

The Corrosion of Electrocoated Steel Studied by a Combination of Accelerated Exposure and Electrochemical Methods

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Acknowledging the contributions from:

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Accelerated corrosion tests vs electrochemical techniques

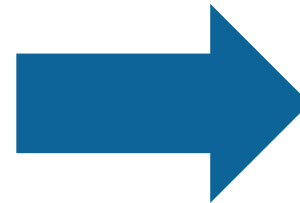
Accelerated corrosion tests

- Use elevated RH, corrosive solutions, elevated T etc. to accelerate corrosion
- Static (B117, HSW) or cyclic (SAE J2334, VDA 233-102...)
- Typical analysis:
Assessment of cosmetic corrosion in 1 or 2 dimensions



Issues:

- Confounding of multiple experimental variables
- Effects of different coating properties are confounded
- Different tests can rank coatings differently
- Interpretation of corrosion mechanisms can be difficult



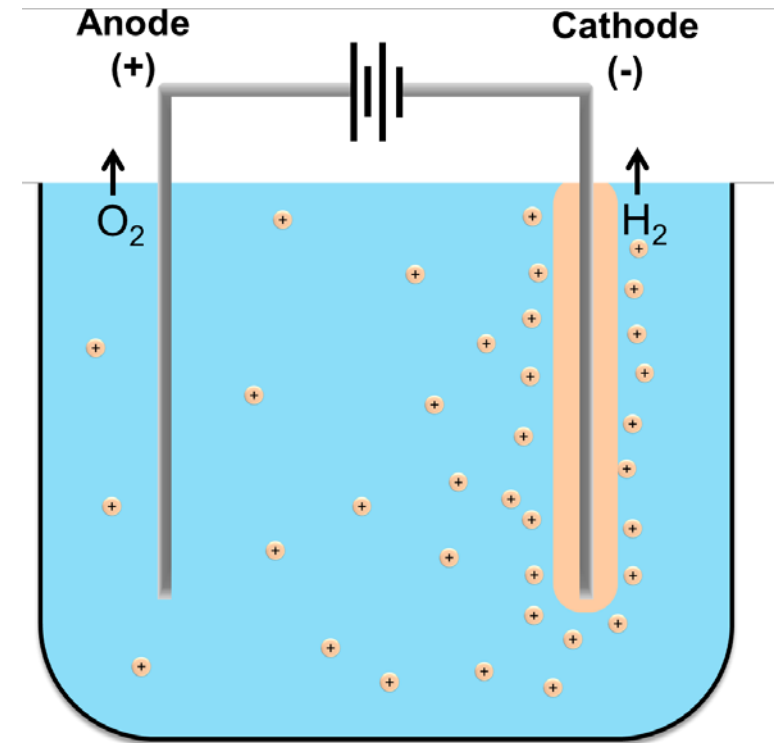
Electrochemical techniques:

- Provide information of how and why corrosion happens
- **Can be used to extract useful properties of the system**
- **Interpretation of mechanisms**

Introduction

Electrocoating

- Electrophoretic deposition of paint
- Hydrogen evolution $\rightarrow$ OH^- generation on the cathode surface
- Positively charged particles get neutralized and coagulate on the cathode
- After curing, a uniform, adherent, corrosion protective film (15 – 25 μm) is obtained



Goal of this study

Develop an electrochemical methodology that can help understand the corrosion behavior of Electrocoats.

Experimental

Metallic Materials and Coatings

- Cold-rolled AISI 1008 Steel
- Zinc phosphate pre-treatment
- 4 different cationic electrocoats (EC1-4)

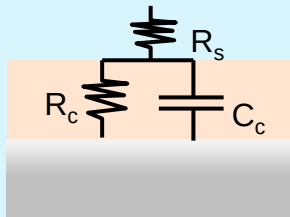
Corrosion tests

- SAE J2334
- Hot Salt Water dip test (HSW)

Electrochemical tests

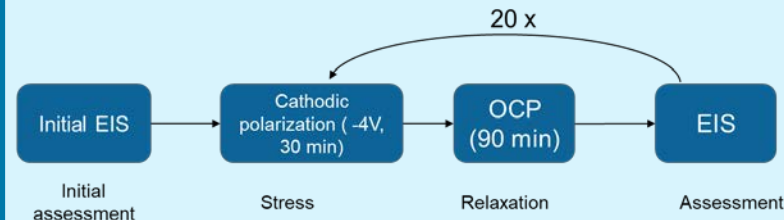
Electrochemical Impedance Spectroscopy

- After full immersion in 5 wt.% NaCl, 50° C
- after SAE J2334



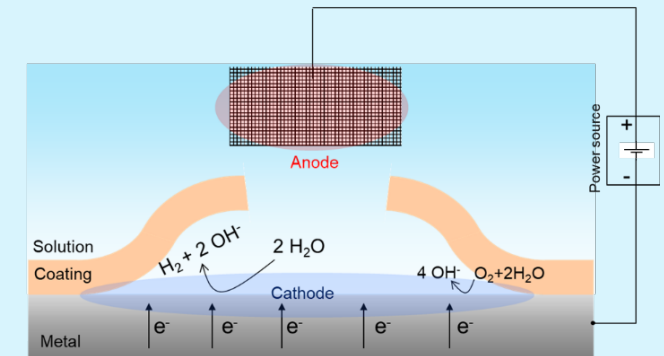
AC/DC accelerated testing

- In 5 wt.% NaCl
- EIS + CP for 20 cycles

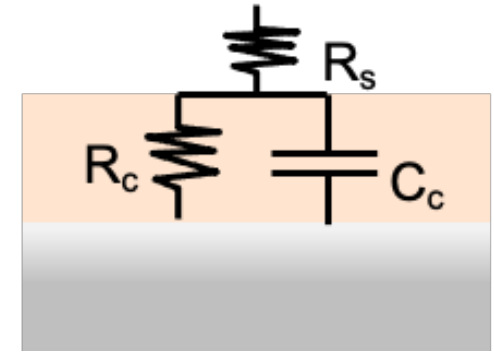
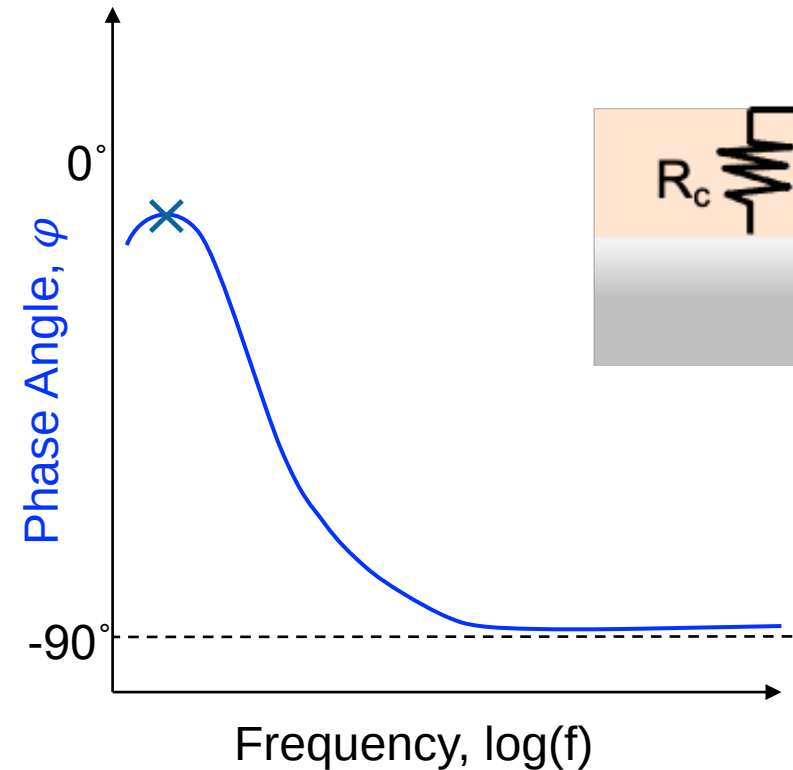
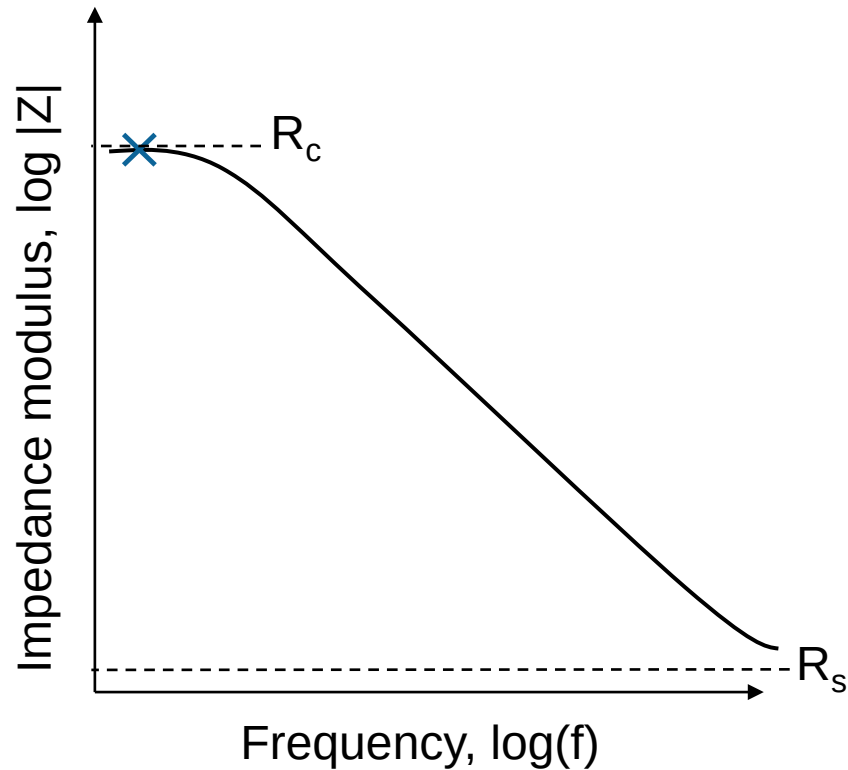


Cathodic polarization

- In 5 wt.% NaCl



Electrochemical Impedance Spectroscopy (EIS)



Assumptions:

- $|Z|$ at low frequency is a good approximation of barrier property (R_c)
- $|Z|$ at 10 kHz reveals capacitive reactance from the coating

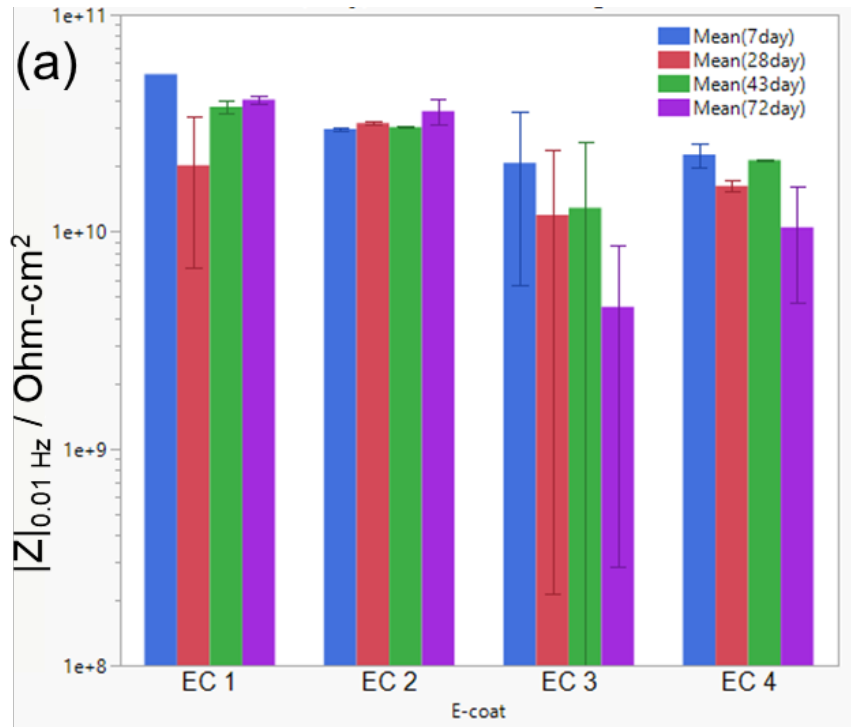
Part 1 – Effect of barrier on scribe corrosion performance

How can we use barrier property to rank E-coat performance?

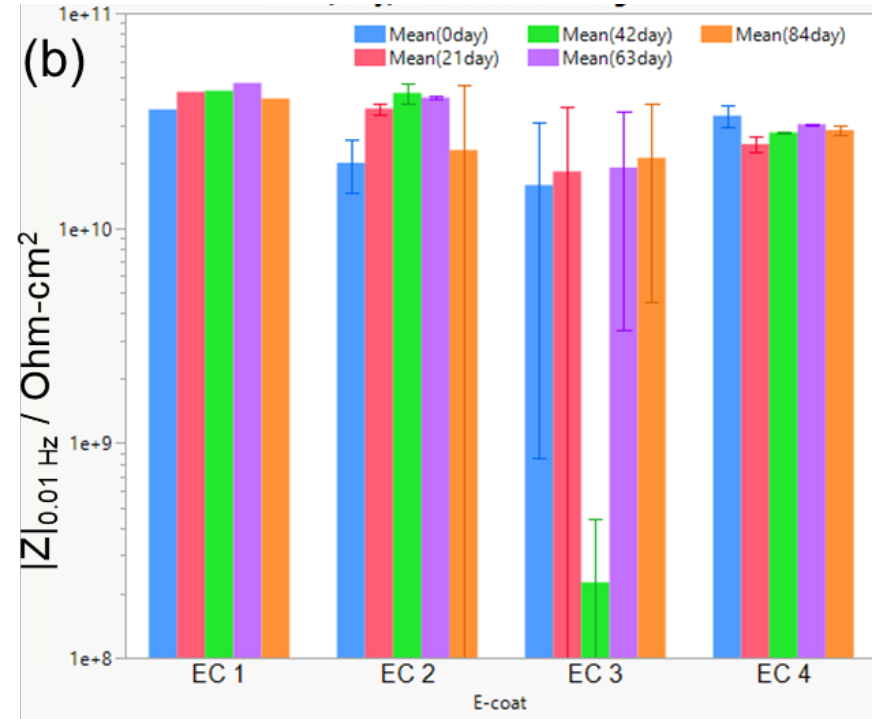


EIS measurements after aging (intact samples)

EIS after Full immersion aging



EIS after SAE J2334

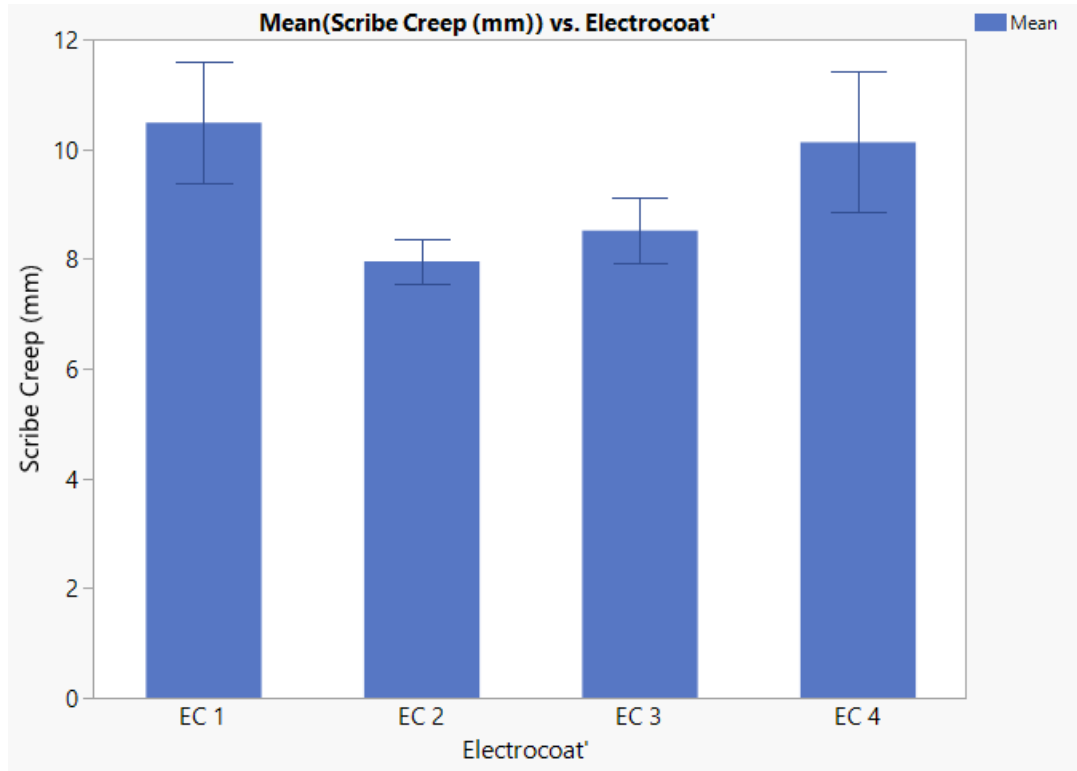


- Results from the two exposure methods are in agreement
- Both show a **very slow decrease** in impedance
- EIS after intermittent periods in SAE J2334 shows more noise results vs time – effect of area selection

Ranking by impedance:
EC 3 < EC 4 < EC 2 < EC 1

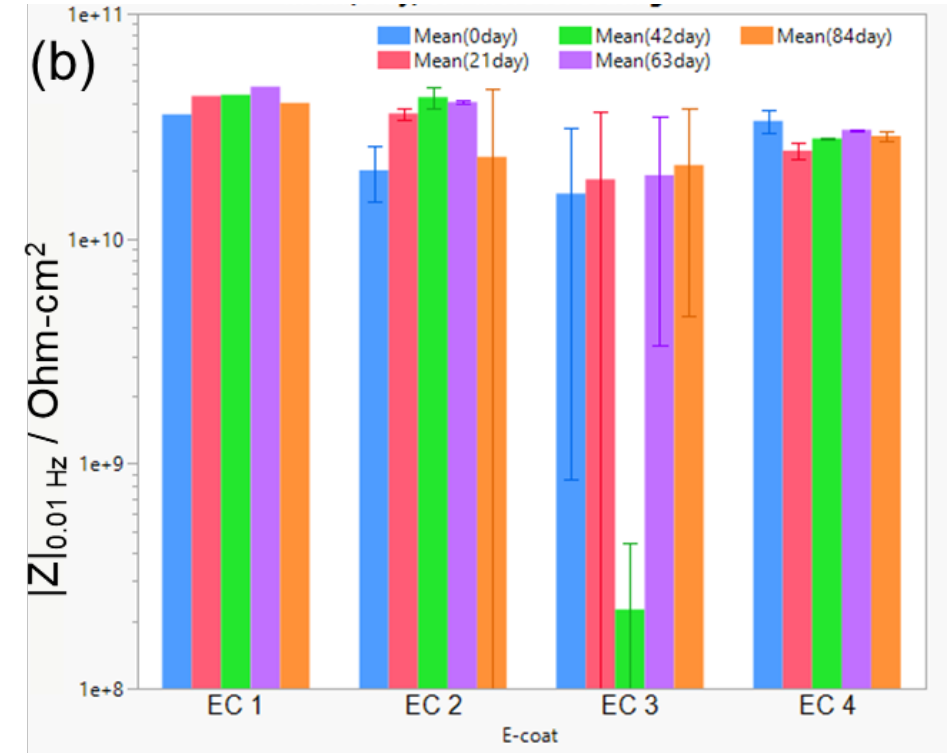
EIS measurements after exposure

SAE J2334 creep



Ranking by creep:
EC 1 < EC 4 < EC 3 < EC 2

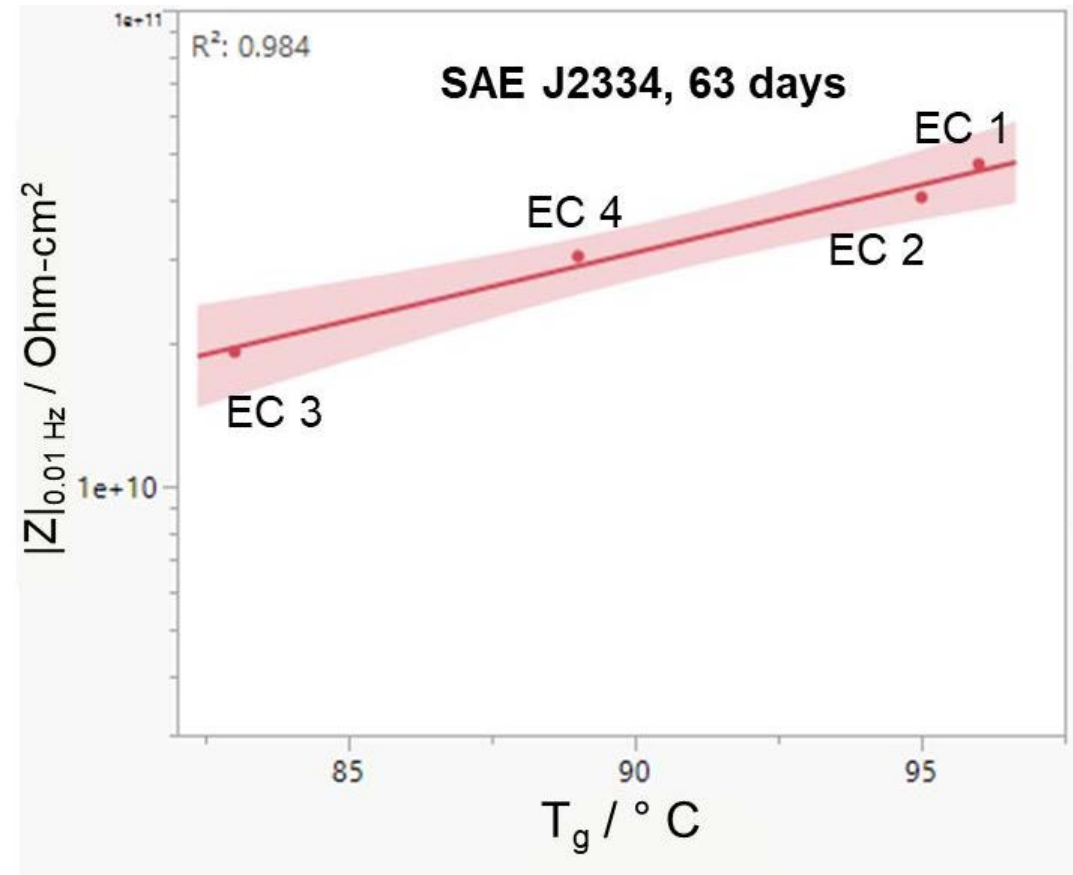
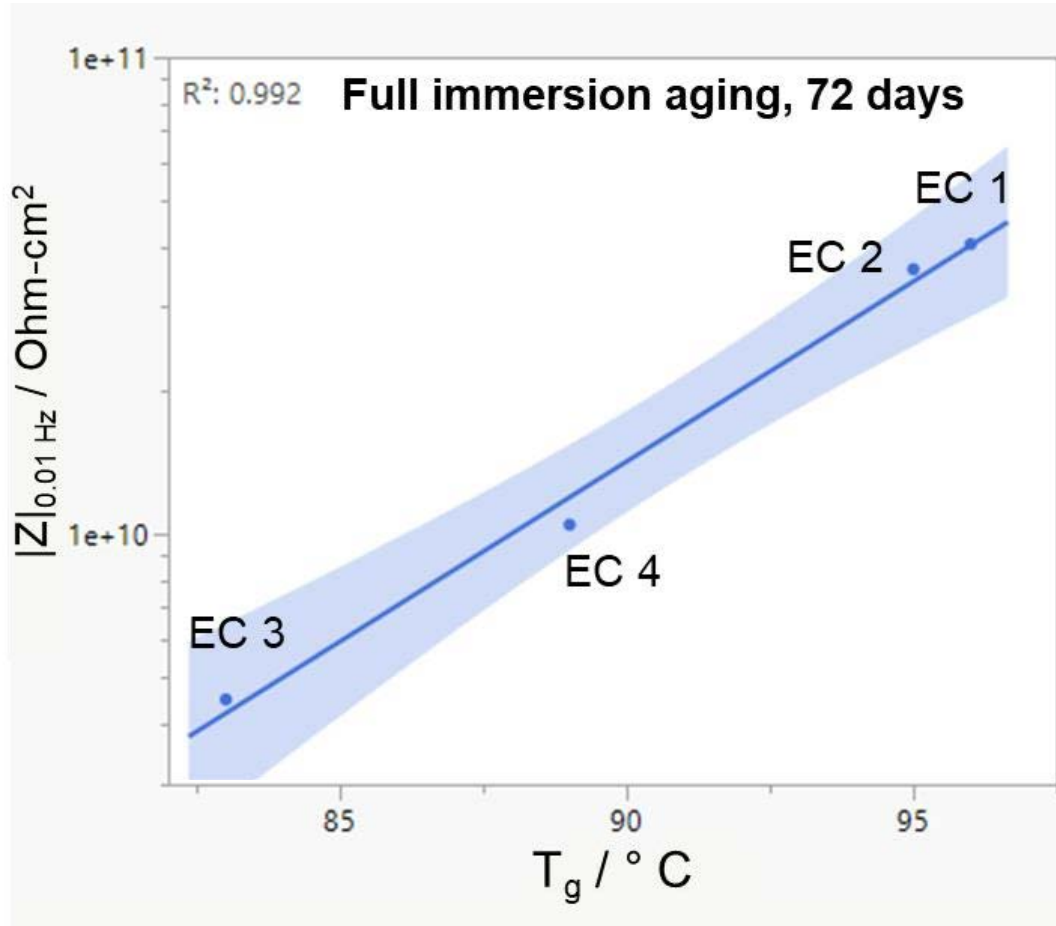
EIS after SAE J2334



Ranking by impedance:
EC 3 < EC 4 < EC 2 < EC 1

Evolution in low-frequency impedance is not a good proxy for scribe creep performance in cyclic test

EIS measurements after exposure



Impedance measurements from both approaches correlate with resin T_g

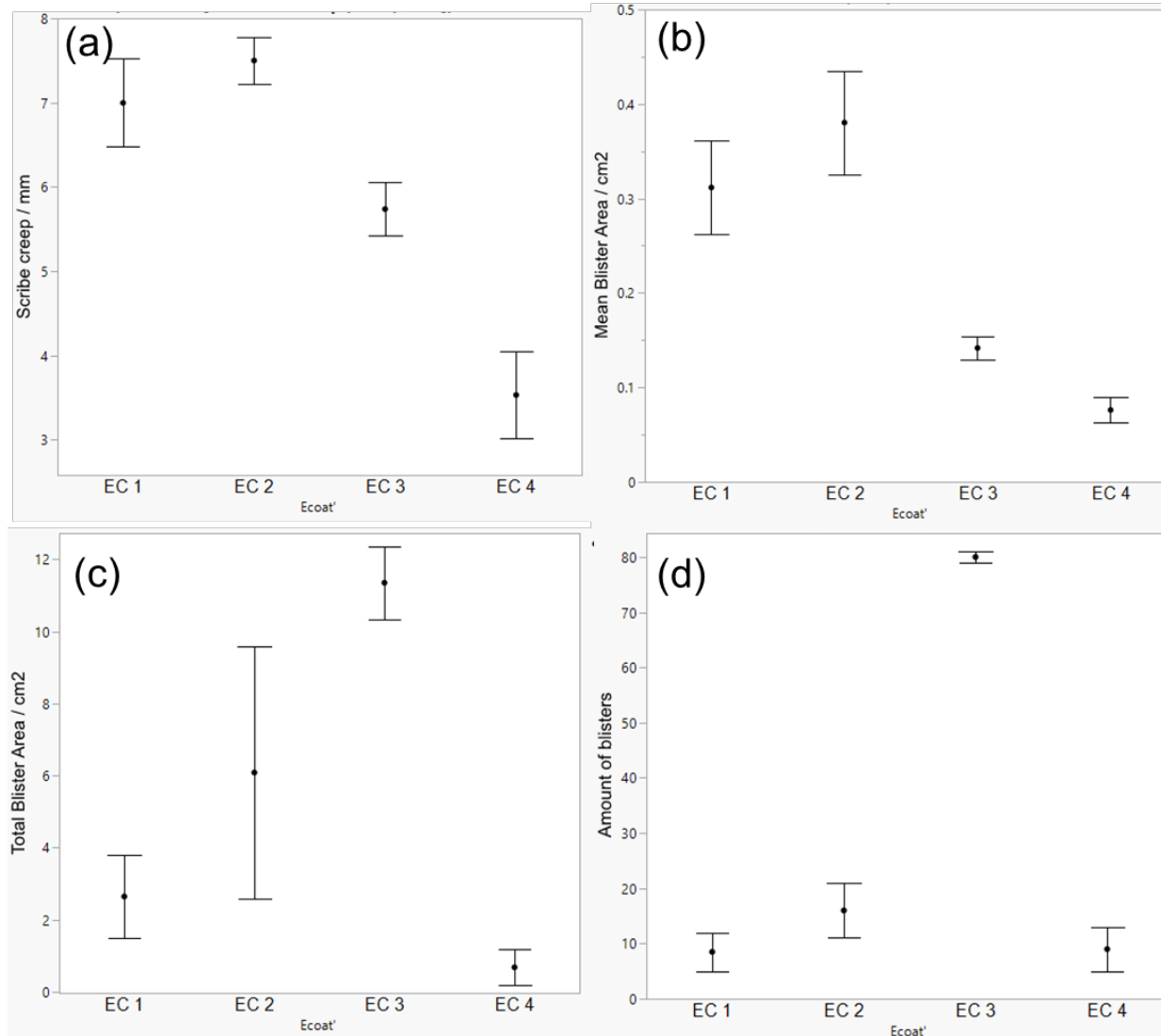


EIS estimates barrier property during aging, but **small differences in barrier property do not necessarily impact scribe creep**

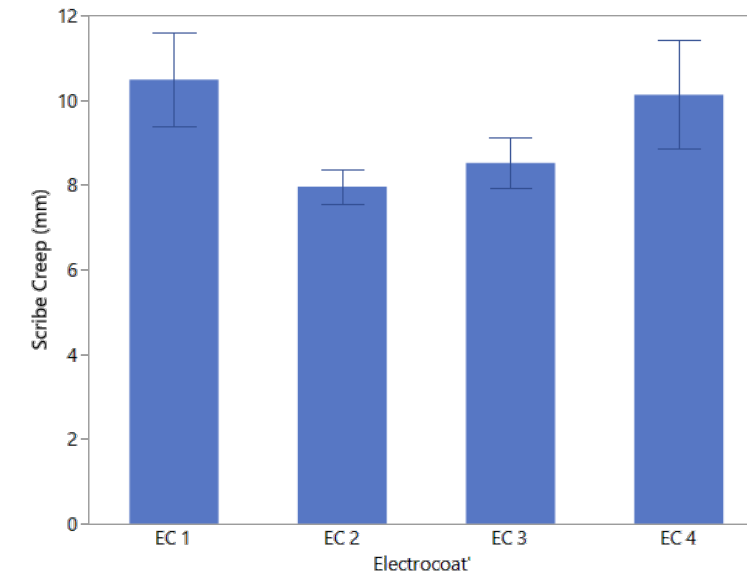
Cyclic vs continuous corrosion exposure



Hot Salt Water dip



SAE J2334



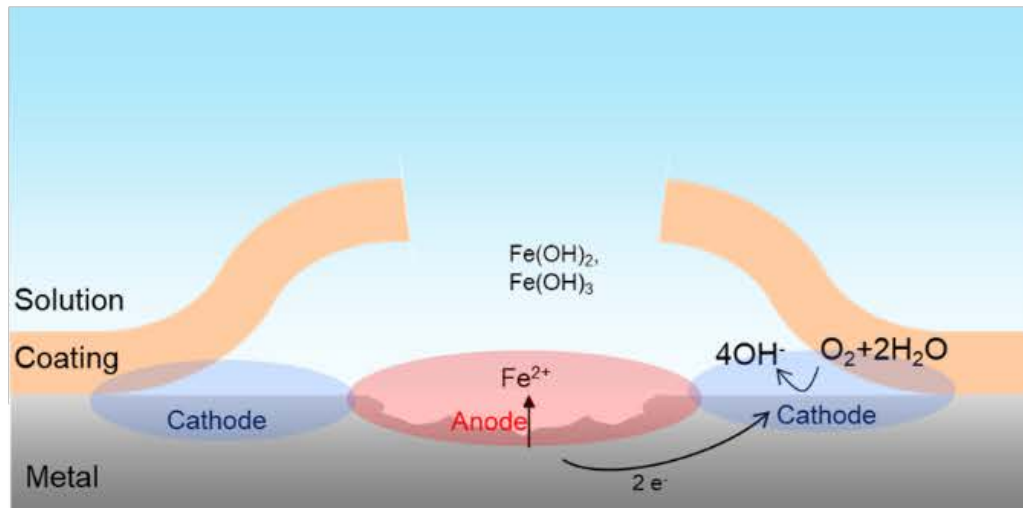
- HSW and SAE J2334 scribe creep trends disagree. **Neither correlates with $|Z|$ measurements**
- **Mean blister area correlates with scribe creep**, pointing to similar mechanisms of creep and blister growth.
- Blister nucleation depends on different properties – with exception of EC 4, **higher $|Z|$ and higher T_g contribute lower blister nucleation**

What other electrochemical tests could we use to study the mechanism?



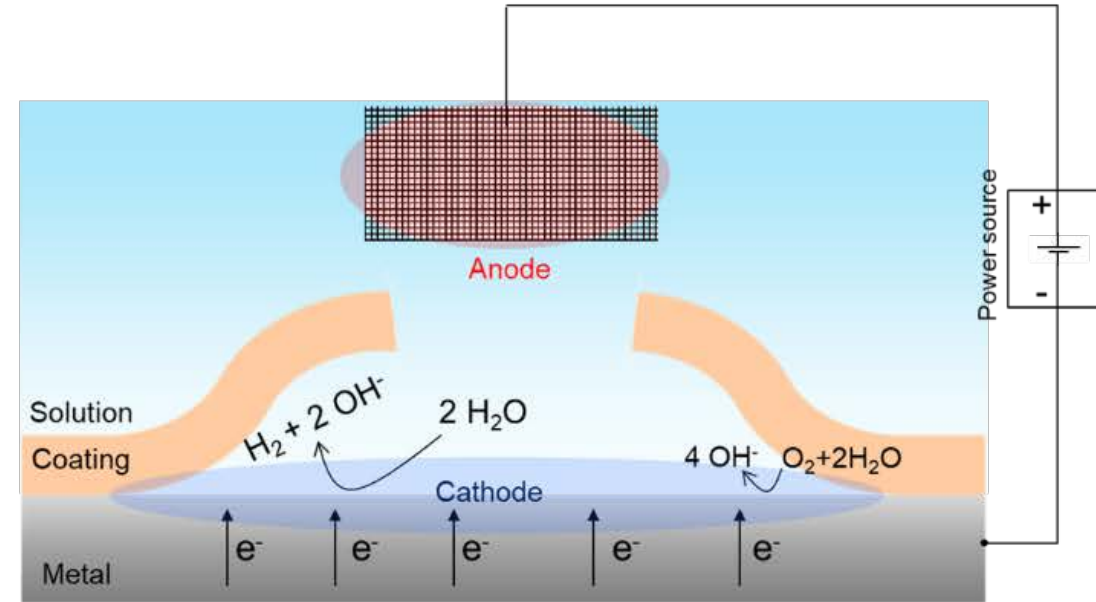
Cathodic polarization

Corrosion



On Iron and Zinc, coating damage often progresses by cathodic disbondment

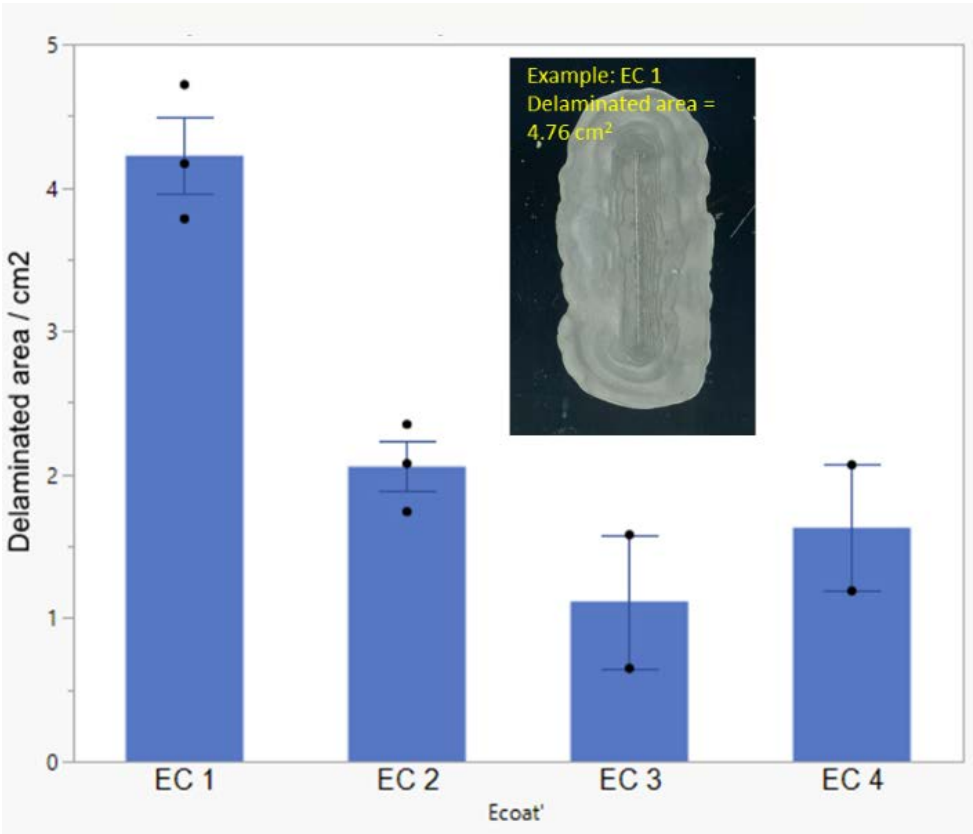
Cathodic Polarization



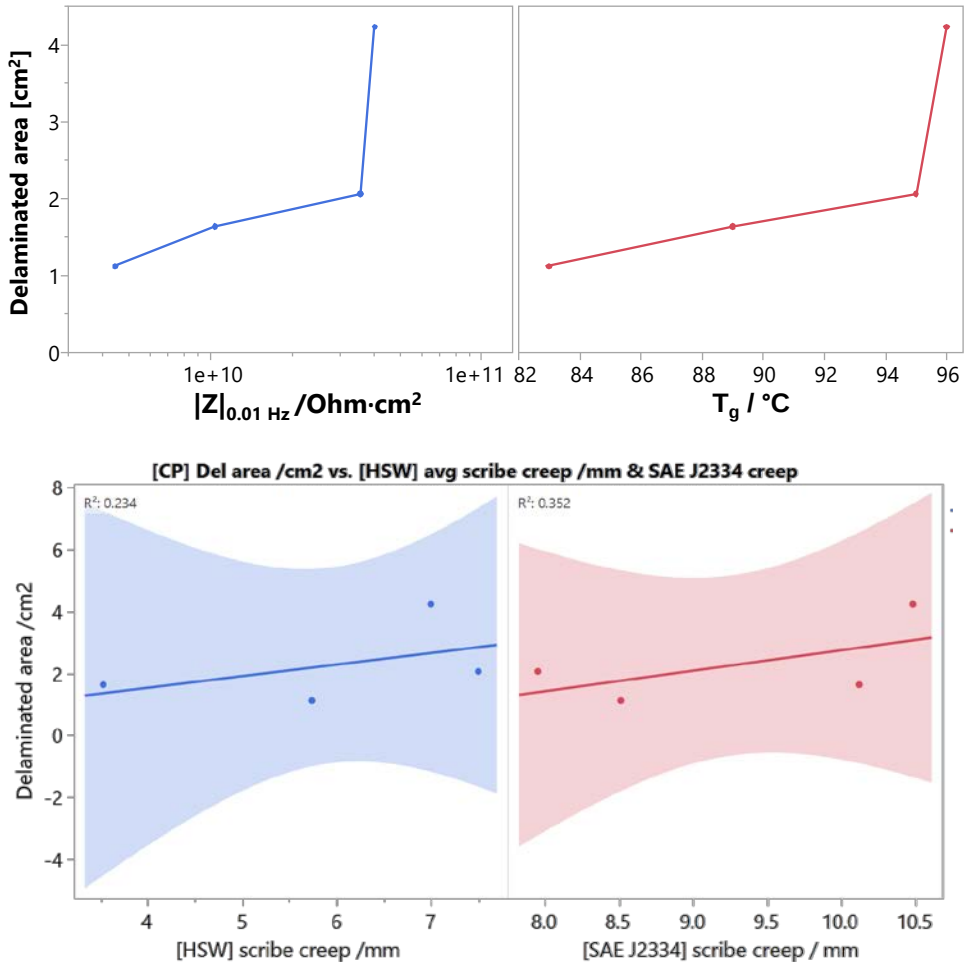
Electrochemical methods can be used to accelerate the disbondment mechanism

Cathodic polarization

Delaminated area after CP and tape pull



Correlation with impedance and T_g

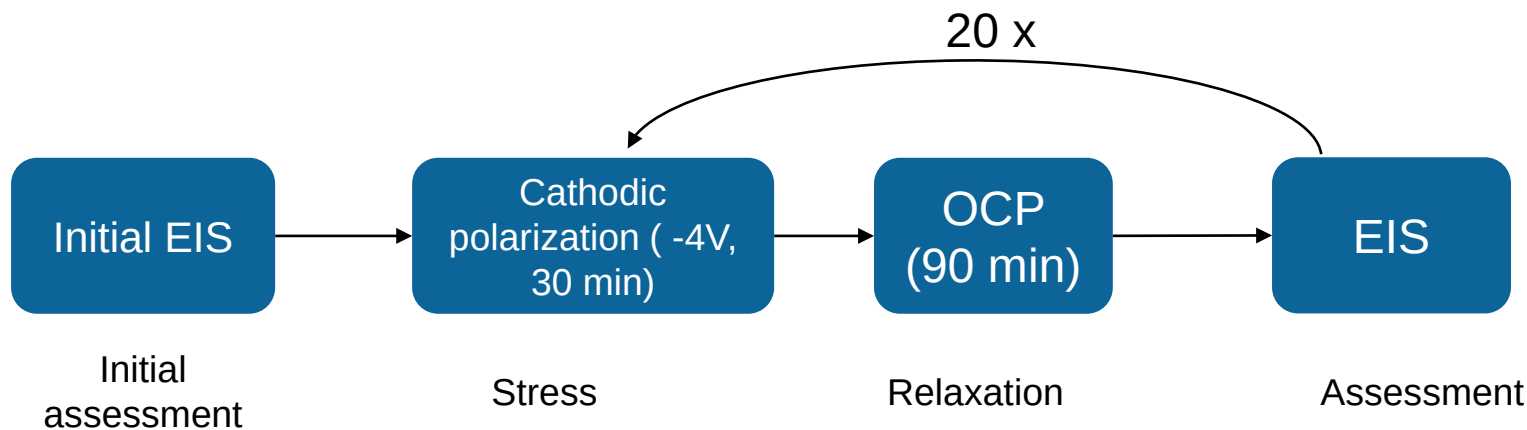


- CP and EIS data correlate inversely
- CP delaminated area increases with binder T_g

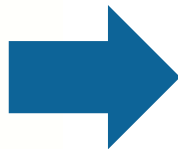
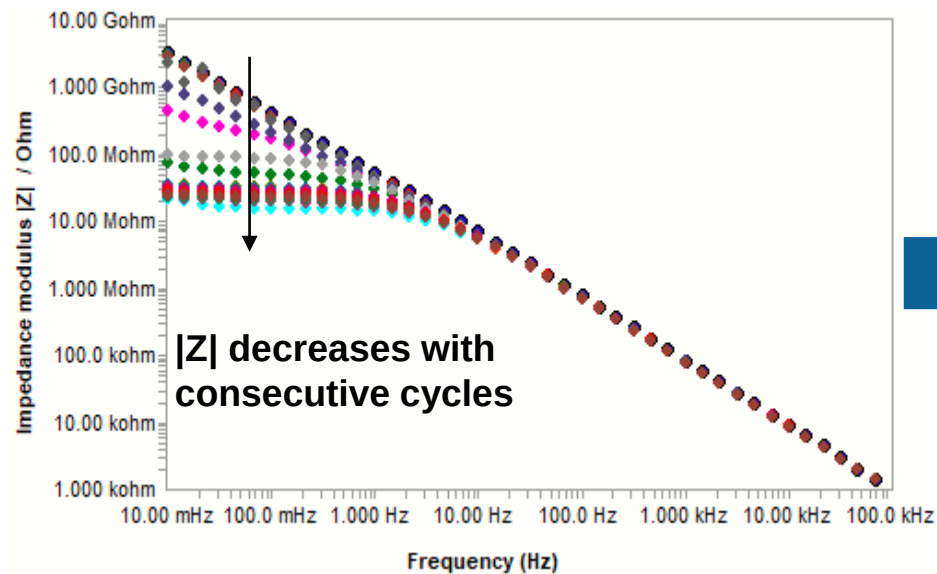
Effect on mechanical properties?

CP delaminated area was not a good proxy for scribe creep

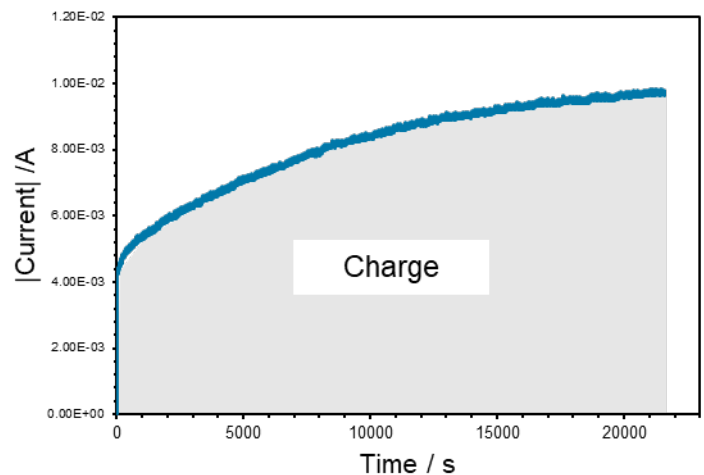
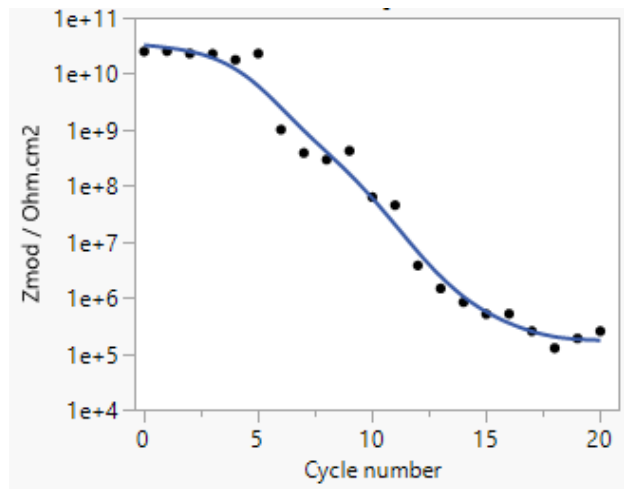
AC/DC method



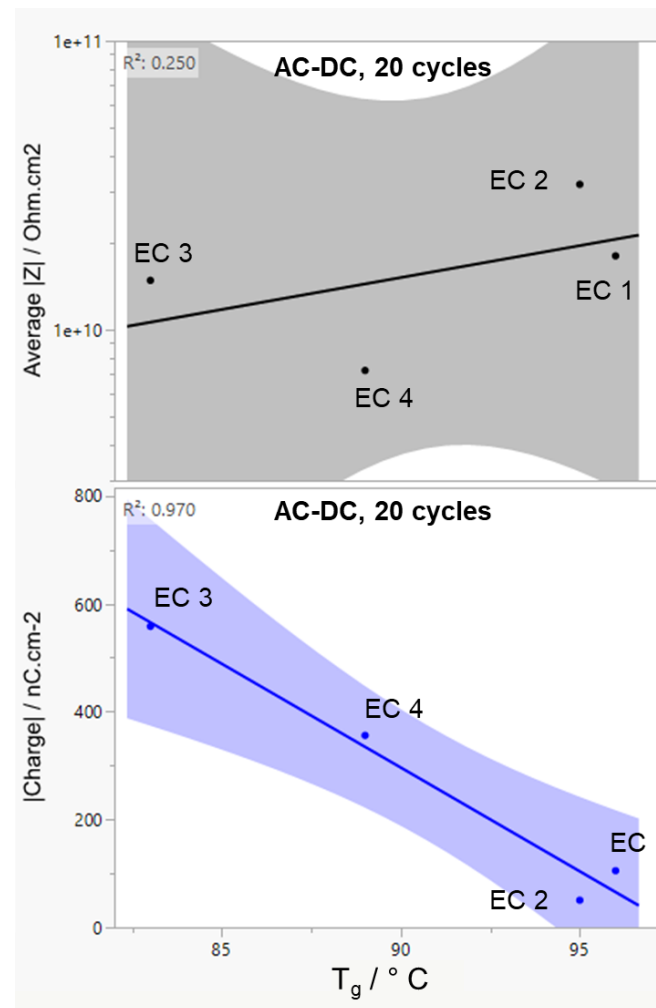
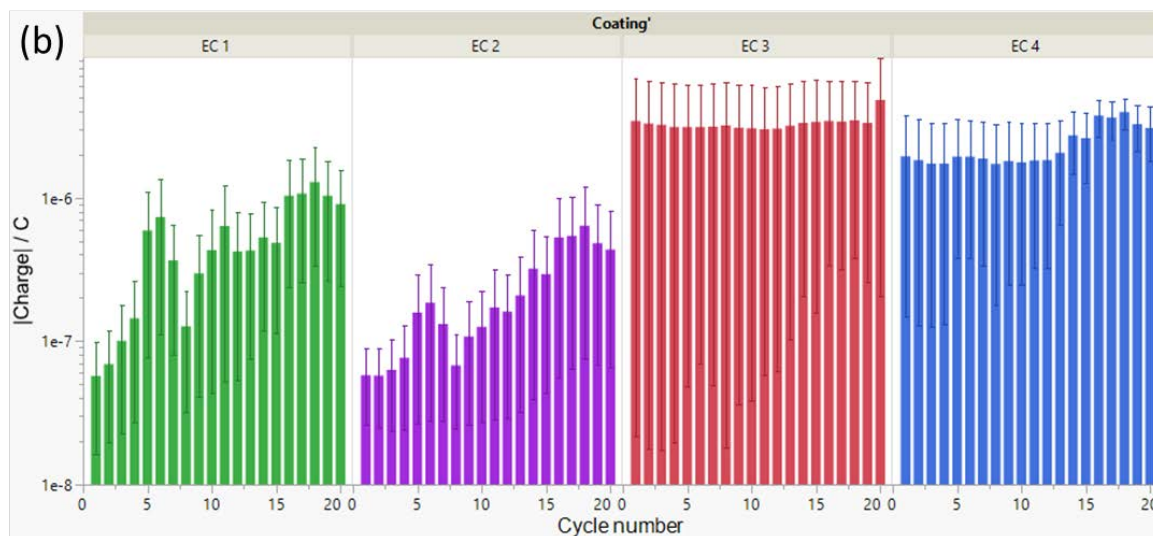
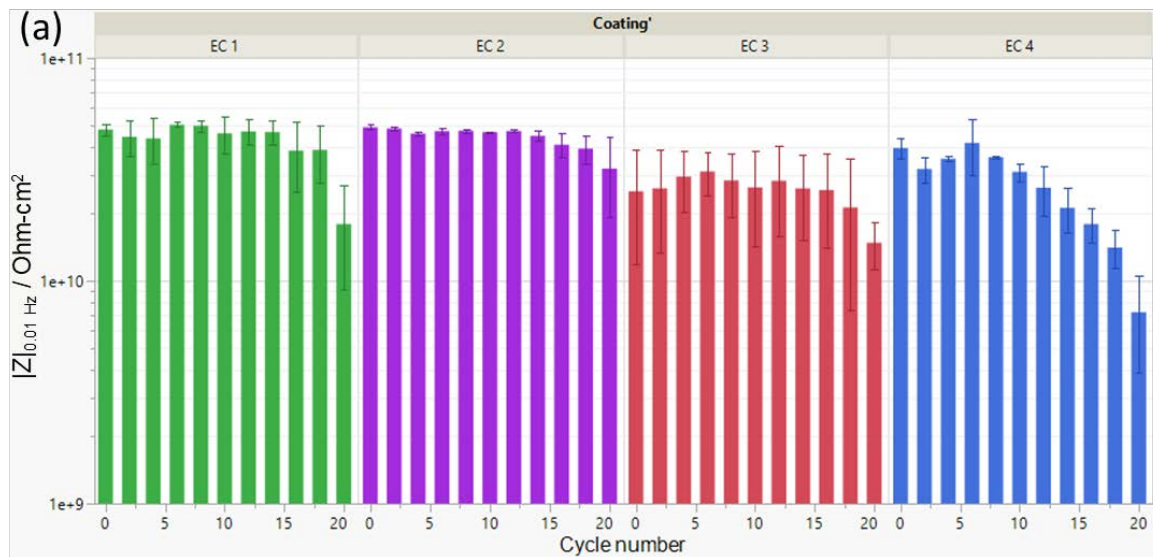
- Cathodic polarization degrades the coating;
- EIS and current are used to assess degradation over time



Outputs: **Impedance** and cathodic **charge** vs time



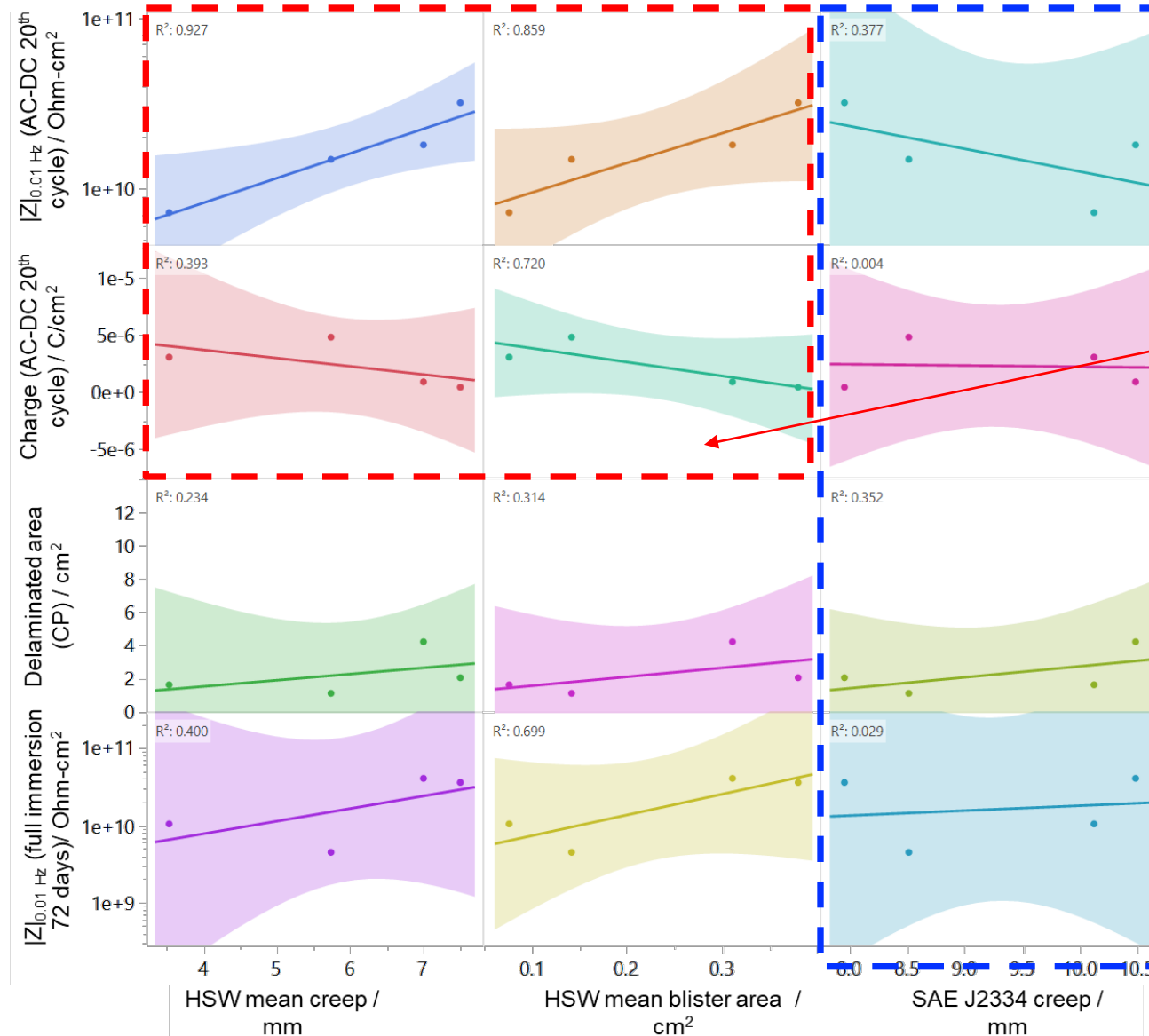
AC/DC method



- General impedance trend agrees with other exposure methods (full immersion and SAE J2334)
- Correlation between $|Z|$ and T_g is more noisy

- Charge during cathodic polarization has good agreement with binder T_g .

Correlation between E-chem variables and cabinet corrosion tests



SAE J2334 creep showed little correlation with e-chem properties

Higher barrier property from AC/DC tests correlate with higher creep and mean blister area in HSW test

The unexpected impact of higher coating resistance and T_g may be due to impact on mechanical properties and their effect on the interface

Conclusions

SAE J2334

- Small decrease in barrier property
- the **three EIS approaches** – EIS after full immersion exposure, after SAE J2334 exposure, or in an AC-DC protocol – **presented similar trends, but no correlation with creep**

HSW

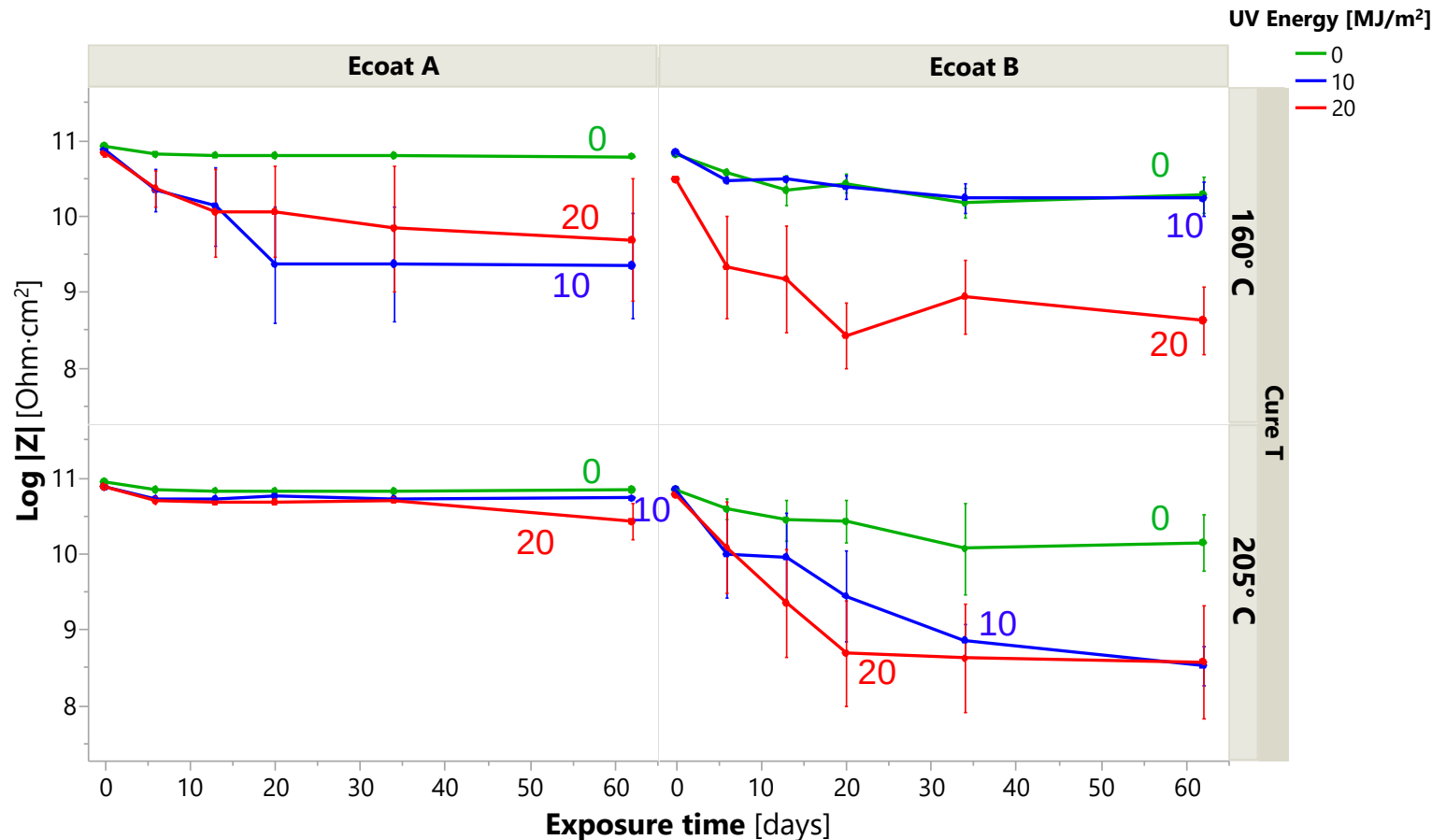
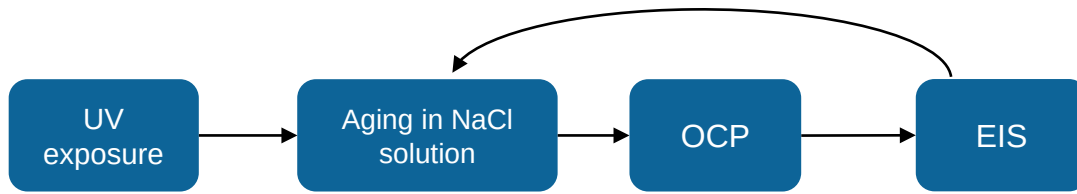
- Ecoats with higher barrier (and higher T_g) typically showed worse scribe creep, analogously to what was observed in CP tests.
- More similarities with CP

More barrier is not always better - The delaminated area from CP tests showed an inverse correlation with impedance measurements of intact coatings. This may indicate a relationship between mechanical properties of the E-coat and delamination rate in CP tests.

Part 2 – Effect of UV exposure

- Does barrier property have a higher impact on creep after UV damage?

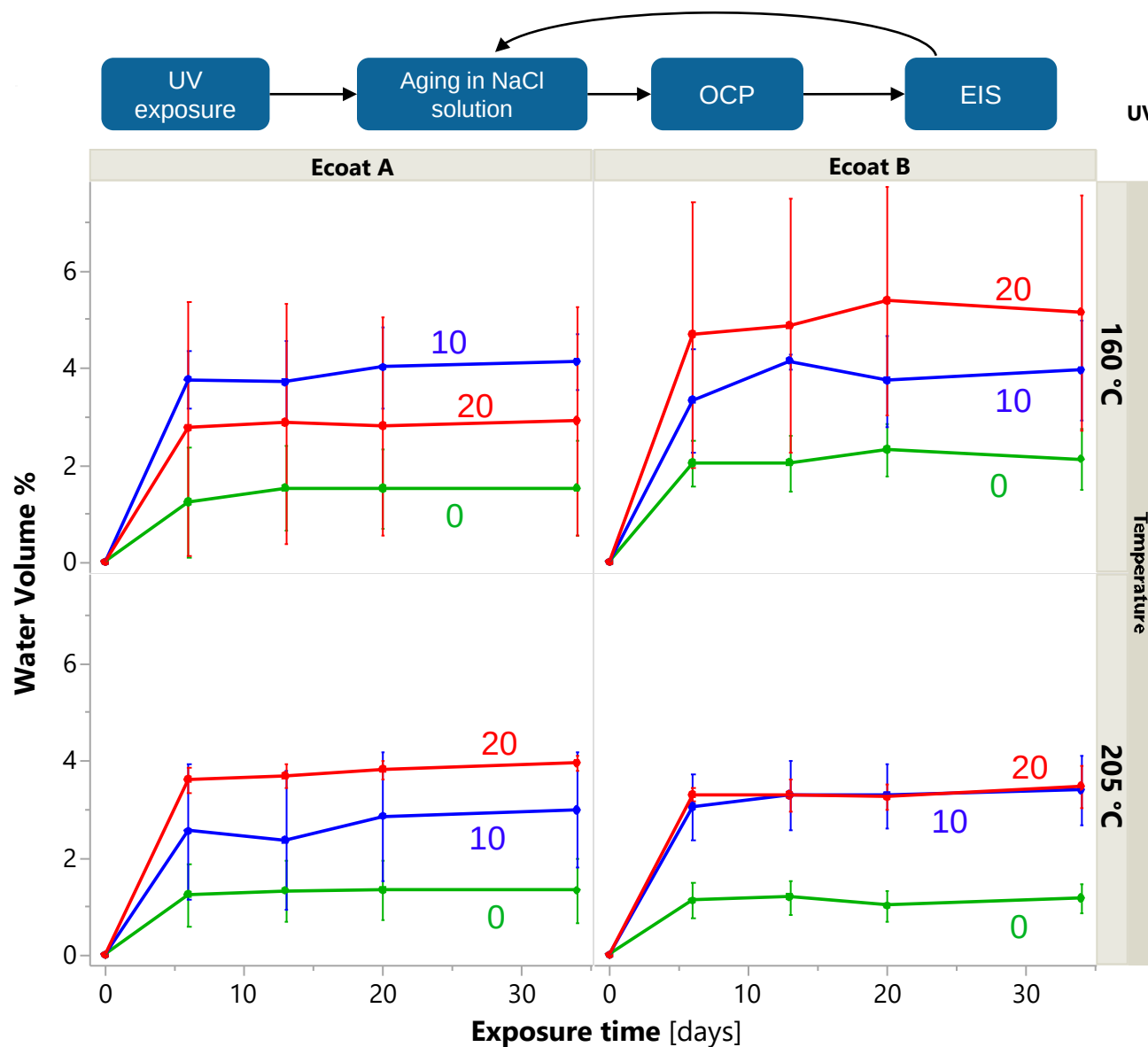
EIS measurements after UV exposure – 5-week update



Assumption: Low-frequency impedance (point nearest to $\phi = 0^\circ$) represents barrier property (R_{coat})

- Ecoat A shows a higher resistance to UV damage than Ecoat B – barrier property does not decrease as much
- UV has small effect on initial measurements, but it causes a **faster degradation of the barrier property** in corrosive solution
- A higher bake temperature results in **higher resistance to UV** – especially for Ecoat A

EIS measurements after UV exposure – 5-week update



Assumptions for single frequency capacitance estimation approach:

$$|Z|_{10kHz} \approx X_c$$

$$X_c = \frac{1}{2\pi f C_{coat}} \quad \Phi_w = \frac{\log\left(\frac{C_t}{C_0}\right)}{\log \epsilon_w}$$

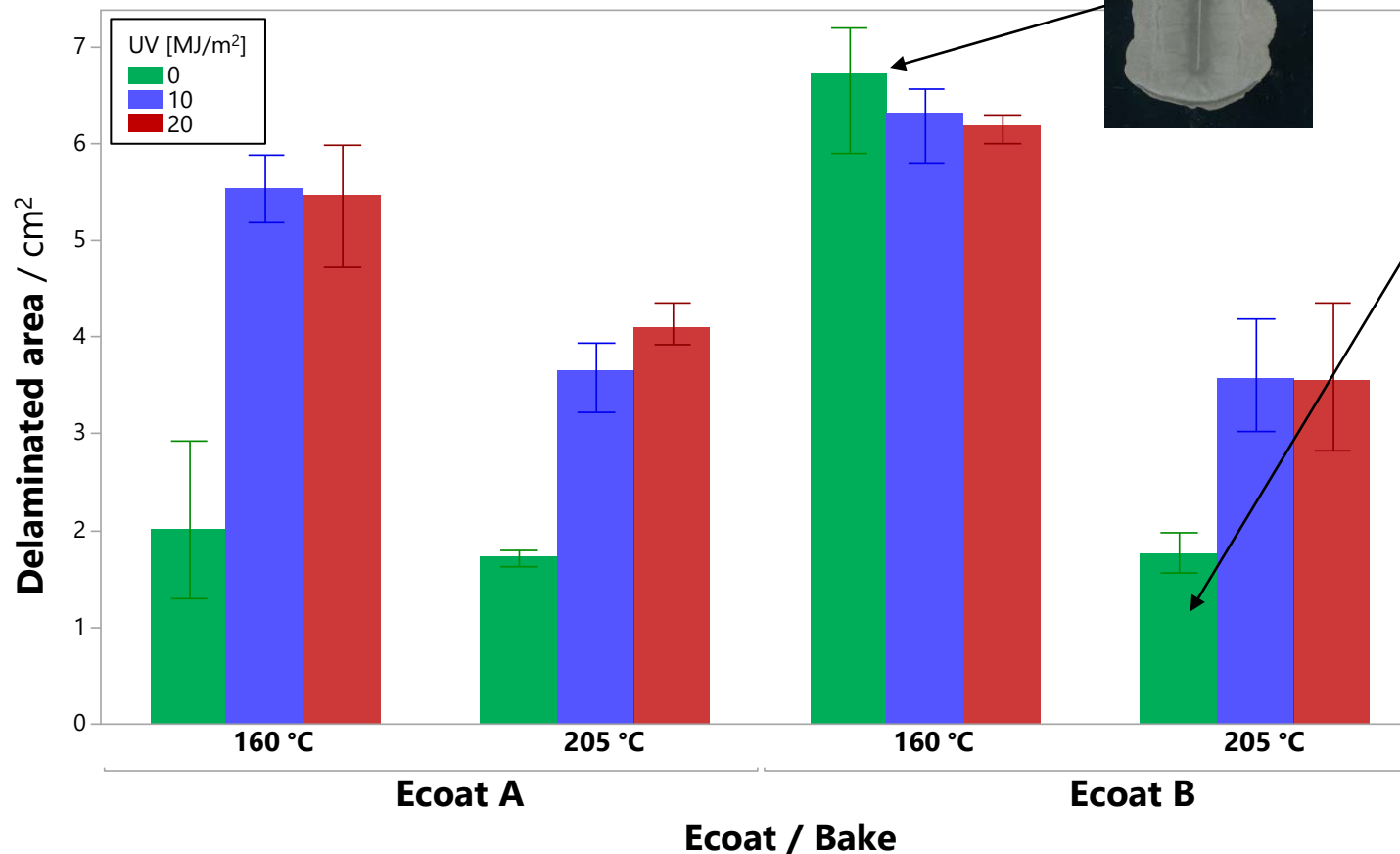
Time = 0 measurement taken after 1h exposure.

- **UV exposure increases water uptake** for all coatings/bakes
- **Water uptake is lower at 205° C than at 160° C**
- Most of water uptake takes place before 6 days in solution
- At 160° C, water uptake is generally smaller for Ecoat A than for Ecoat B

Cathodic polarization

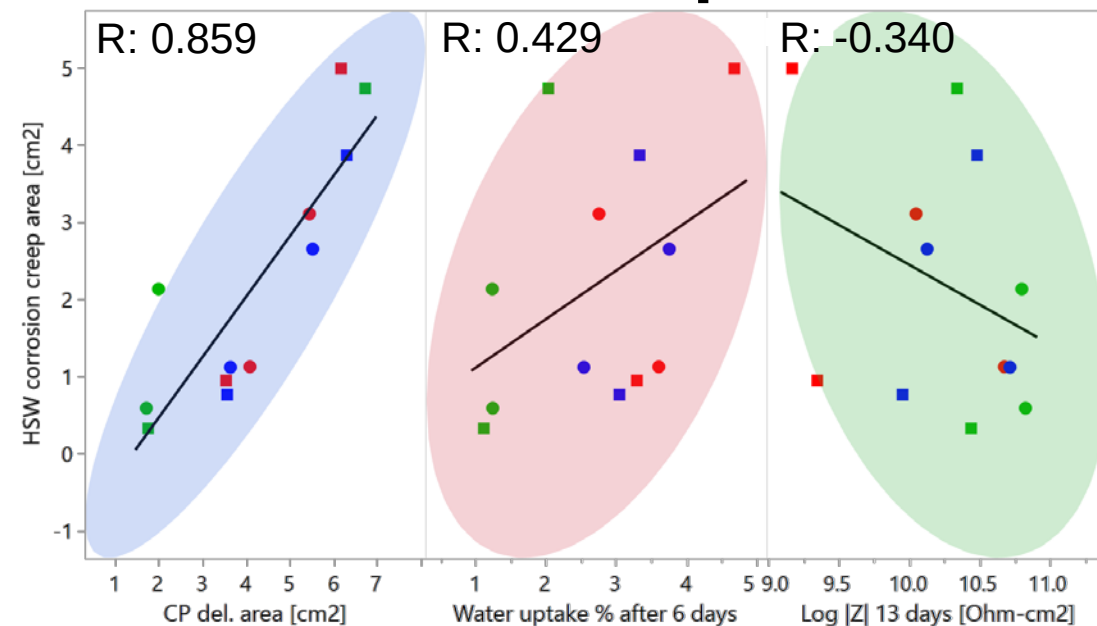
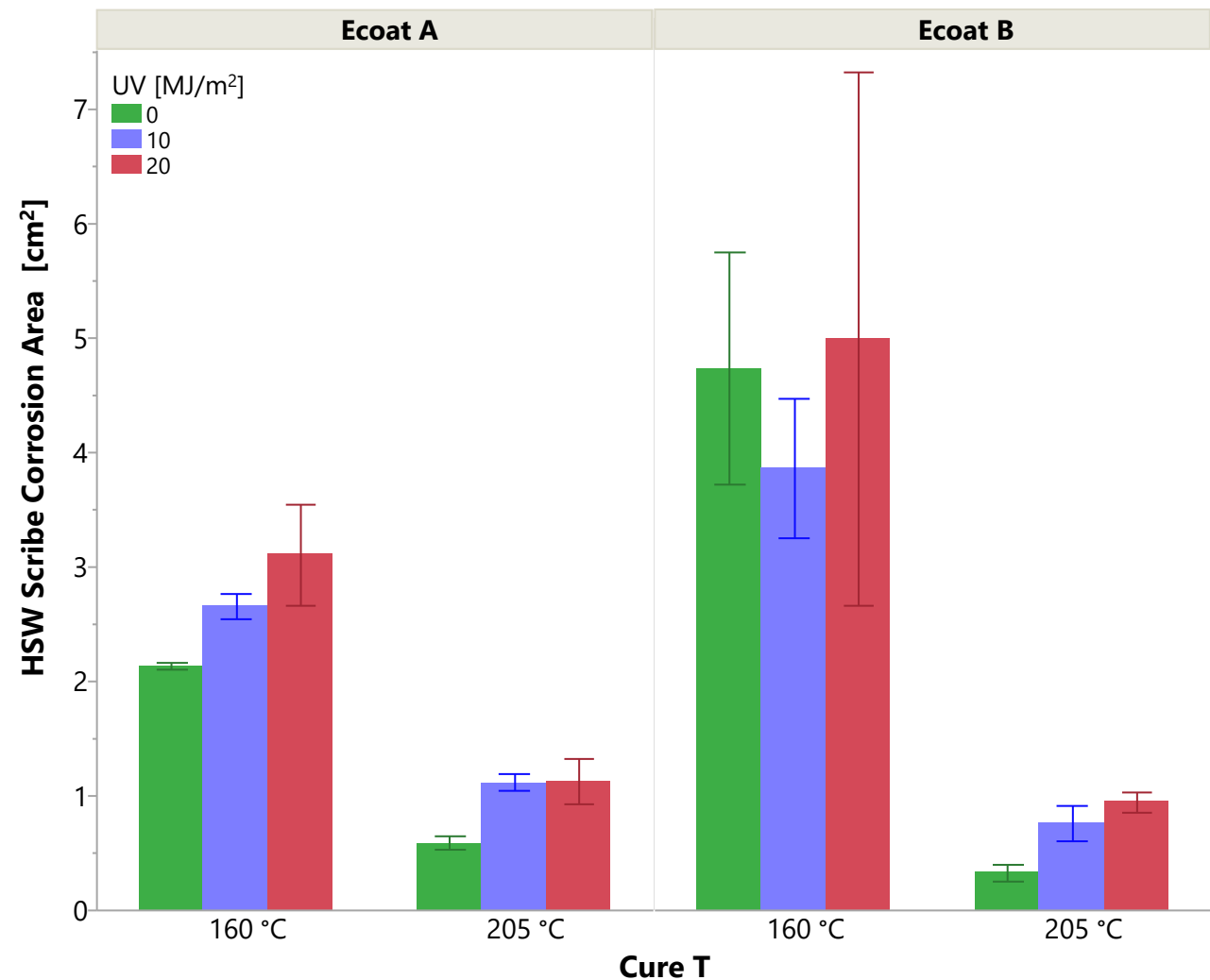


Delaminated areas after CP and tape pull

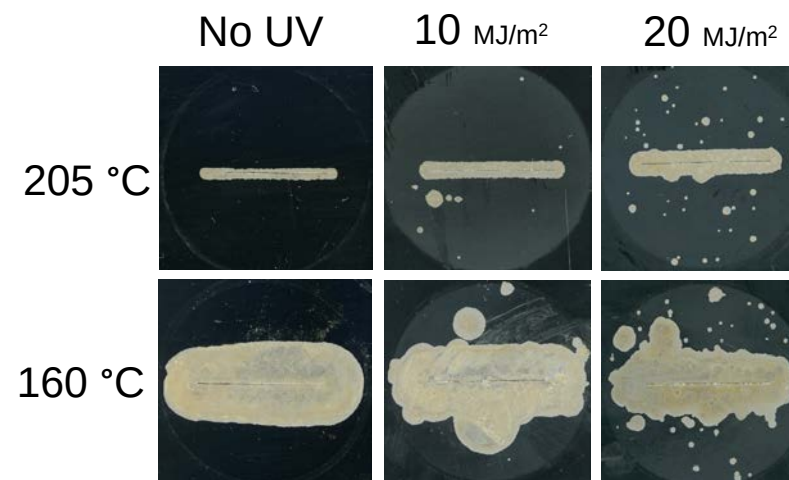


- At 160 °C bake, Ecoat A has a better resistance to cathodic delamination than Ecoat B. At 205 °C bake, results are similar.
- Higher UV exposure => higher cathodic delamination. Exception: Ecoat B, 160 °C.
- Higher bake temperature diminishes effects of UV

Correlations between electrochemical and corrosion exposure tests



Best correlation with scribe creep was found for CP tests



UV exposure increases blister nucleation

Conclusions

Effect of UV

- UV high-energy damage to E-coats increased water uptake and decreased barrier property.
- Overbaked E-coats are more resistant to UV damage.

Coating electrochemical properties

- With larger differences in **barrier property**, low frequency $|Z|$ modulus has better (but not great) correlation with scribe creep.
- **Low barrier** promotes face blistering – corrosion assessment should not be limited to assessment of scribe creep.
- **Cathodic polarization** results had good correlation with scribe creep in HSW test. Water uptake also seems to correlate well.

Electrochemical tests with scribed samples are more adequate for scribe creep prediction

- Need better accelerated electrochemical tests with scribed samples
- Better understanding of delamination process of commercial E-coats with localized techniques

Acknowledgements

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