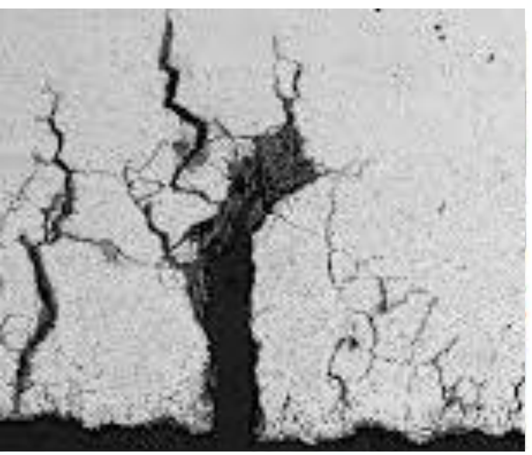
PASSIVE FILM EVOLUTION OVER 2.5 YEARS OF LEAN-DUPLEX STAINLESS STEEL REINFORCEMENTS EMBEDDED IN MORTAR CONTAINING CHLORIDES

1st Corrosion and Materials Degradation Web Conference

Ulises Martin, Juan Bosch, Jacob Ress, Dr. D.M. Bastidas



DEPARTMENT OF CHEMICAL, BIOMOLECULAR AND CORROSION ENGINEERING

The University of Akron

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CONTENT

- Introduction to Corrosion of Reinforced Concrete Structures
- Passive film of Stainless Steels
- Materials and Techniques
- Results and Discussion
- Conclusions

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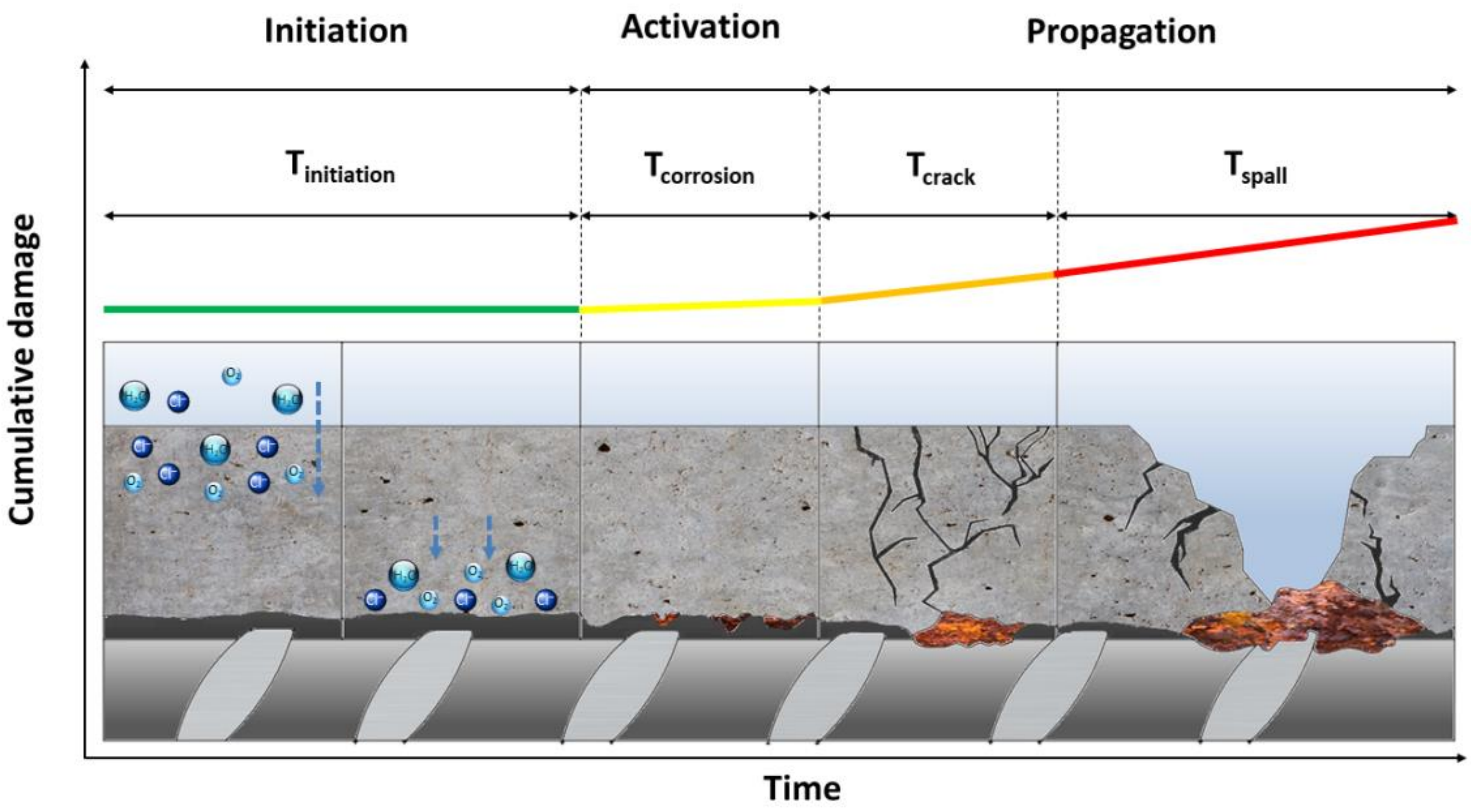
Introduction to Corrosion of Reinforced Concrete Structures

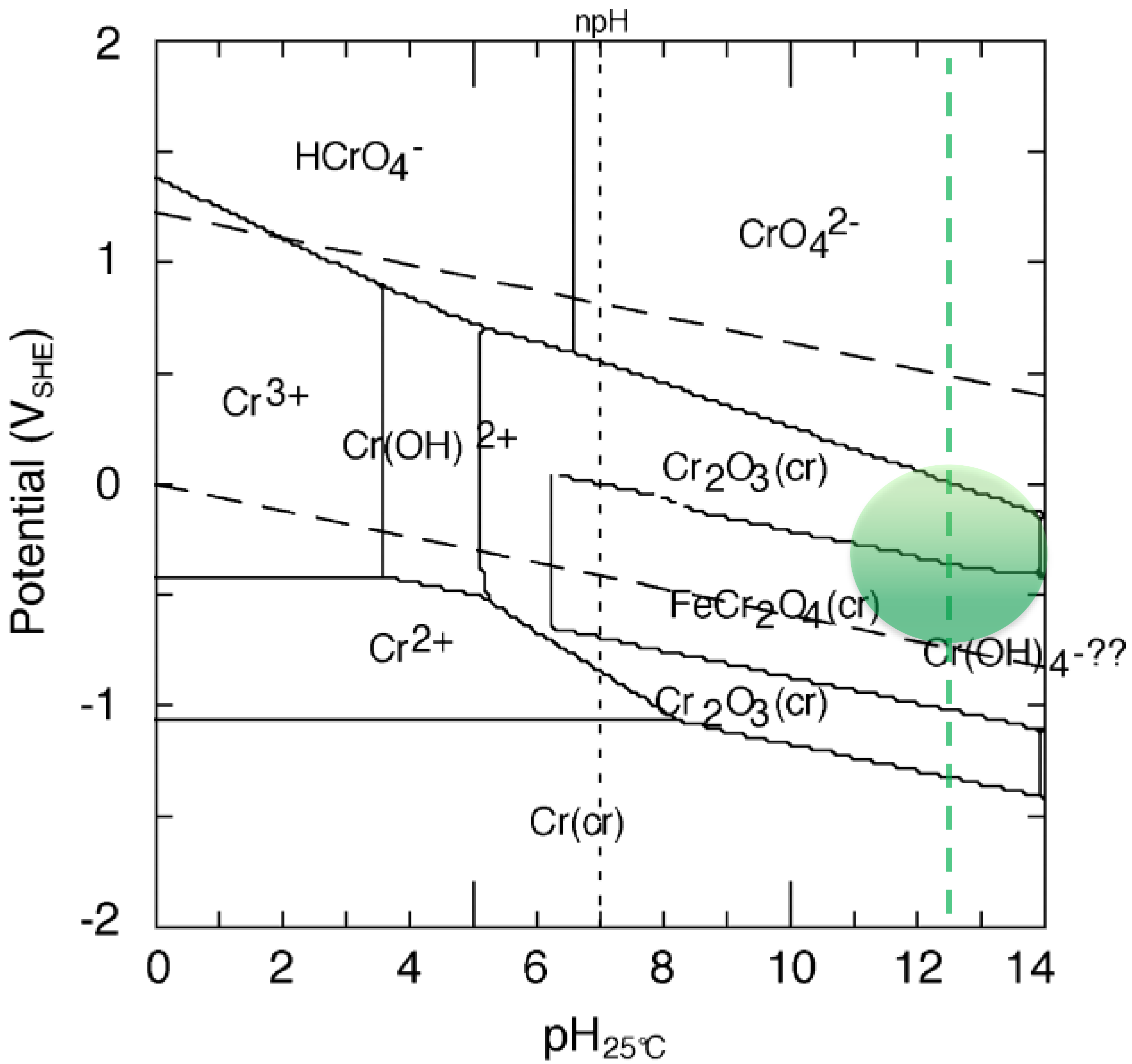


Tuutti model for the corrosion of RCS

- Stages for the corrosion of RCS:
  - **Initiation** → Ingress of chlorides, carbonation,…
  - **Activation** → First dissolution of the passive film, pit nucleation
  - **Propagation** → Pit growth, cracking of concrete cover, spallation

Tuutti, K. Corrosion of steel in concrete, PhD Thesis, Swedish Cement and Concrete Research Institute, Stockholm, 1982.

Passive film of Stainless Steels



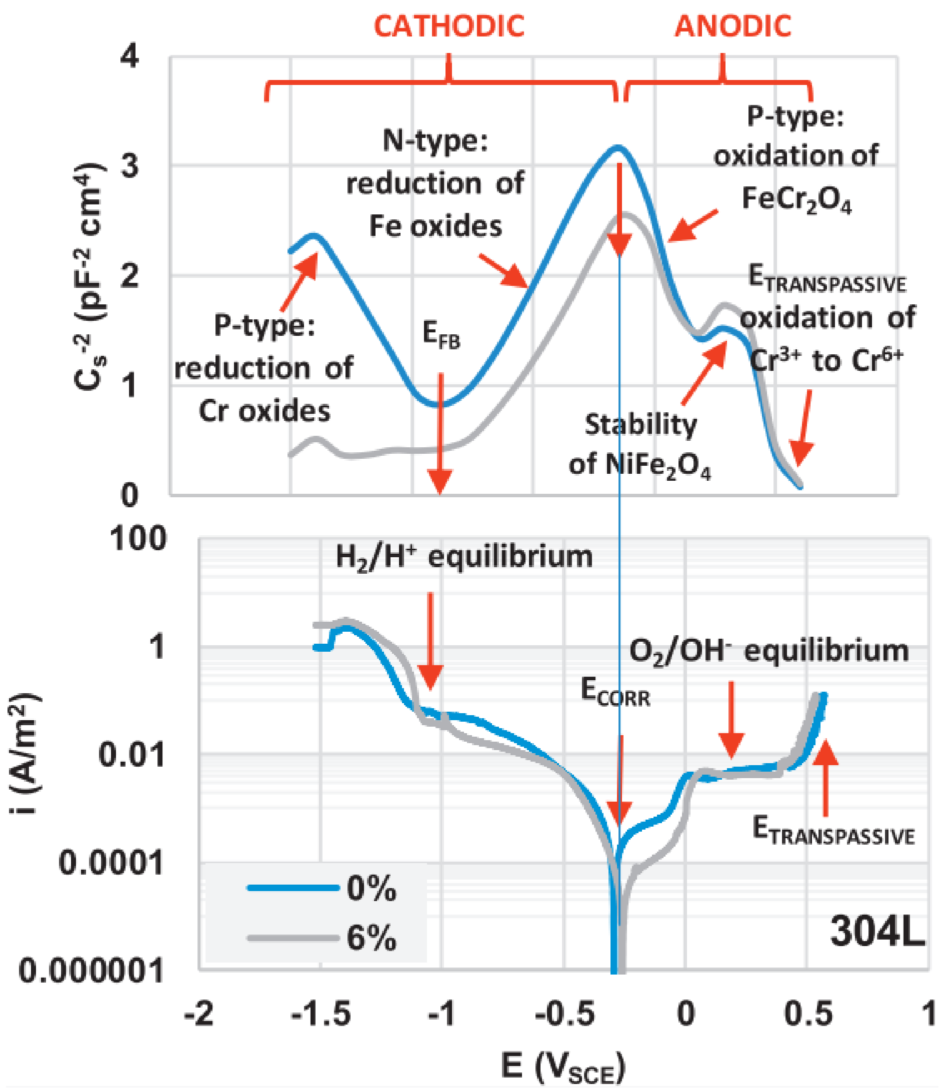
Pourbaix diagrams for chromium species in the ternary system of Fe-Cr-Ni at 25 ºC from Puigdomenech et al.

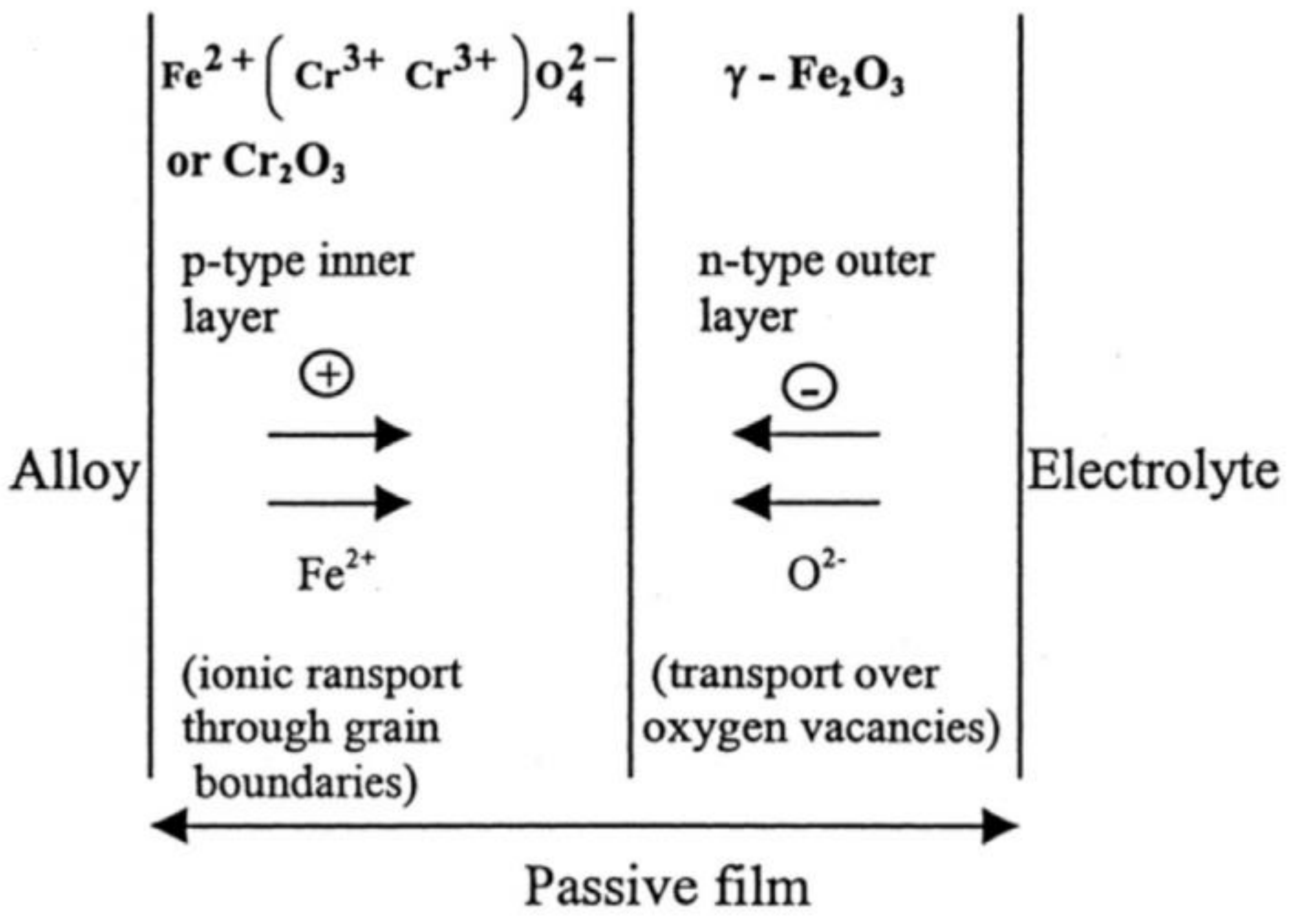
Concrete has a **12.6 pH**

- Formation of $\mathbf{Cr_2O_3 + FeCr_2O_4}$ ***p*-type** semiconductors, reducing the defects inside the passive film as electrons flow from the solution to the film

Beverskog, B.; Puigdomenech, I. Pourbaix diagrams for the ternary system of iron-chromium-nickel. *Corrosion* **1999**, *55*, 1077–1087, doi:10.5006/1.3283945.

Passive film of Stainless Steels

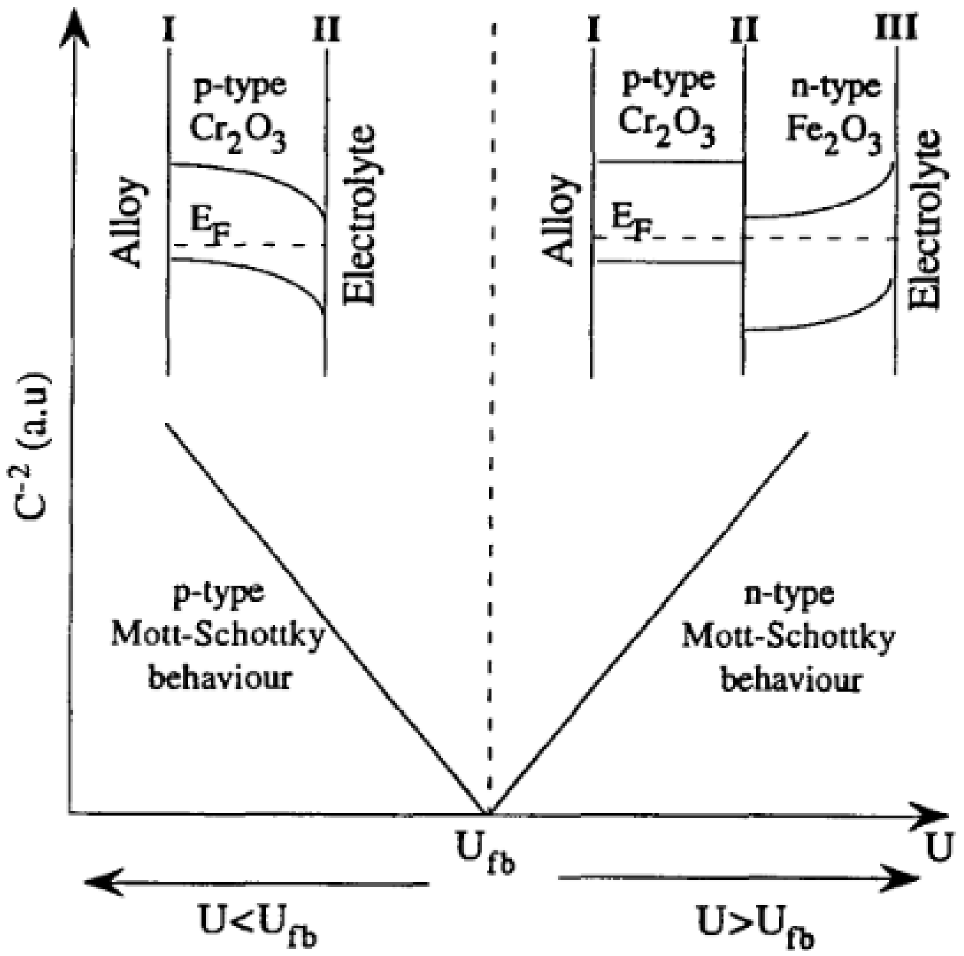


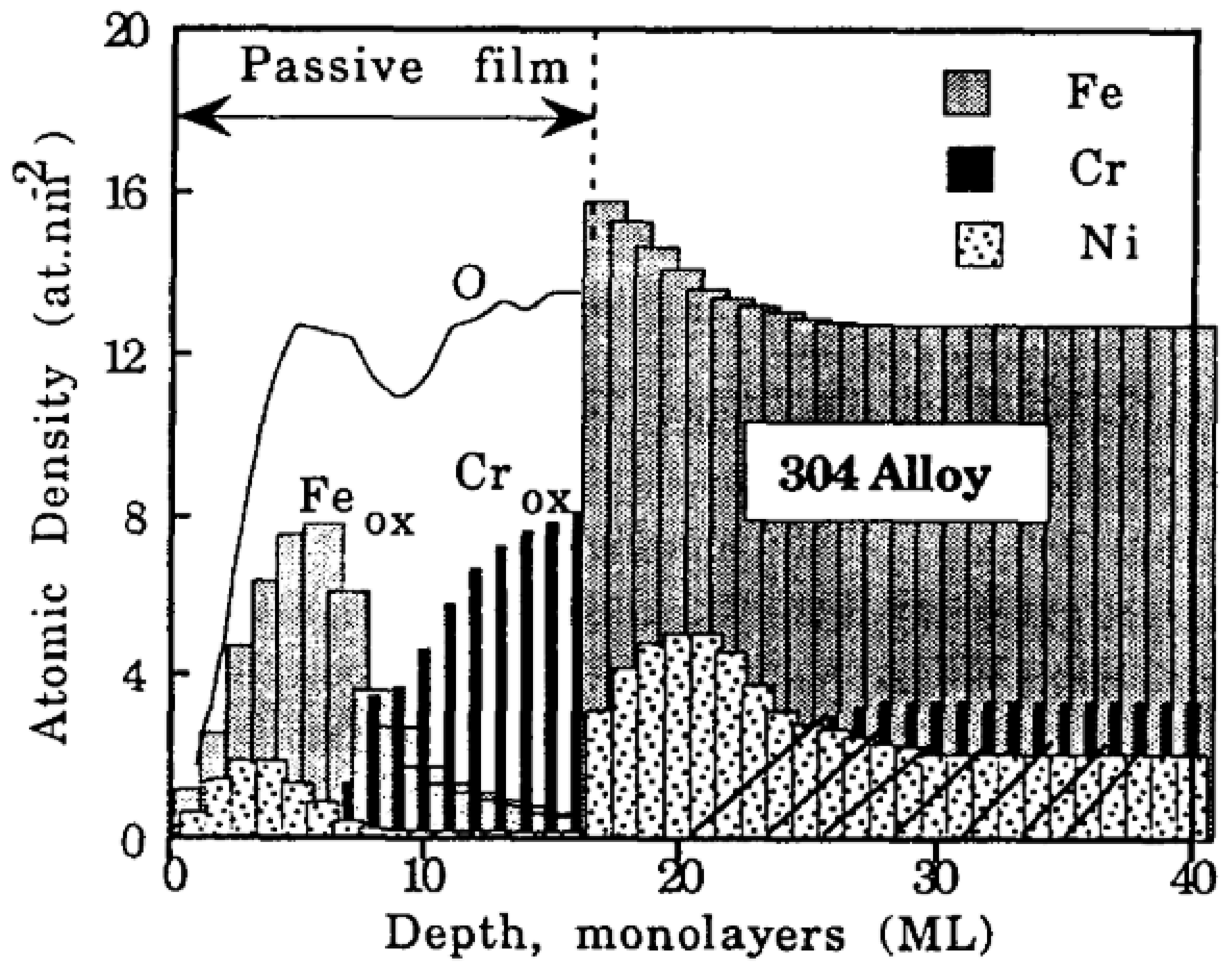


Ogunsanya, I.G.; Hansson, C.M. The semiconductor properties of passive films and corrosion behavior of stainless steel reinforcing bars in simulated concrete pore solution. *Materialia* **2019**, *6*, 100321, doi:10.1016/j.mtla.2019.100321.

Hakiki, N.E.; Montemor, M.F.; Ferreira, M.G.S.; Da Cunha Belo, M. Semiconducting properties of thermally grown oxide films on AISI 304 stainless steel. *Corros. Sci.* **2000**, *42*, 687–702, doi:10.1016/S0010-938X(99)00082-7.

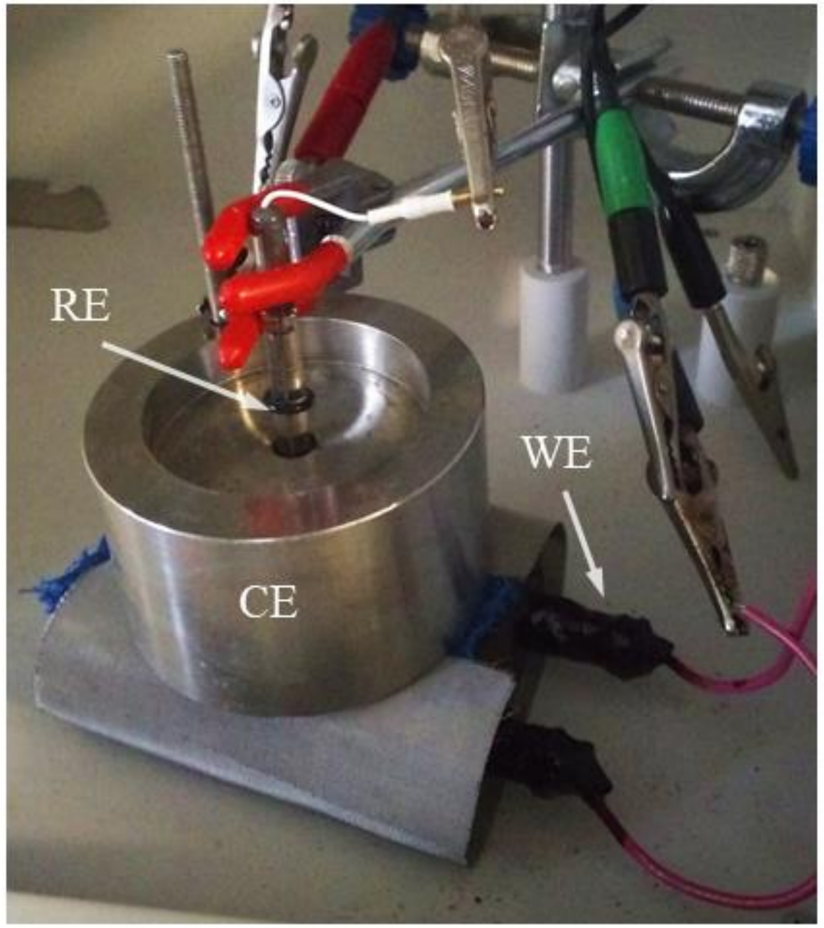
Passive film of Stainless Steels





Hakiki, N.B.; Boudin, S.; Rondot, B.; Da Cunha Belo, M. The electronic structure of passive films formed on stainless steels. *Corros. Sci.* **1995**, *37*, 1809–1822, doi:10.1016/0010-938X(95)00084-W.

Materials and Techniques



Materials

Sample	C	Si	Mn	P	S	Cr	Ni	Cu	N	Mo
LDSS 2001	0.028	0.65	4.19	0.023	0.010	20.07	1.78	0.08	0.129	0.22
LDSS 2304	0.019	0.35	0.81	0.029	0.010	22.75	4.32	0.31	0.138	0.29
AISI 304	0.023	0.28	1.41	0.034	0.023	18.07	7.93	0.33	0.050	0.22

Ordinary Portland Cement (OPC) with 0, 0.2, 2 and 4 wt.% Cl^-

Electrochemical setting

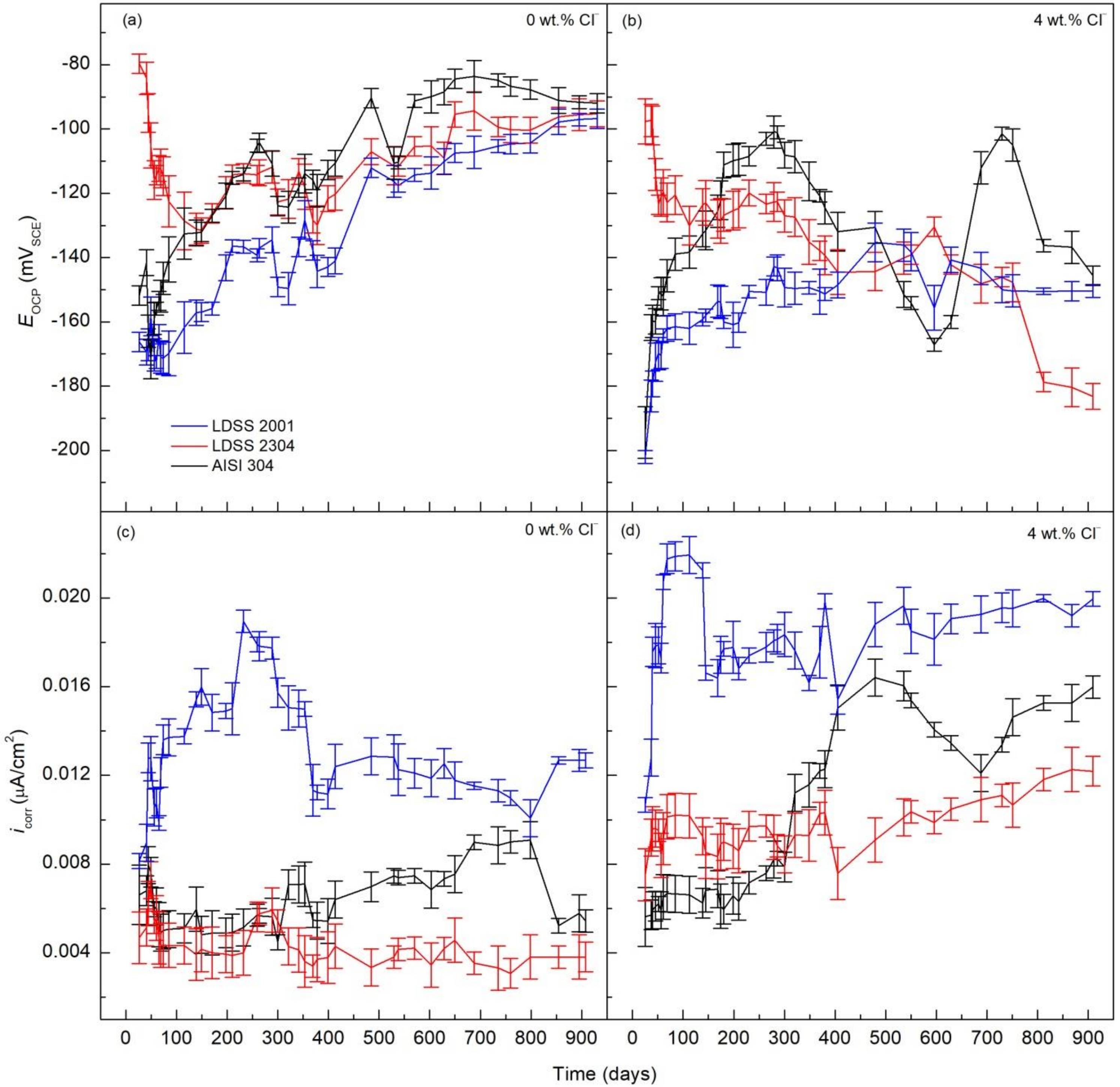
LPR, EIS, CPP, Mott-Schottky

Equipment: Potentiostat/galvanostat Gamry Reference 600. Three-electrode configuration cell setup. Saturated calomel electrode (SCE) as RE, and stainless steel mesh plus guard ring as CE.

Electrochemical standards: ASTM G-1-03, ASTM G61-86 and ASTM G3-14

Martin, U.; Bosch, J.; Ress, J.; Bastidas, D.M. Long-term stability and electronic properties of passive film of lean-duplex stainless steel reinforcements in chloride containing mortar. *Constr. Build. Mater.* **2021**, *291*, 123319, doi:10.1016/j.conbuildmat.2021.123319

Results and Discussion



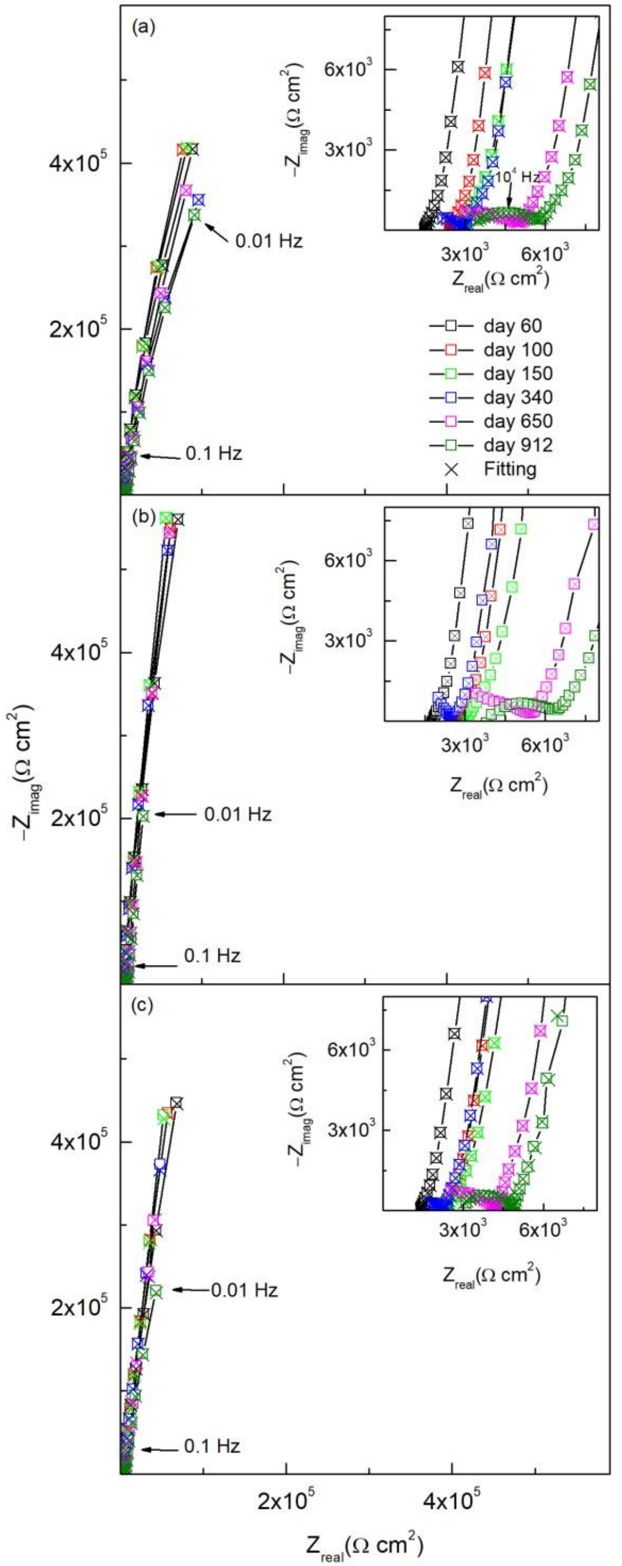
E_{corr} and i_{corr} **monitoring** over **912 days.**

All SS reinforcements **improve** their E_{corr} **over time,** increasing the potential towards more positive values, as the **passive film is growing.**

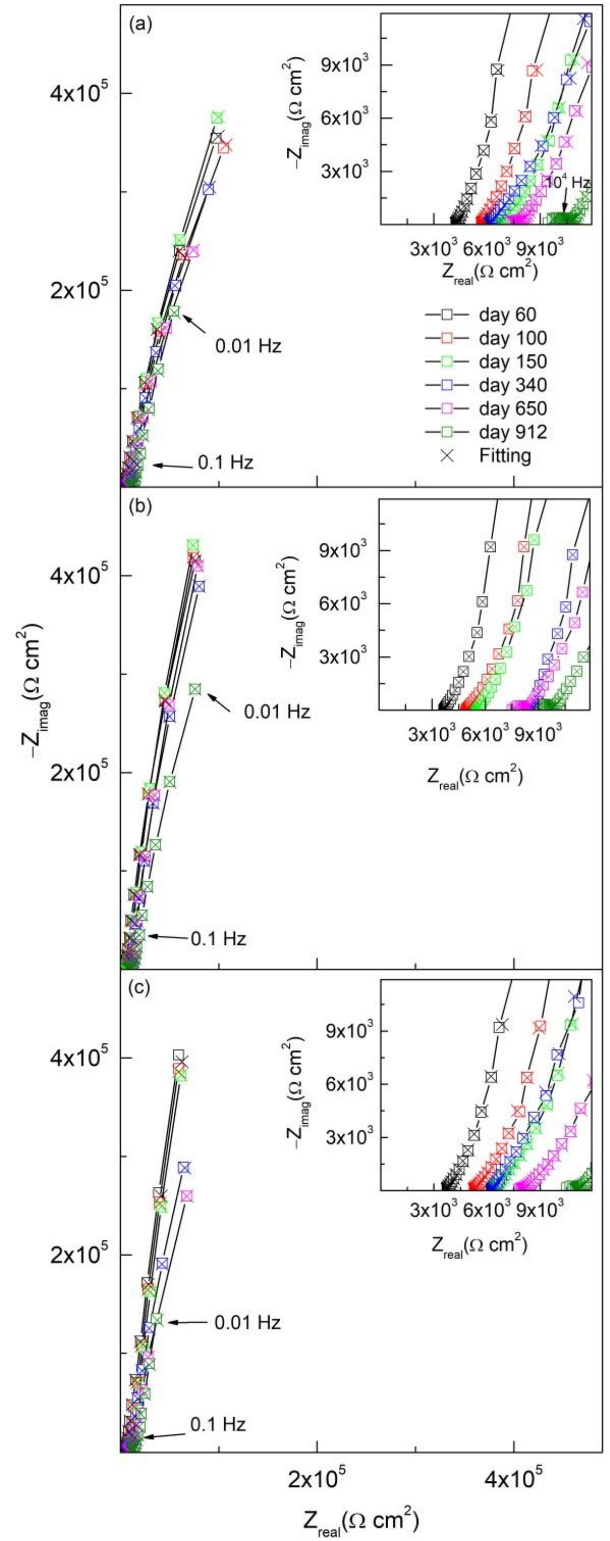
Similarly, the i_{corr} **decreases or stabilizes** and **does not** considerably **change** over the entire testing.

Results and Discussion

0 wt.% Cl⁻



4 wt.% Cl⁻



LDSS 2001

LDSS 2304

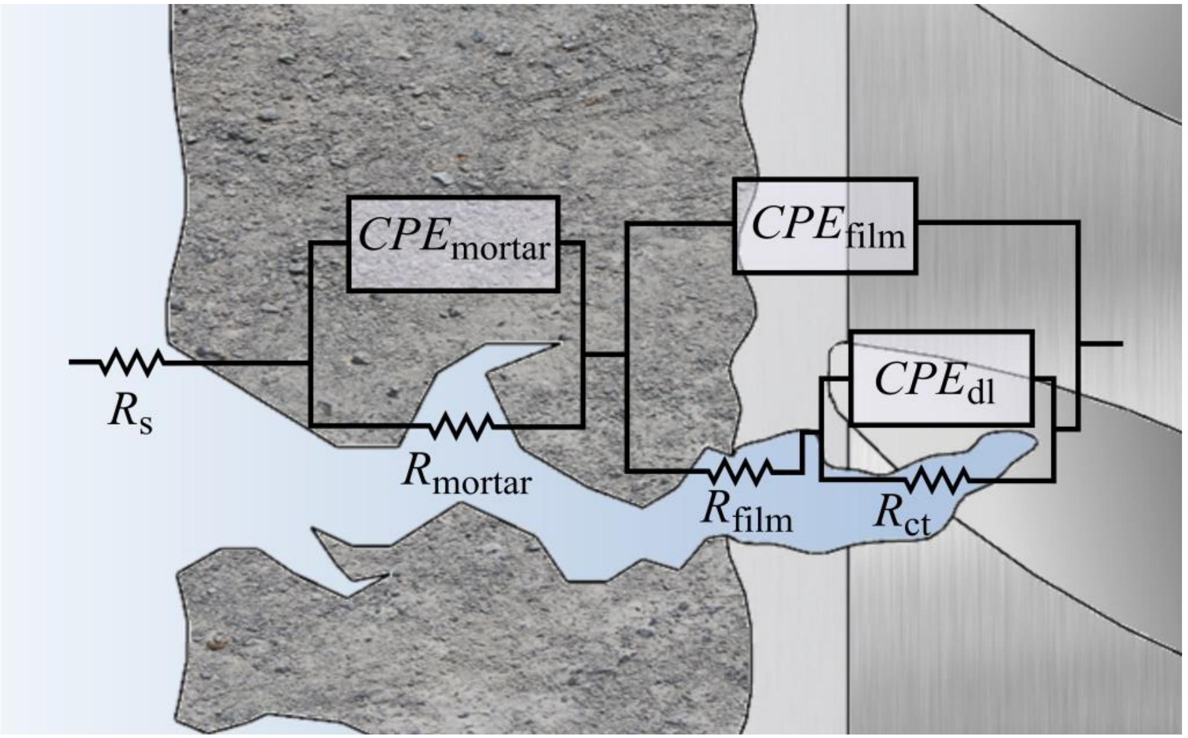
AISI 304

Nyquist plot of all SS reinforcements for **0** and **4 wt.% Cl⁻**.

The **0 wt.% Cl⁻ does not change** the **shape** regardless of the **time of exposure, only** some **minor decrease** in **impedance**

The **4 wt.% Cl⁻ experiences** some **small decrease** in the **impedance** with **time. However,** the **impedance values remain** in the **same order** of as the **0 wt.% Cl⁻.**

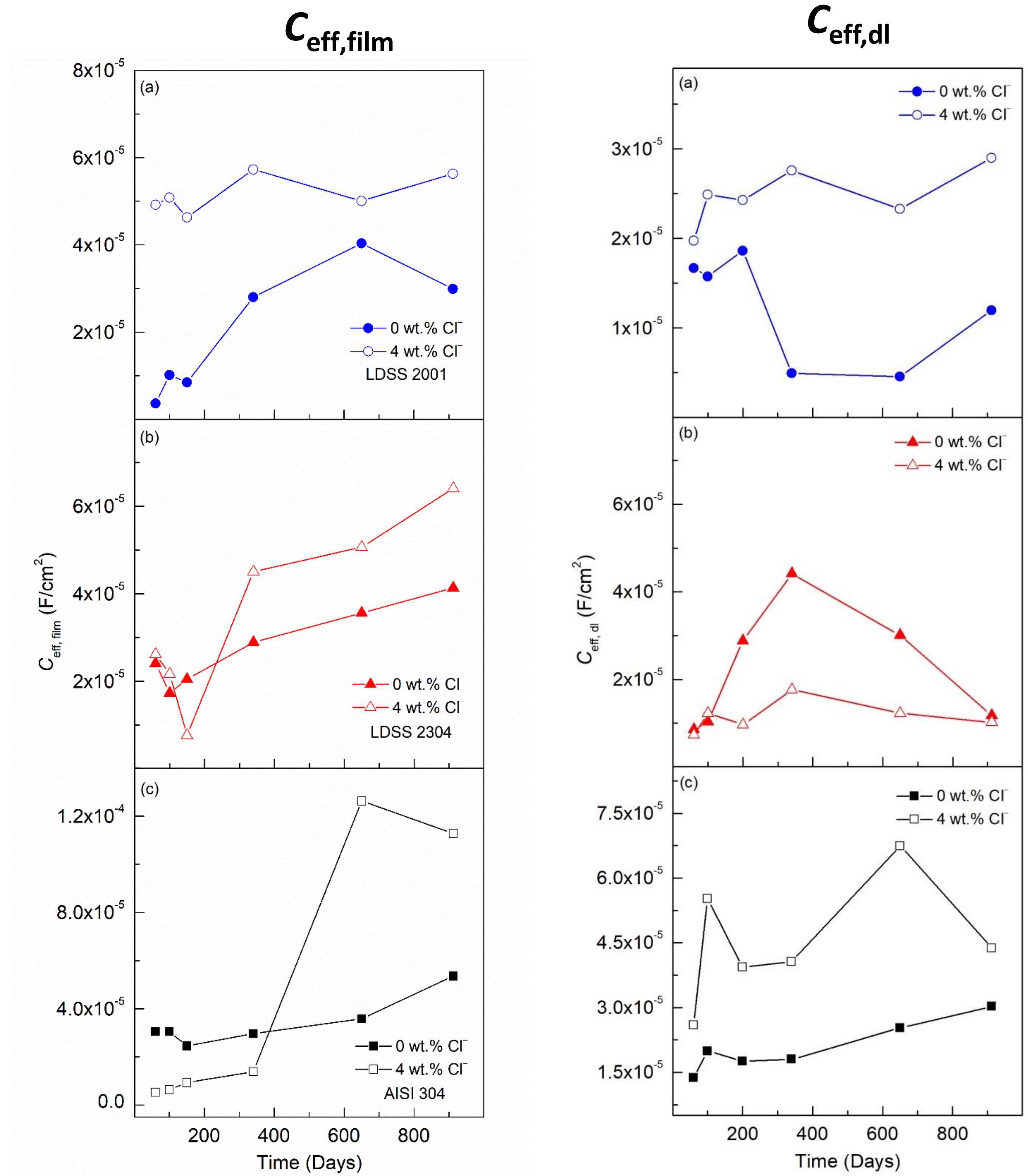
Results and Discussion



Electric equivalent circuit **(EEC)** with **three times constants** and effective capacitance of the film **($C_{eff,film}$)** and double layer **($C_{eff,dl}$).**

$$C_{\mathrm{eff,film}} = Y_{\mathrm{film}}\left(\omega_{\mathrm{m}}^{"}\right)^{n_{\mathrm{film}}-1}$$

$$C_{\mathrm{eff,dl}} = \left[Y_{\mathrm{dl}}\left(\frac{1}{R_{\mathrm{s}}}+\frac{1}{R_{\mathrm{ct}}}\right)^{(n_{\mathrm{dl}}-1)}\right]^{\frac{1}{n_{\mathrm{dl}}}}$$

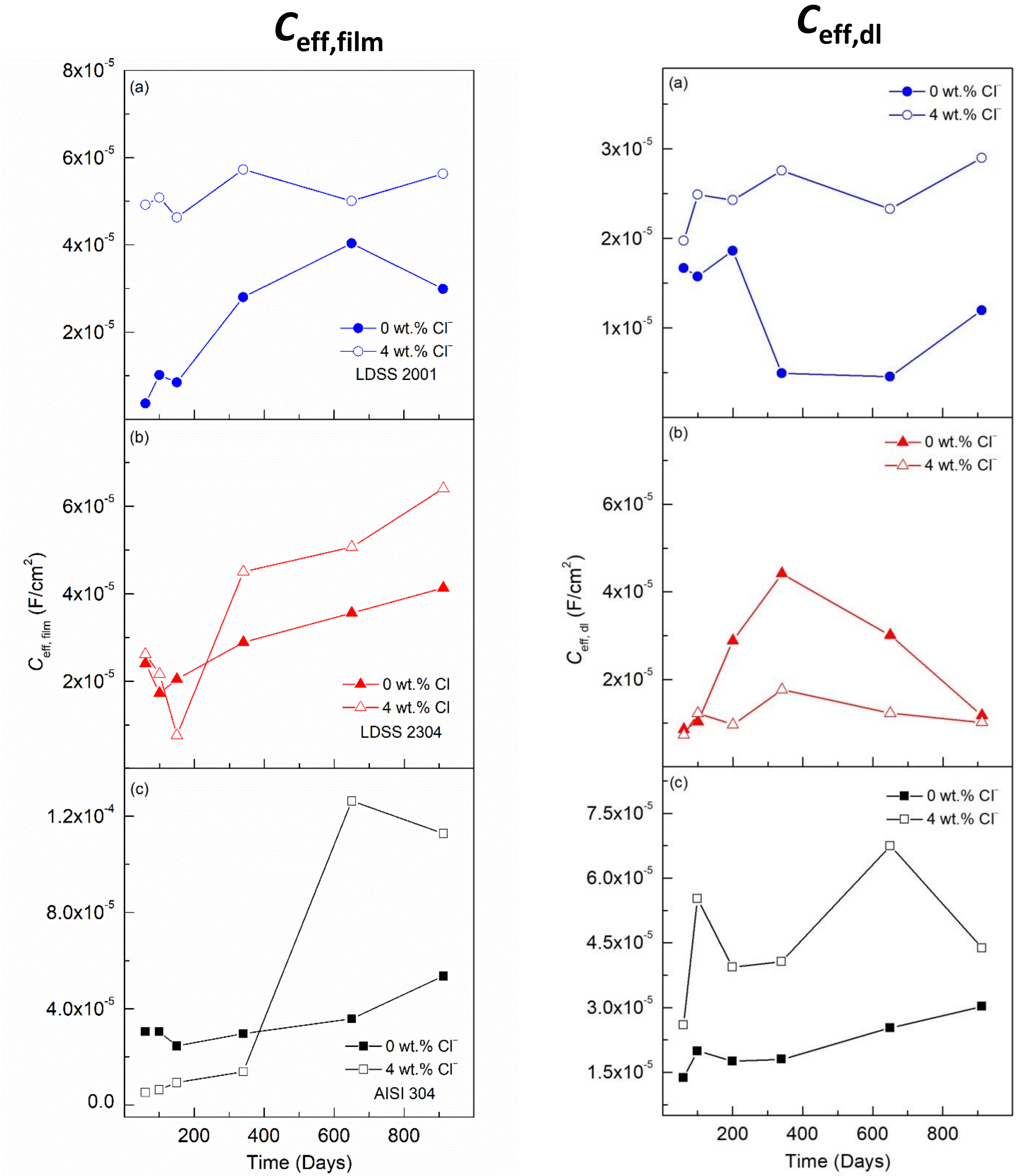


Results and Discussion

Day	Thickness of the electrochemical double layer (*d*, nm)					
	LDSS 2001		LDSS 2304		AISI 304	
	0 wt.% Cl^-	4 wt.% Cl^-	0 wt.% Cl^-	4 wt.% Cl^-	0 wt.% Cl^-	4 wt.% Cl^-
60	0.83	0.70	1.60	1.88	1.00	0.53
100	0.88	0.55	1.33	1.12	0.69	0.25
150	0.74	0.57	0.48	1.43	0.78	0.35
340	2.81	0.50	0.31	0.78	0.76	0.34
650	3.05	0.59	0.46	1.13	0.55	0.20
912	1.15	0.48	1.18	1.35	0.46	0.32

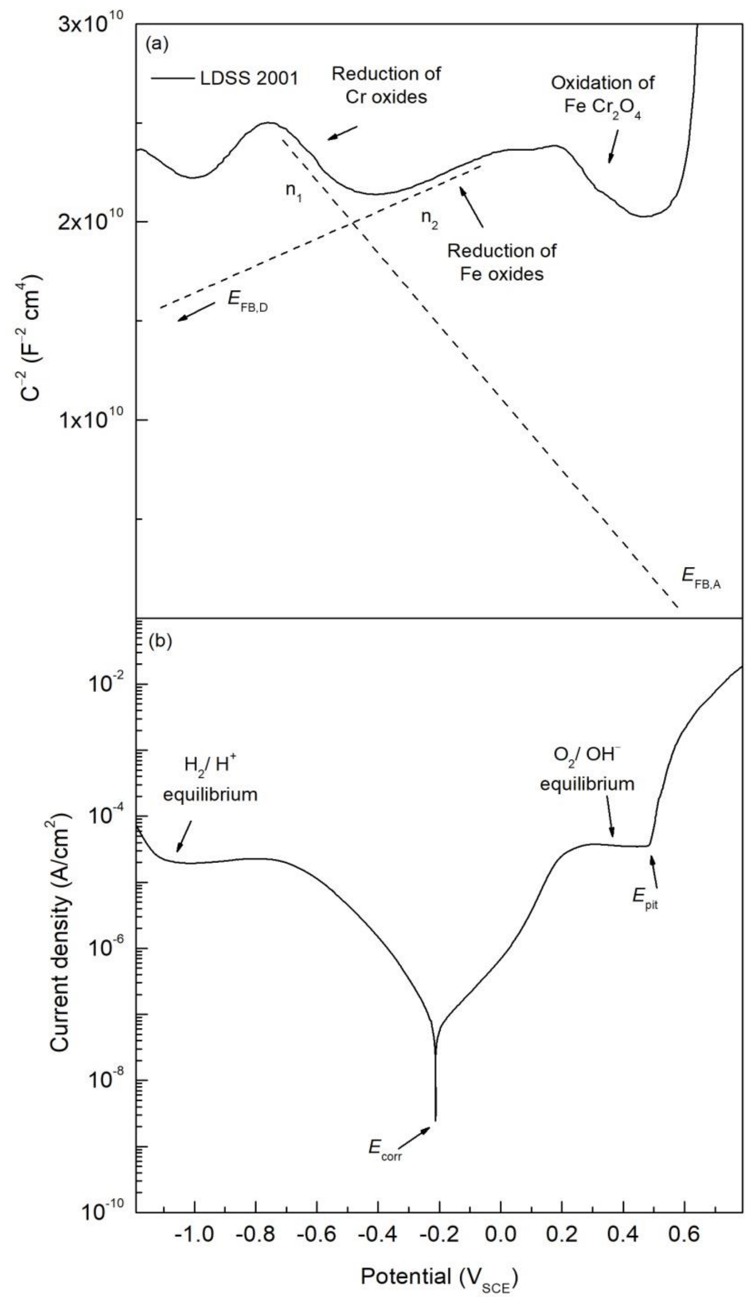
Thickness of the **double layer** based on the fitting parameters.

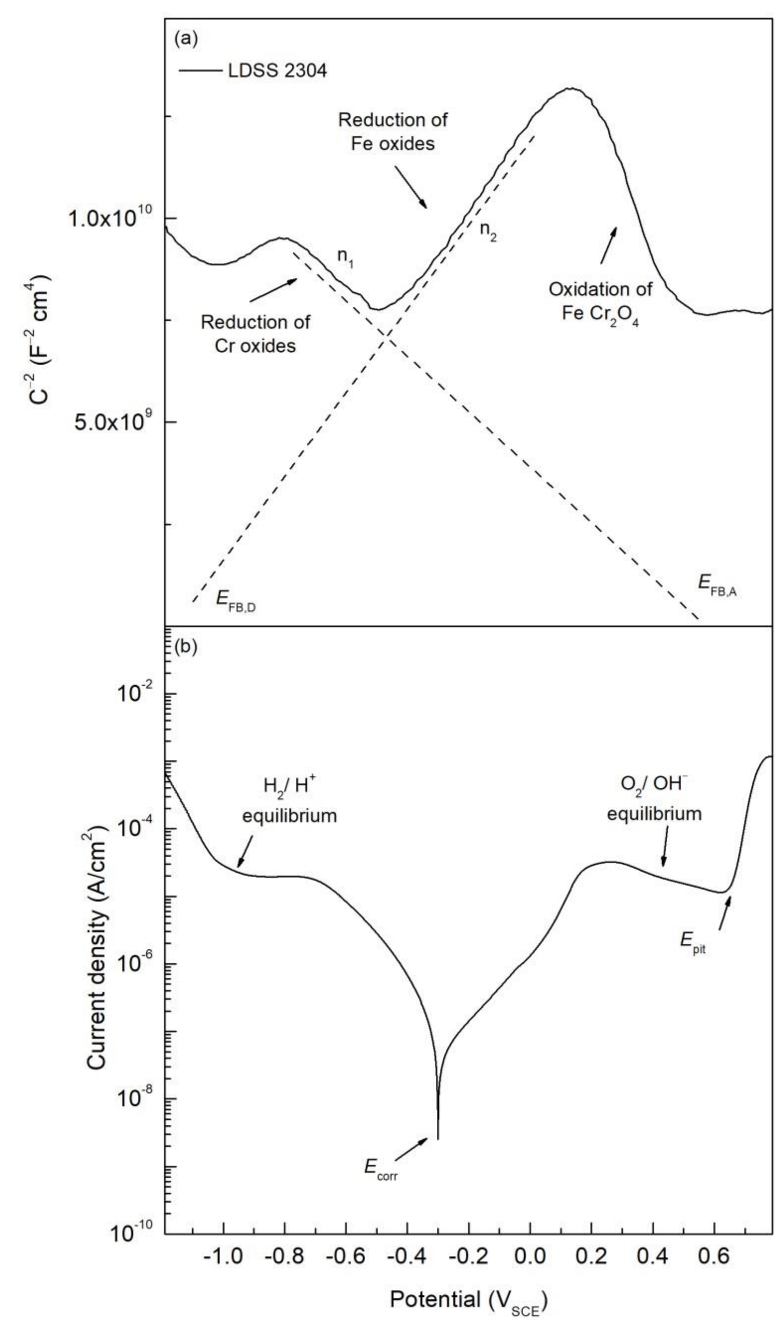
$$C_{\mathrm{eff,dl}} = \frac{\varepsilon_o \, \varepsilon_{\mathrm{film}} \, A}{d}$$

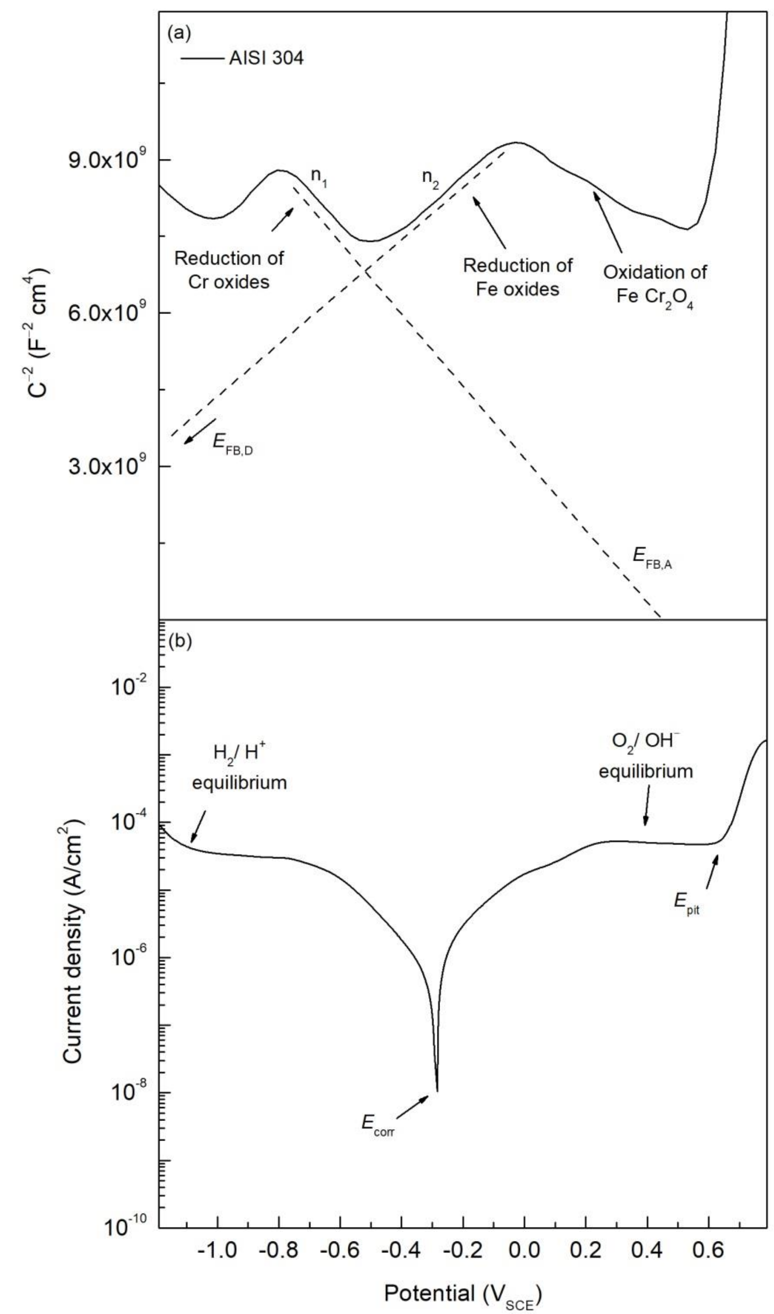


Results and Discussion

Mott-Schottky and **CPP** plots of OPC with **4 wt.% Cl⁻** after **912 days** for all SS reinforcements.



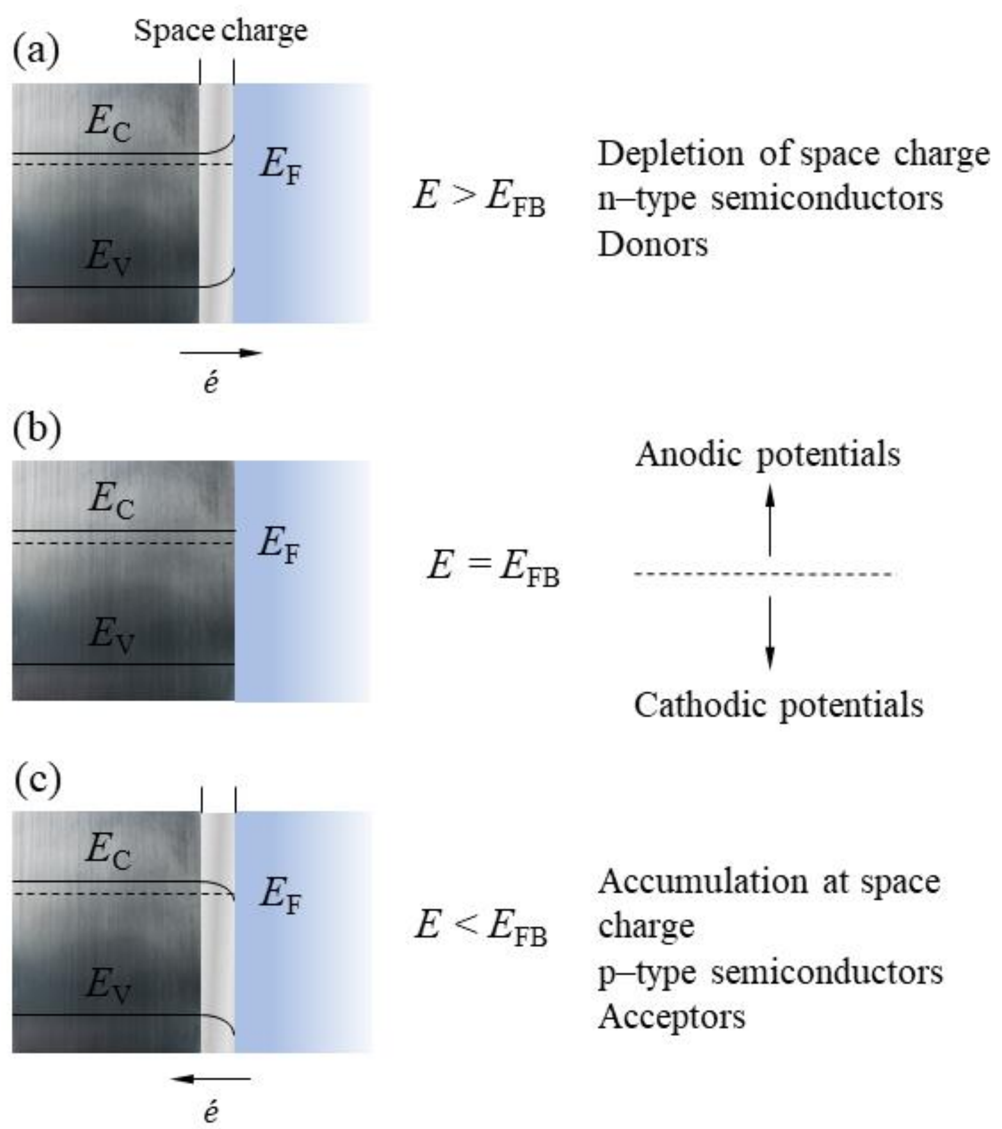




Results and Discussion

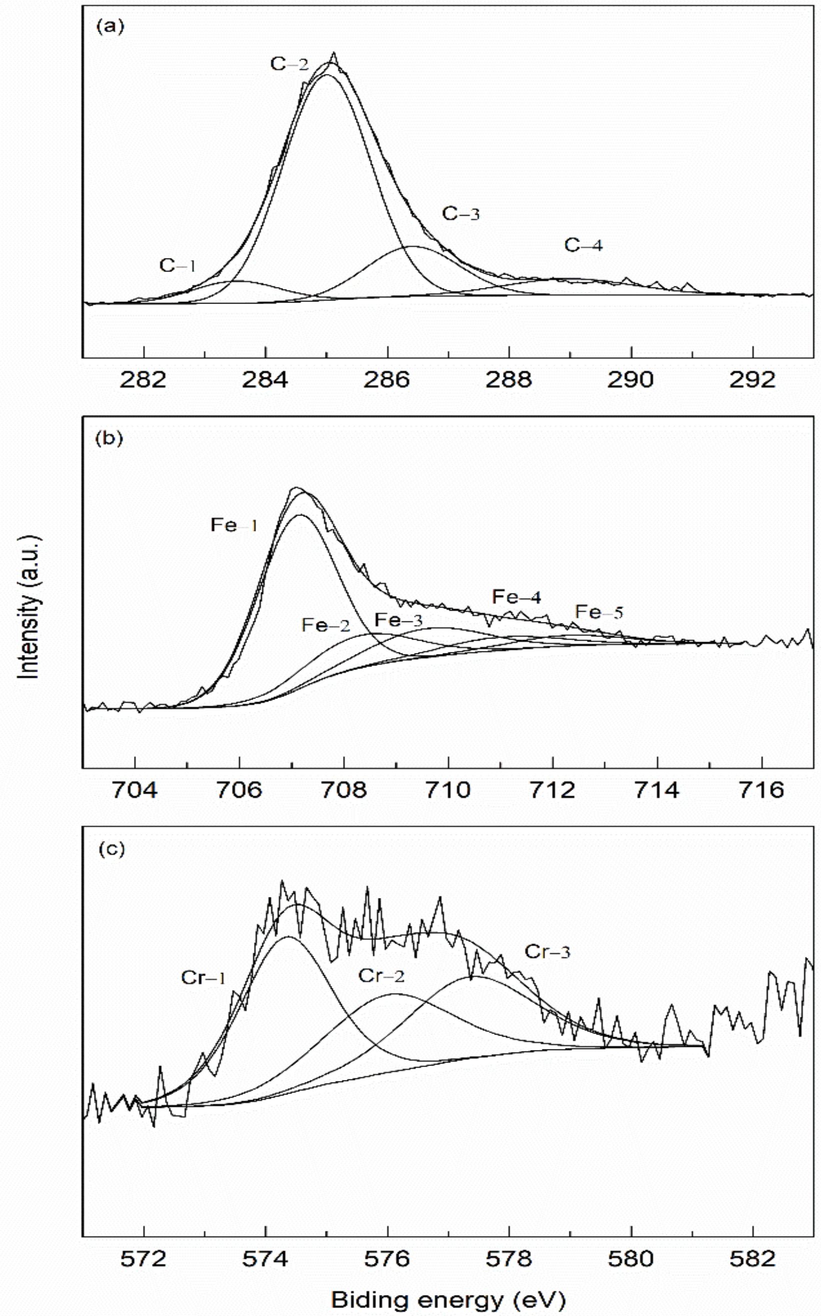
Mott-Schottky results of OPC with **4 wt.% Cl⁻** after **912 days** c.

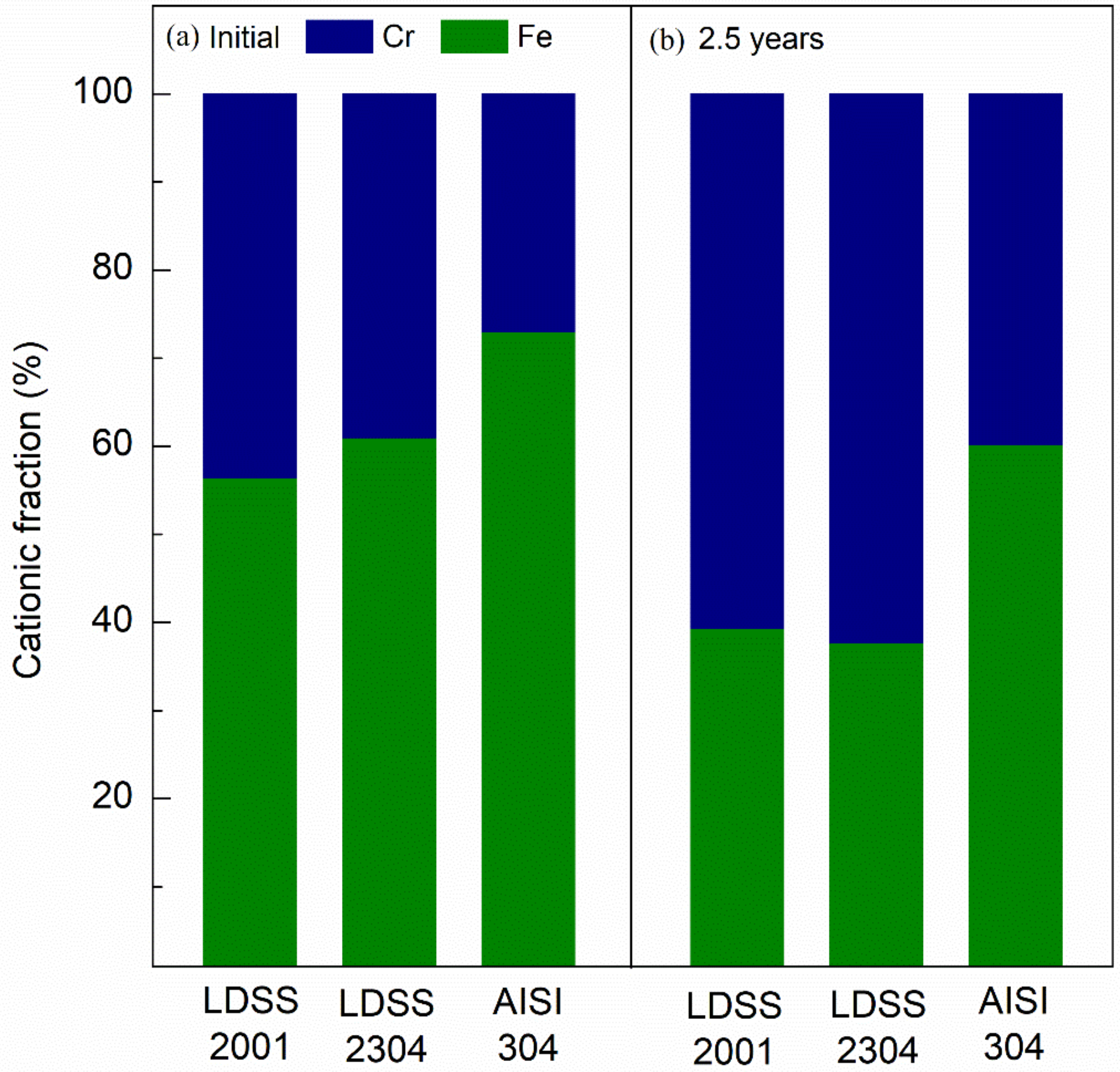
	Cl^-	$E_{FB,A}$	$E_{FB,D}$	N_A	N_D
	wt.%	V_{SCE}		cm^{-3}	
LDSS 2001	0	–0.51	–0.18	1.50×10^{15}	4.52×10^{15}
	0.4	–0.10	–0.22	9.05×10^{15}	1.13×10^{17}
	2	0.07	–0.42	1.29×10^{18}	1.29×10^{19}
	4	0.86	–3.61	1.51×10^{18}	2.26×10^{19}
LDSS 2304	0	–0.31	–0.53	4.51×10^{16}	9.05×10^{16}
	0.4	–0.11	–0.50	4.52×10^{17}	1.13×10^{18}
	2	0.25	–1.20	1.50×10^{19}	1.51×10^{19}
	4	0.45	–1.17	9.05×10^{19}	2.26×10^{19}
AISI 304	0	–0.32	–0.25	4.52×10^{15}	1.29×10^{16}
	0.4	–0.19	–0.36	2.26×10^{17}	3.01×10^{17}
	2	0.52	–0.42	4.52×10^{18}	3.02×10^{18}
	4	0.62	–1.81	1.13×10^{19}	1.01×10^{19}



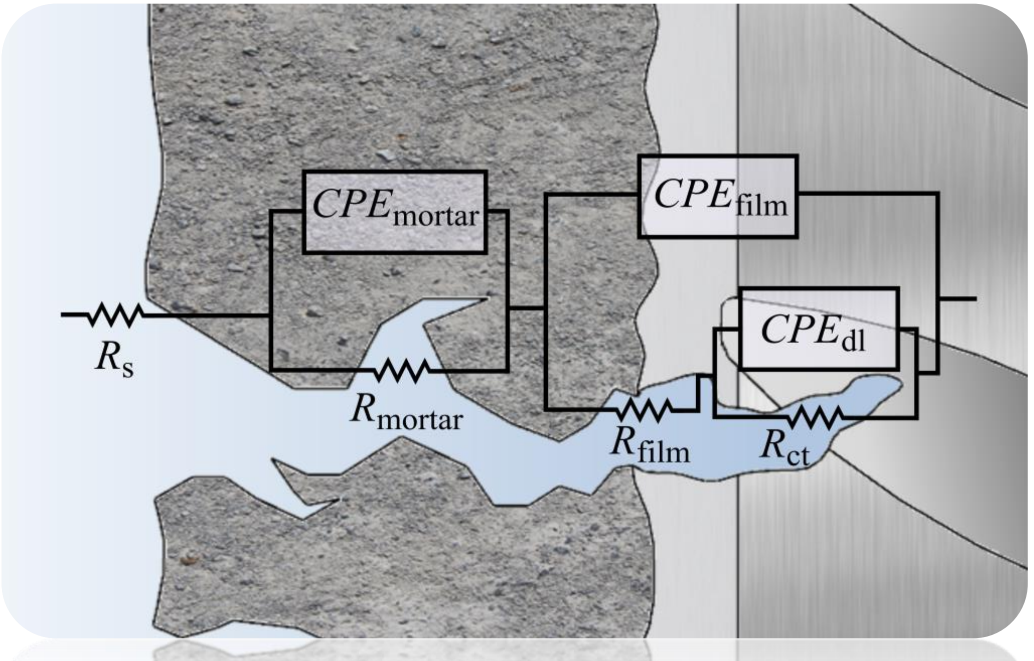
Results and Discussion

XPS and **cationic fraction** section for all SS reinforcements.



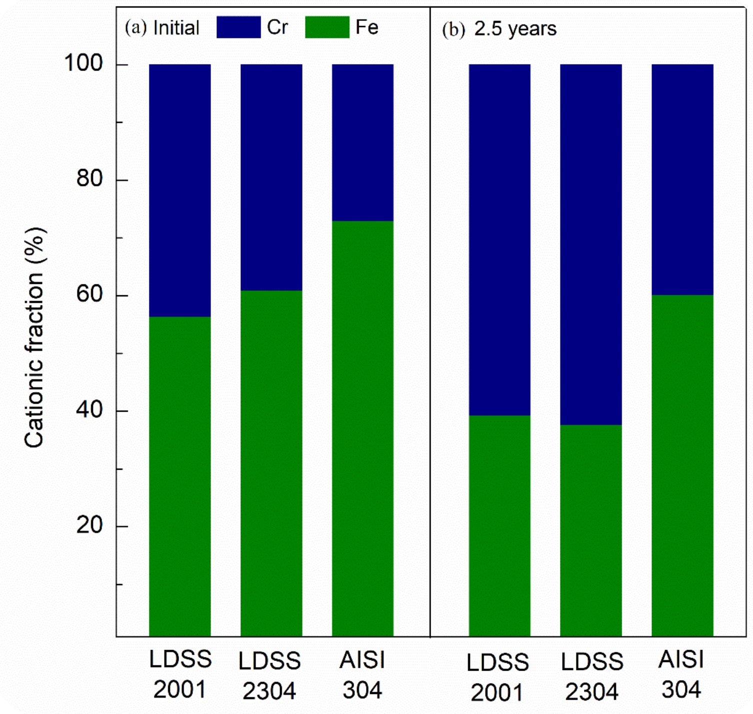


Conclusions



- The i_{corr} values of **all SS** reinforcements were far **below** the corrosion **limit** threshold of **0.1 µA/cm².** Proving the **outstanding corrosion performance** of **LDSS 2001** despite **having** the **smallest Ni content**
- The **impedance** for **all SS** reinforcements remained **above 100 kΩ cm²** during the **912 days**, hence **no passivity breakdown** was shown.

- **After 912 days** both LDSS, 2304 and 2001, had **Cr enrichment in their passive film**, from 40 to 63% and from 44 to 61% cationic fraction respectively**.**
- The $E_{FB,D}$ **of LDSS 2001** rapidly **shifts towards negative potentials**, **generating** more **oxygen vacancies** and worsening the corrosion properties, as the **Cl⁻ concentration increases.**



Thank you for your time!!