Future Work

- Creation of sensor to account for variable conductivity



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