Characterizing the degradation of Army primers by the AC-DC-AC accelerated test method

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Standard Form 298 (Rev. 8-98)
Prescribed by ANSI Std Z39-18

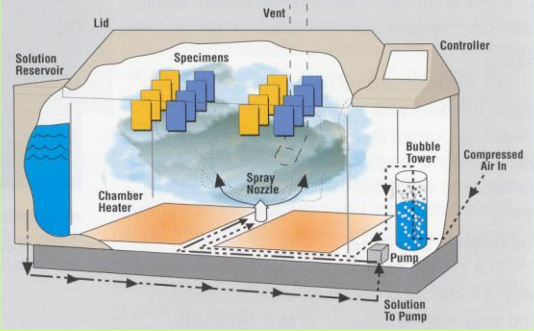
Accelerated Testing Methods

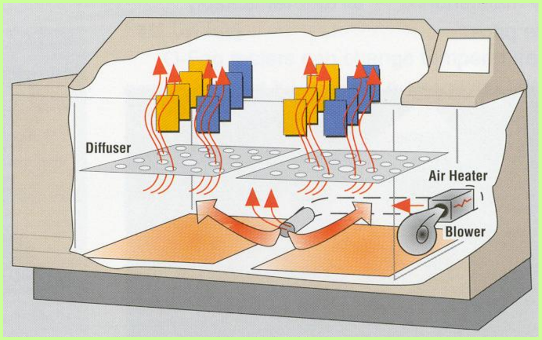
Salt spray

ASTM B-117

Prohesion exposure

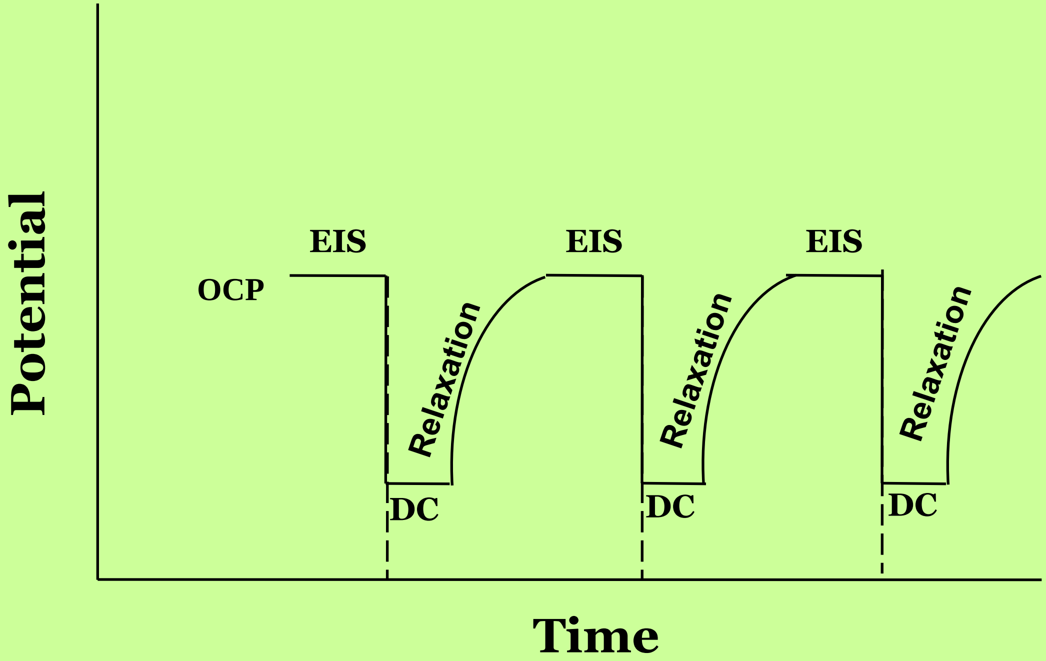
ASTM G85-14





- Simulate weathering conditions
- Periodic testing at given number of cycles
  - Visual inspection for failure, Electrochemical methods (EIS, ENM)
- Exposure times in excess of weeks or months for failure

AC-DC-AC accelerated testing method



Cycles

- AC-step (EIS/ENM, measurement step)
- Cathodic potential dc-step(stressing step)
- Rest/equilibration/relaxation process

Effects

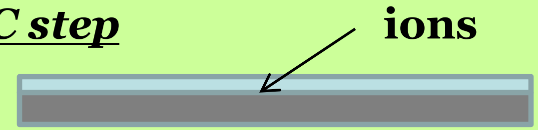
AC step

$Fe \longrightarrow Fe^{2+} + 2e^-$

$O_2 + 2H_2O + 4e^- \longrightarrow 4OH^-$

❖Corrosion reactions at interphase

DC step

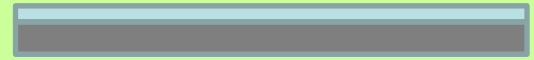


$2H_2O + 2e^- \longrightarrow 2OH^- + H_2$

❖Delamination by OH- and H2

❖ influx of ionic species by ionic current

Relaxation step



$Fe \longrightarrow Fe^{2+} + 2e^-$

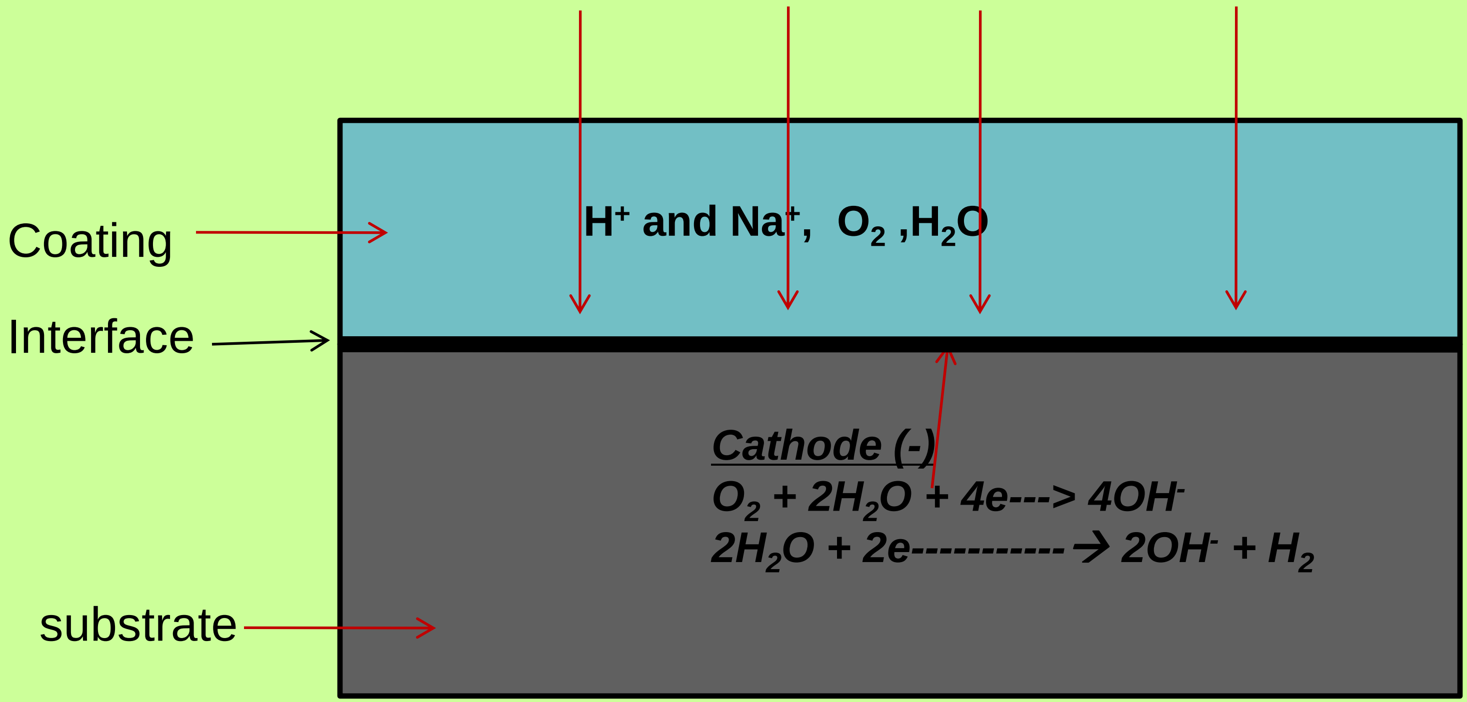
$O_2 + 2H_2O + 4e^- \longrightarrow 4OH^-$

$2H_2O + 2e^- \longrightarrow 2OH^- + H_2$

❖Corrosion reactions , ions/electrolyte exit from primer, pore formation

Hollaender, Ludwig, Hillbrand, Proc. 5th Int Tinplate Conf., 1992

Consequences of the DC condition



- ➢**Passage of ions can cause coating deterioration and formation of transport pathways in coatings**
- ➢**Film delamination at interface if cathodic reactions take place**

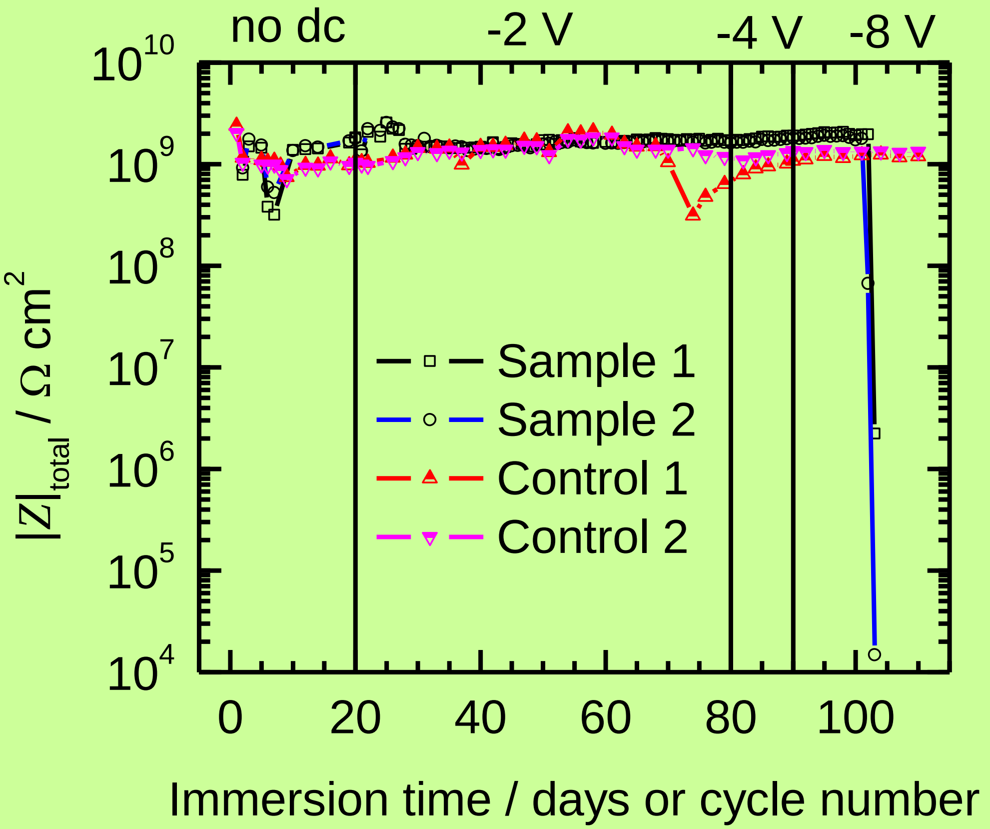
Rodríguez M.T., et al. Progress in Organic Coatings, 50 (2004) 123-131

Army Corrosion Summit 2007

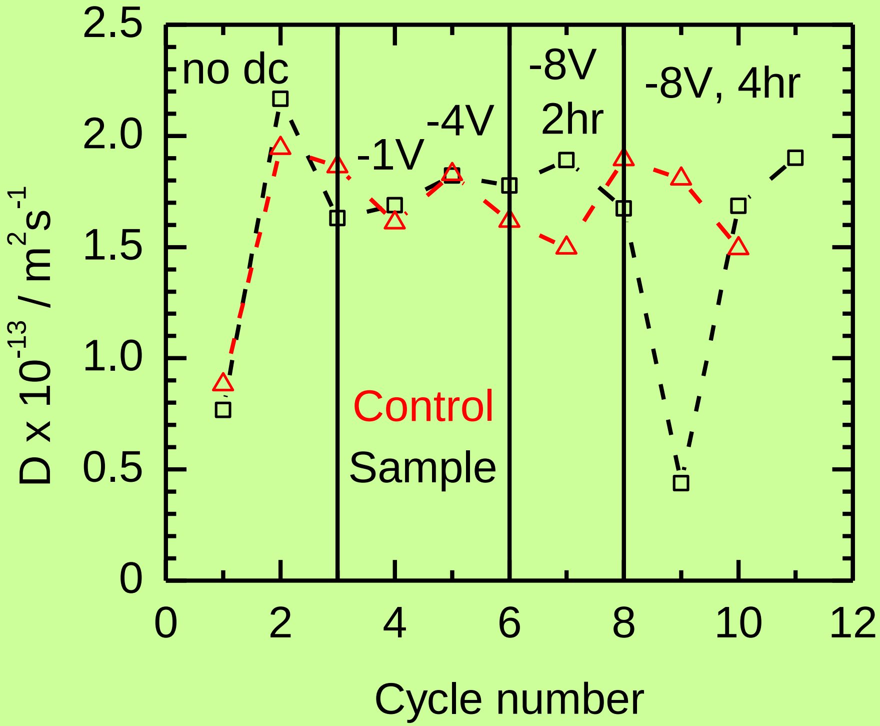
- Steel substrate
- **<u>Polyurethane CARC</u>**
  - **<u>(MIL-DTL-64159 Type 2)</u>**
- Epoxy Primer
  - (MIL-P-53022B Type II,)
- 3.5 wt % NaCl electrolyte

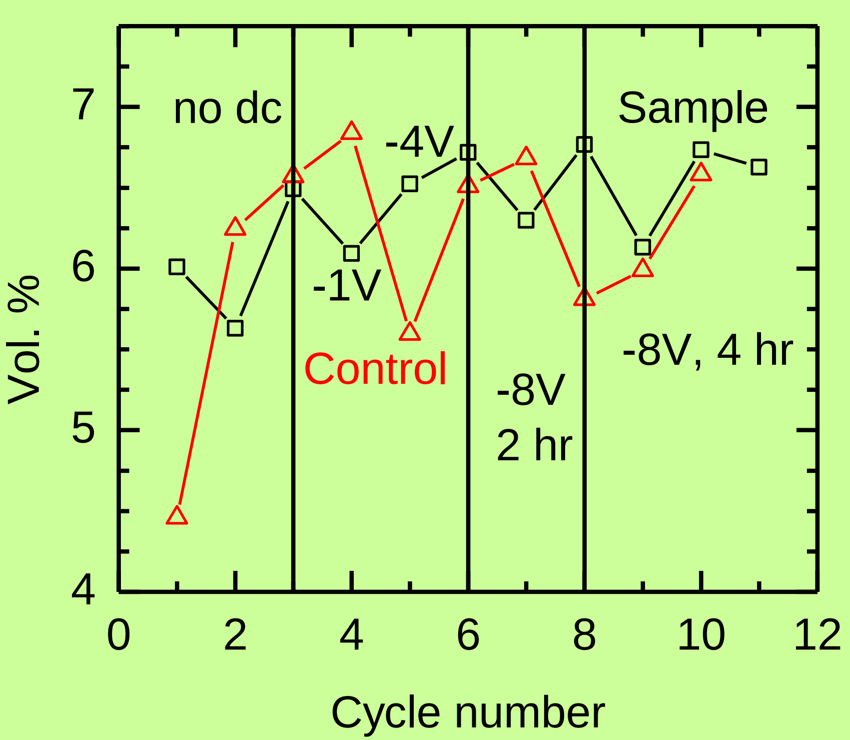
- -2 V and -4 V cycles had no influence

- After 12 -8 V cycles, coating system failed



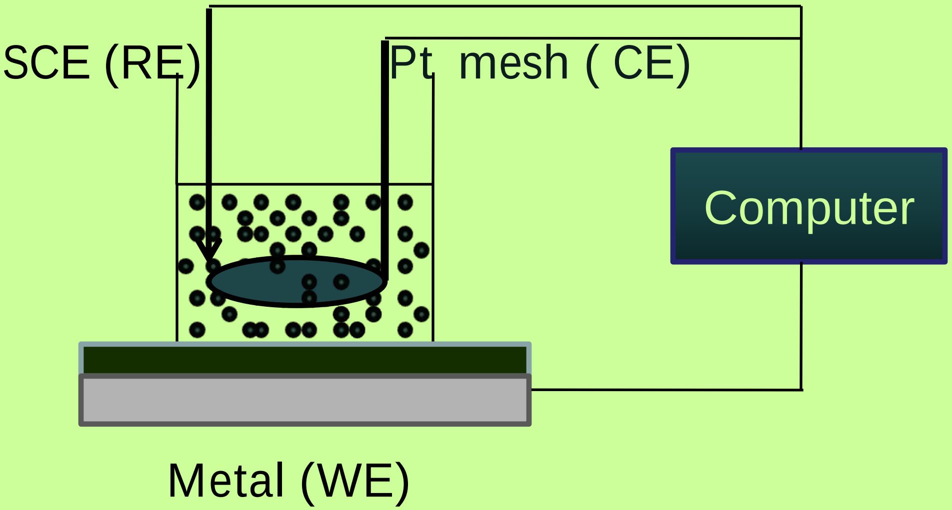
Army Summit 2008





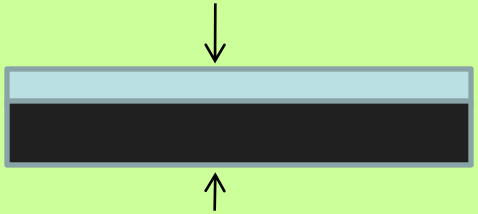
- Steel substrate, Epoxy Primer (MIL-P-53022B Type II,)
- 3.5 wt % NaCl electrolyte
- No observable influence on D_{H2O} and water uptake

Experimental setup



<u>Substrate/Coating Information</u>

Epoxy primer with Inhibitor
MIL-P-53022B Type II epoxy primer



Substrate Steel

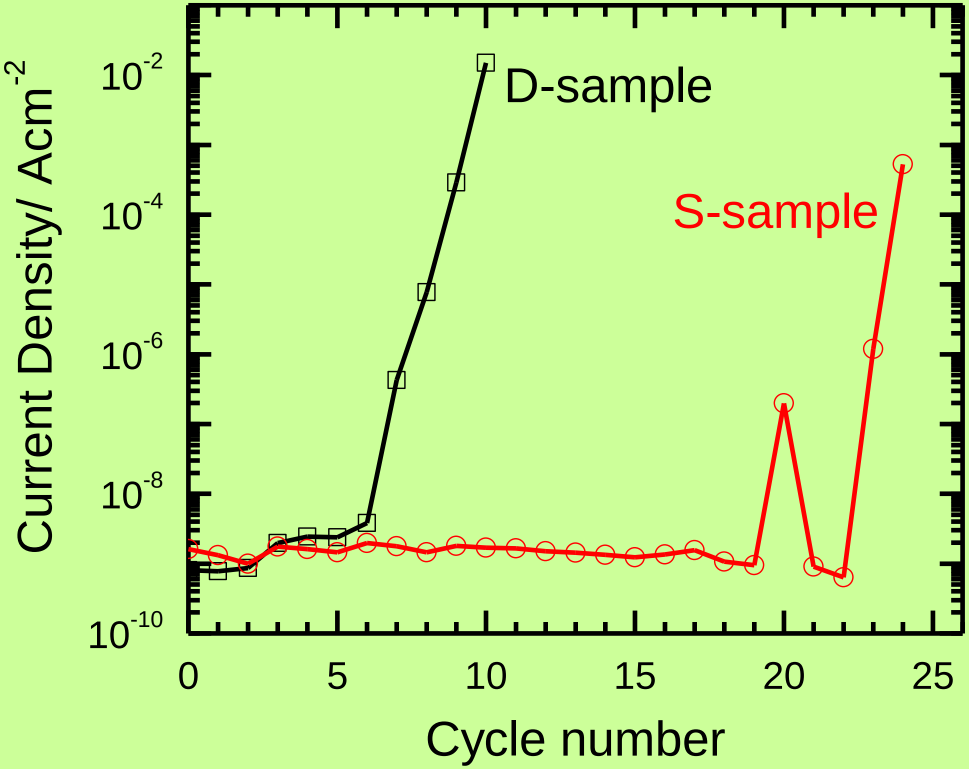
- **Substrate –Steel R-36 supplied by Q-panels**
- **Coatings- 2 epoxy primers with specification of MIL-P-53022b Type II (D and S)**
- **Testing method: AC-DC-AC via Electrochemical Impedance Spectroscopy.**
- **Electrolyte: 5.0 % NaCl**
- **Sample was immersed in 5.0 % NaCl solution during EIS.**

<u>Gamry instrumentation and software</u>

➢**EIS- : 100 kHz to 10 mHz , 10 mV amplitude, 10 points per decade**
➢**Test cell-: clamp-on persplex cylinder with O-ring seal (7.07 cm^2)**
➢**Modeling done using Zsimpwin provided by Princeton applies research**

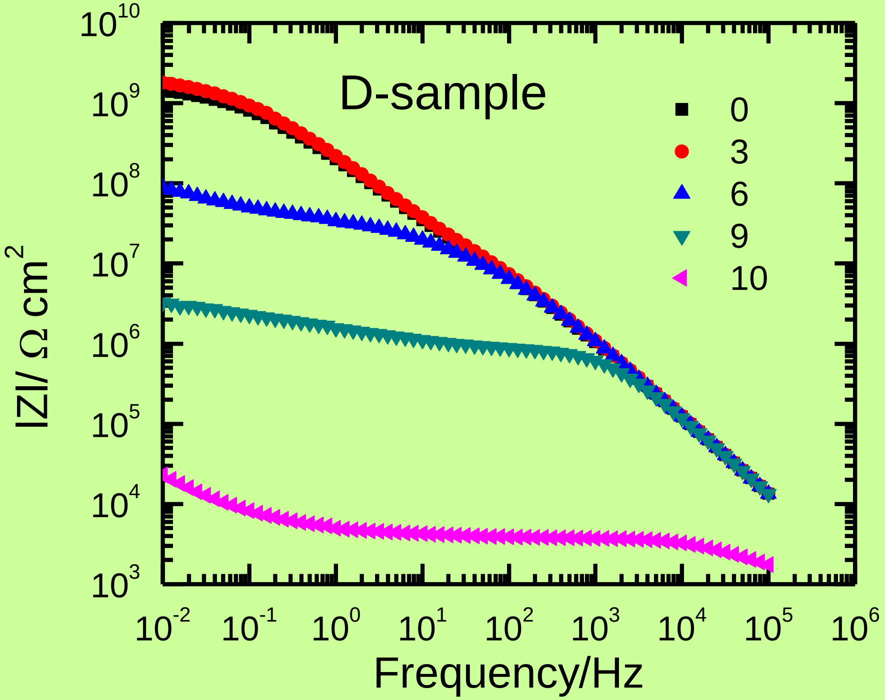
Influence of DC on current density

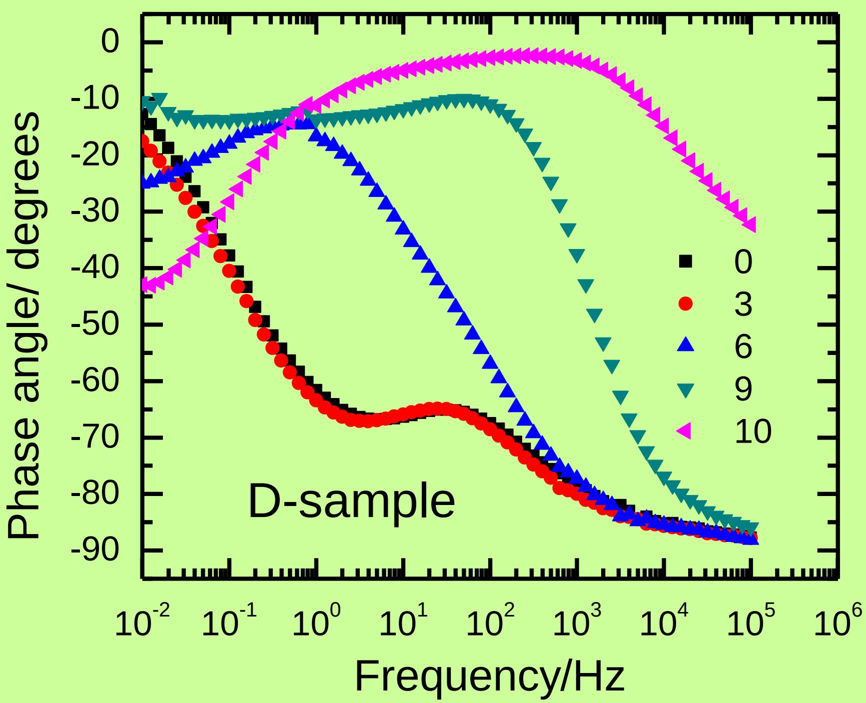
- Cycles 1 to 3: -2 V
- Cycles 4 to 6: -4 V
- Cycles 7 to 9: -6 V
- Cycles 10…: -8 V



- Increase in current density
  - indicates corrosion at the metal coating interface and degraded coating
  - after 6 cycles for D sample compared to 22 cycles for S-sample

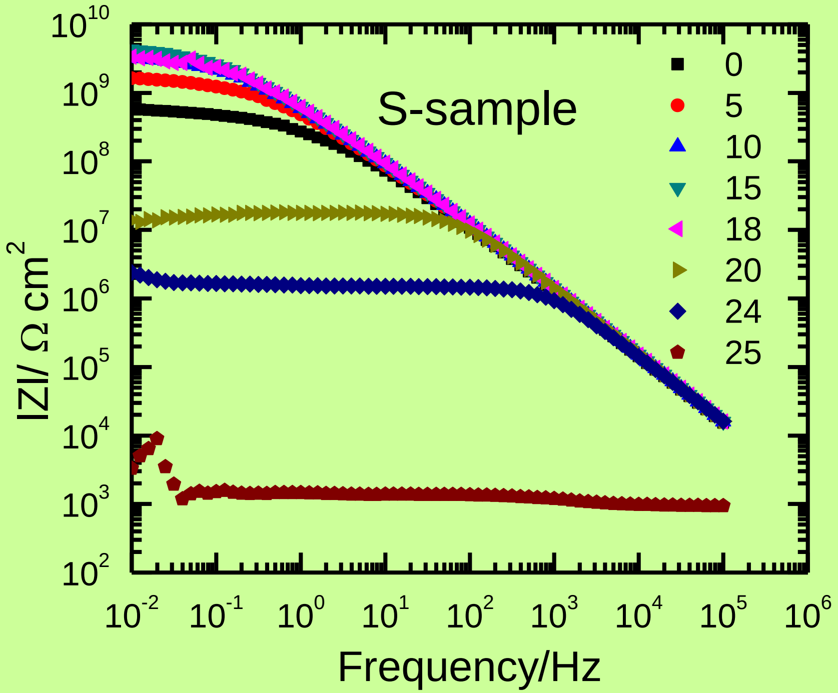
Results for D-primer

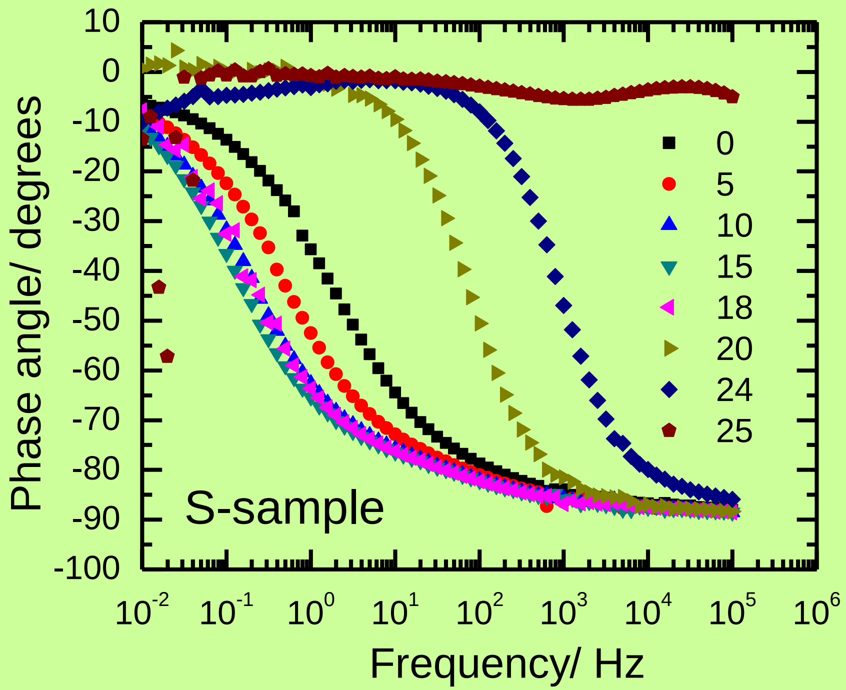




- lZl and Phase angle responds to the applied dc volts
- Failure could be induced by applying dc

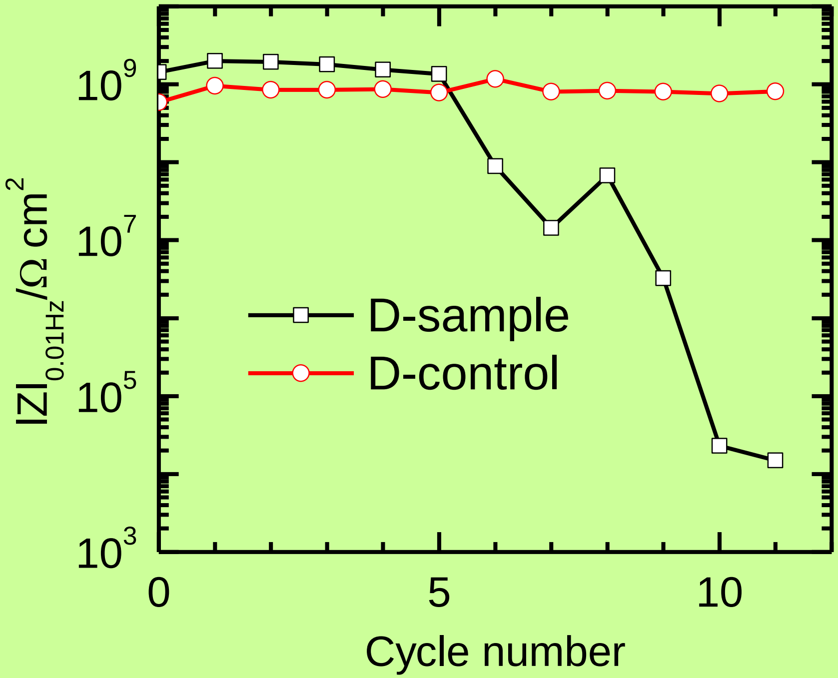
Results for S-primer

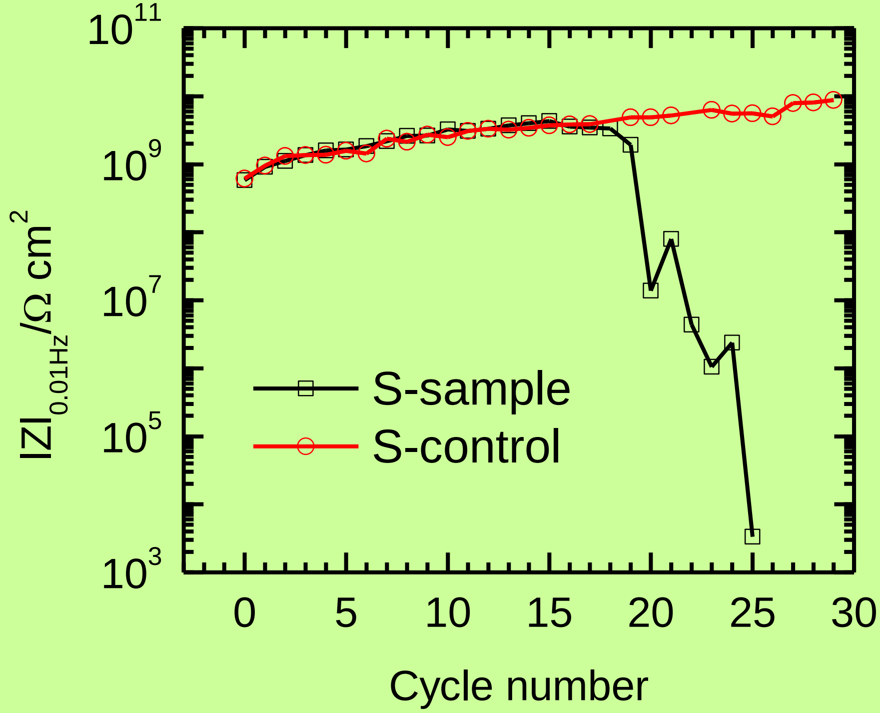




- IZI and Phase angle responds to the applied dc volts
- Failure could be induced by applying dc
- S-sample however fails at higher cycle compared to D- sample

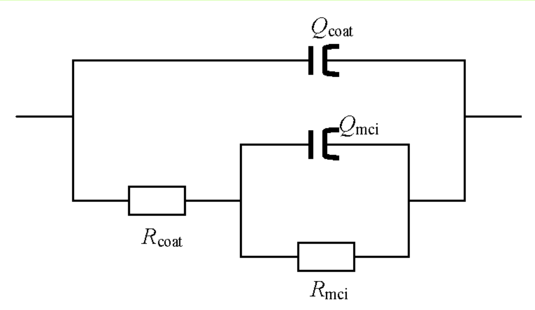
Influence of dc on barrier property

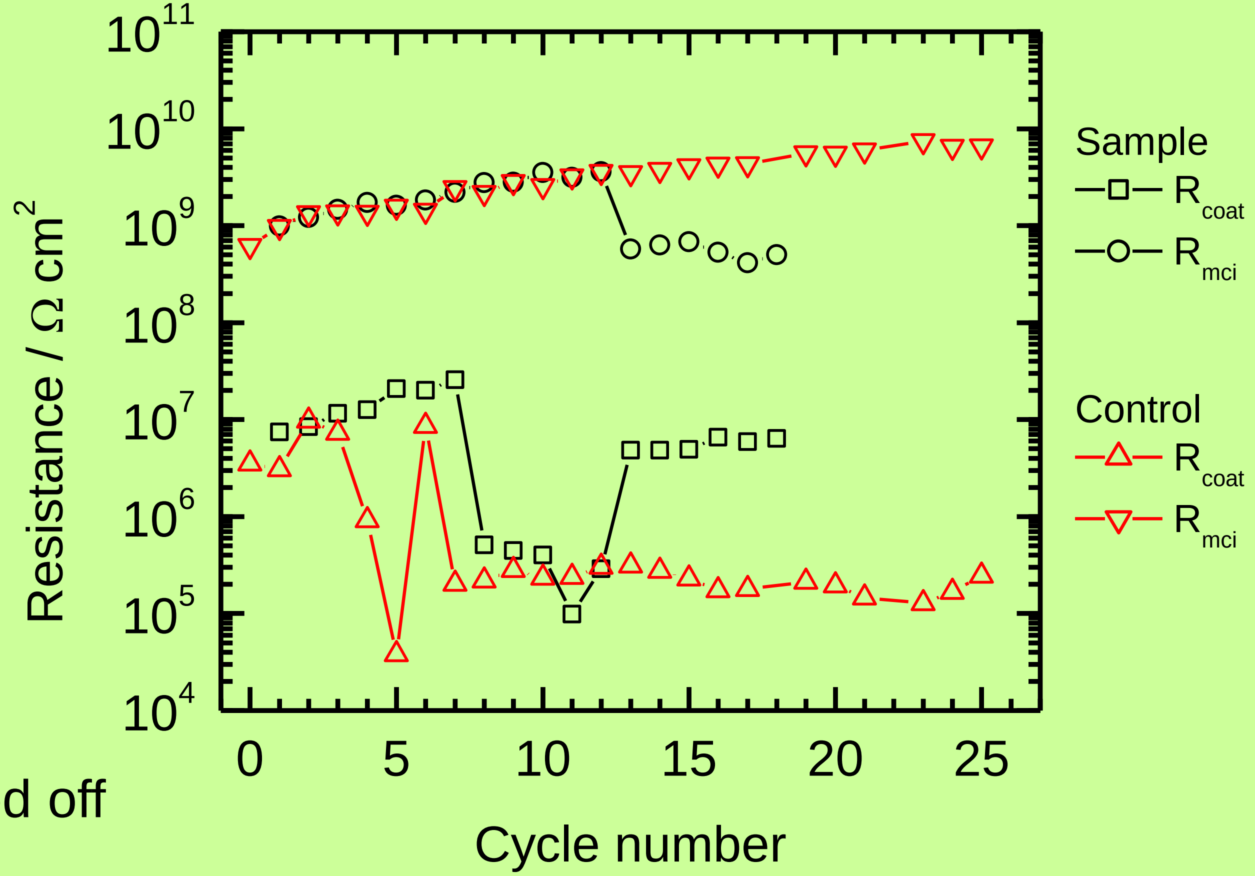




- $|Z|_{0.01Hz}$ dissimilar for control and sample
- Influence of dc on barrier property of both the samples

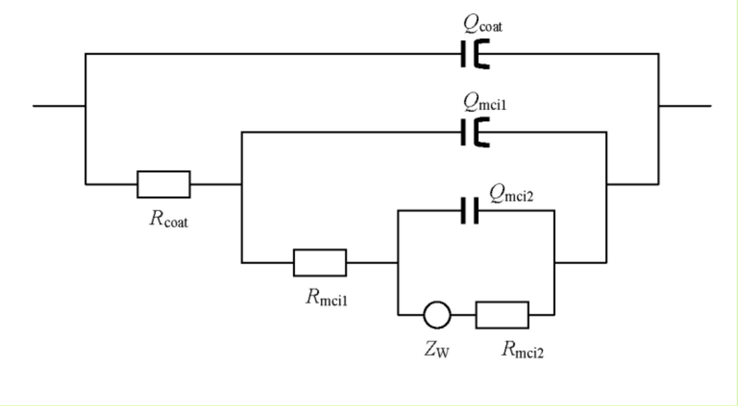
Analysis of S-primer data

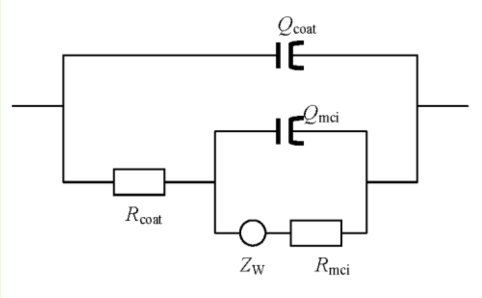


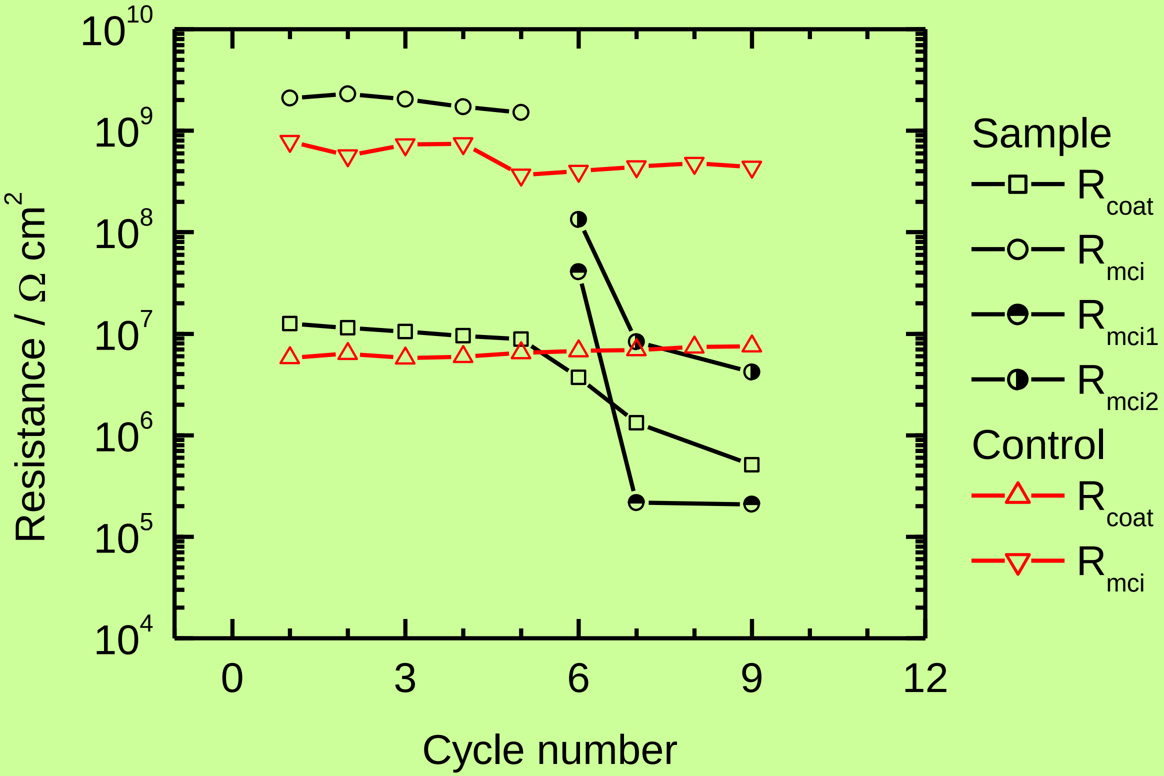


- $R_{mci} > R_{coat}$
- R_{mci} for Sample dropped off after 12 cycles
- Cycles 16, 17 and 18: truncated data set at 0.1 Hz
- Lack of fit for sample data at cycles > 18

Analysis of D-primer data





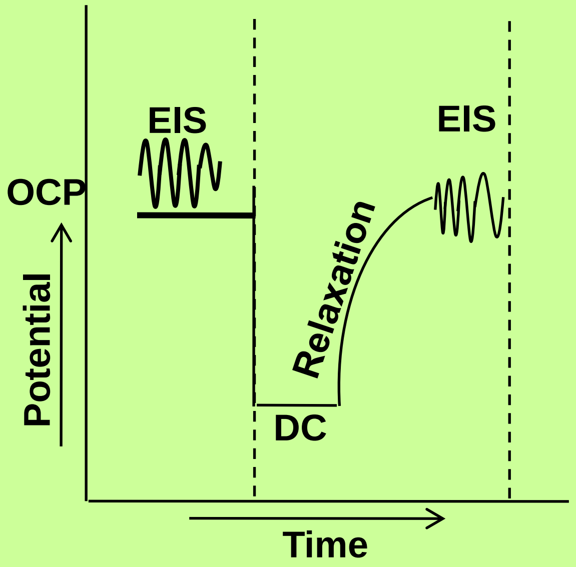


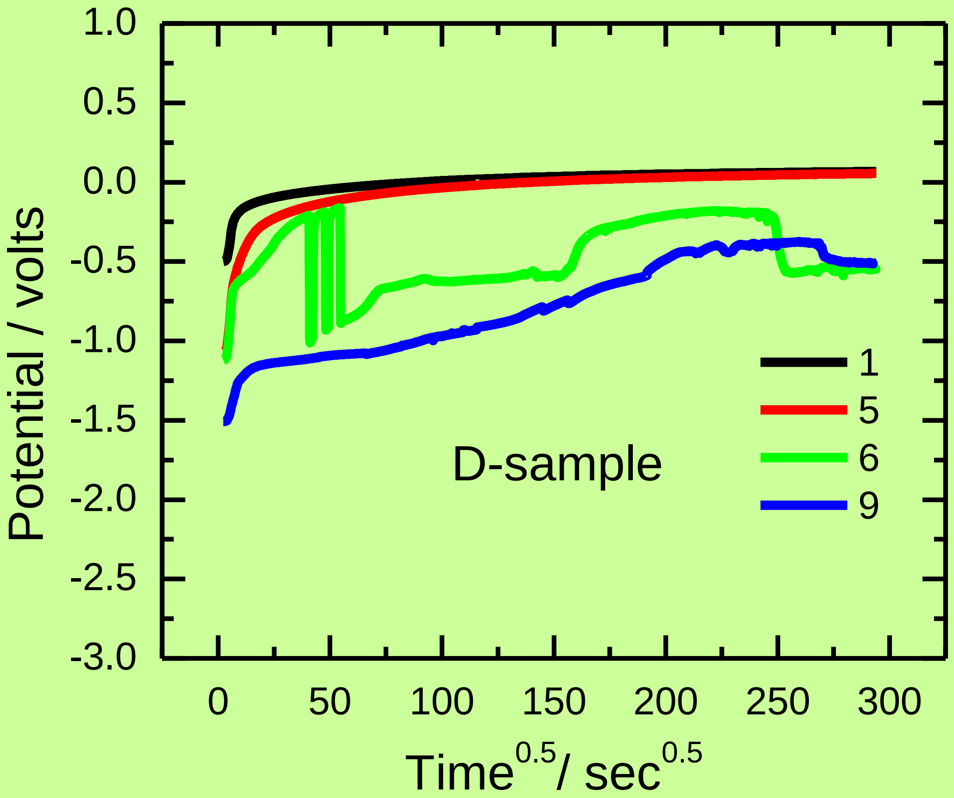
- For D-control : R_{mci} and R_{coat} unchanged
- For D-sample: R_{coat} and R_{mci} similar for first 5 cycles

  R_{mci1} and R_{mci2} required after 5 cycles

  R_{coat}, R_{mci1} and R_{mci2} dropped off after 5 cycles

Post dc potential profile for D-sample

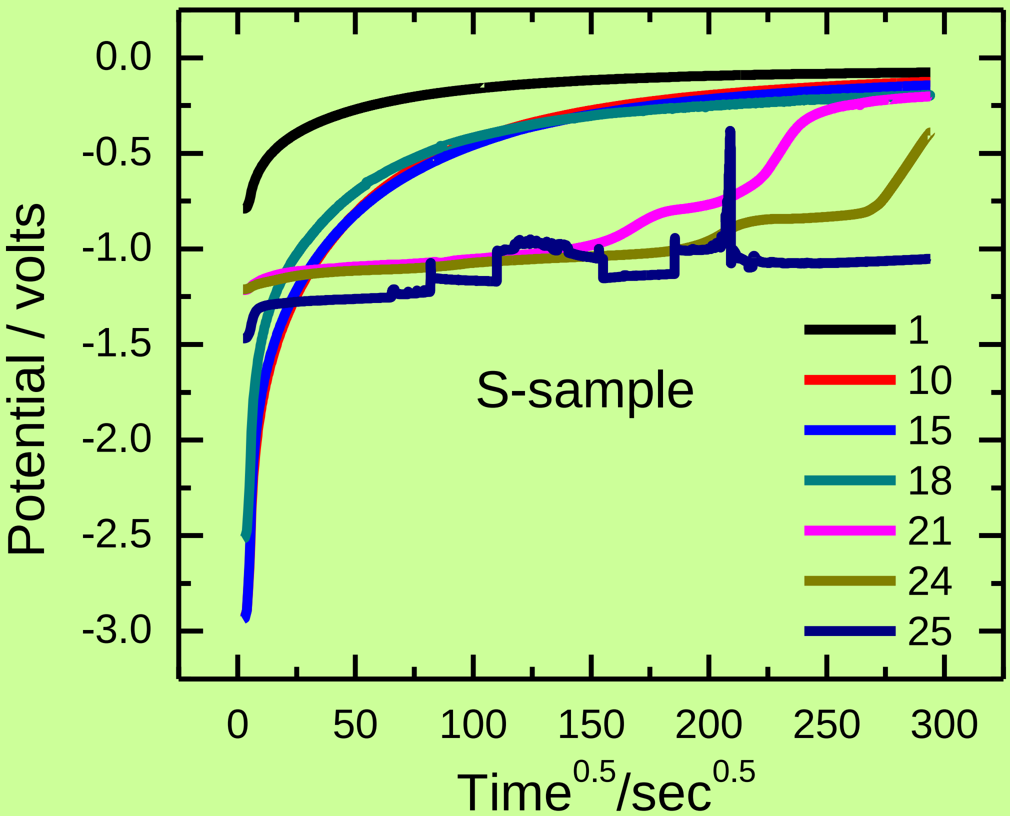




• Up to cycle 5, short time relaxation observed, characteristic of intact coating

• More than one time constant post cycle 5 indicating loss of coating intactness

Post dc potential profile for S-sample



• Relaxation behavior changes from cycle 21 indicating barrier property degradation.

• More than one time constant observed. Cycle 25 displays the OCP of the substrate when the coating fails completely

Application of AC-DC-AC on primers

- Based on barrier property $|Z|_{0.01Hz}$ and current density plots
  - – 3 cycles of -4 V dc degraded D-sample
  - – S-sample degraded after 11 cycles of –8 V dc
- Equivalent circuit analysis of EIS data
  - – S-sample circuit included only R_{bulk} and R_{mci} until failure
  - – D-sample circuit used R_{bulk} and R_{mci} when intact and R_{bulk}, R_{mci1} and R_{mci2} upon failing

- Potential profile post dc also provides signature of coatings ability
- Different relaxation behavior was observed that could discriminate between an intact and degraded coating
- Future effort--- correlate ac-dc-ac findings with B117 exposure data for primers