Nano and microlayers against material deterioration in aggressive environment

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Outline

1. Aim of study
2. Background
3. Experimental
4. Results
5. Conclusion

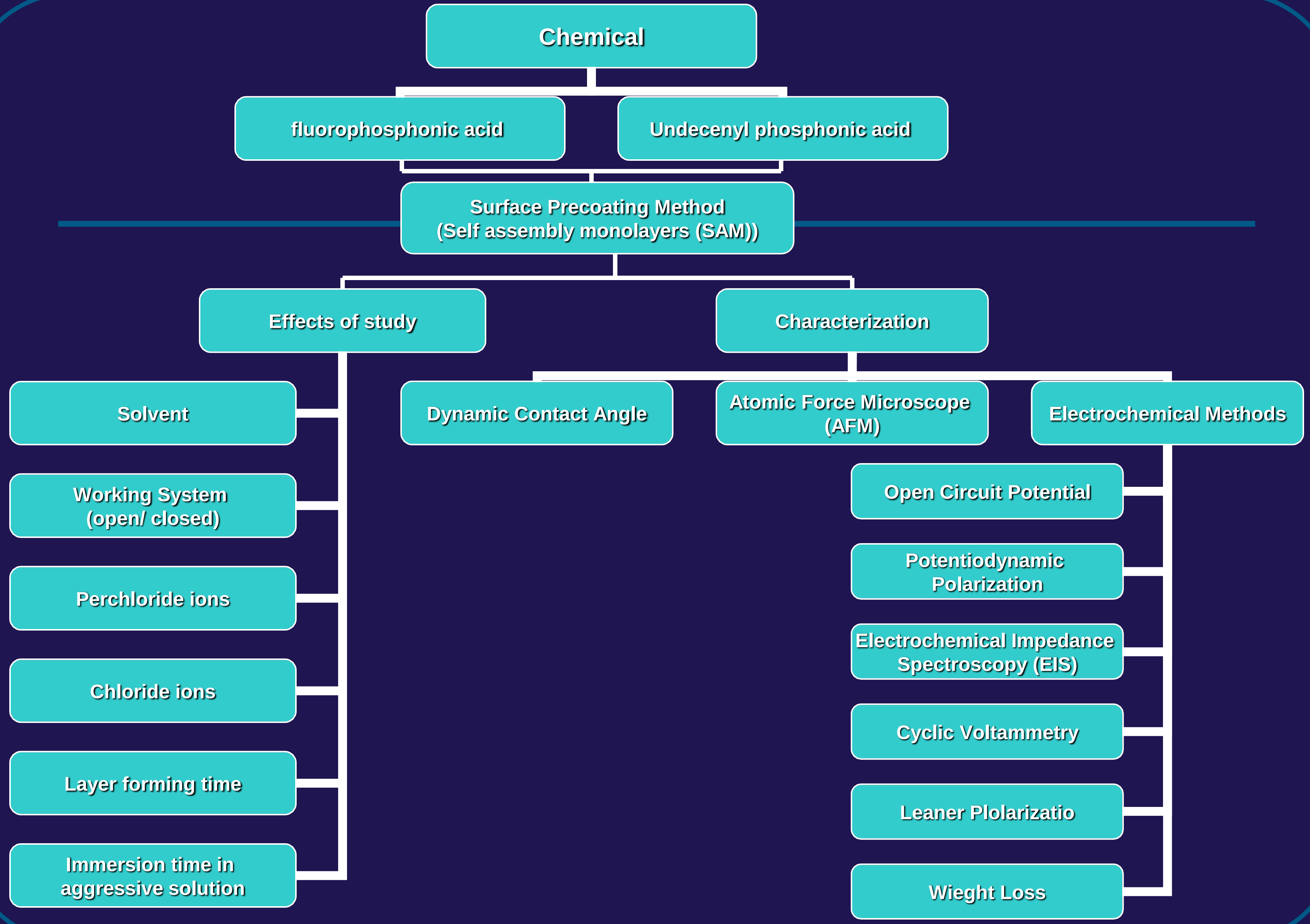
Aim of study

➢Study of

- **formation of self assembled molecular layers (SAM) on carbon steel and aluminum**.
- **influence of different variables** (solvent, oxide layer, working system (open or closed), temperature,pH, chloride ions, perchloride) **on the protective layer formation**.

➢Characterization of the formed layers

- **Contact angle measurement** (presence of the layer)
- **Atomic force microscopy** (morphology of the layer)
- **Electrochemical measurements**: cyclic voltammetry (compactness of the layer), potentiodynamic polarization techniques, and electrochemical impedance spectroscopy (anticorrosion activity).


Chemical
fluorophosphonic acid
Undecenyl phosphonic acid
Surface Precoating Method
(Self assembly monolayers (SAM))
Effects of study
Characterization
Solvent
Working System
(open/ closed)
Perchloride ions
Chloride ions
Layer forming time
Immersion time in
aggressive solution
Dynamic Contact Angle
Atomic Force Microscope
(AFM)
Electrochemical Methods
Open Circuit Potential
Potentiodynamic
Polarization
Electrochemical Impedance
Spectroscopy (EIS)
Cyclic Voltammetry
Leaner Plolarizatio
Wieght Loss

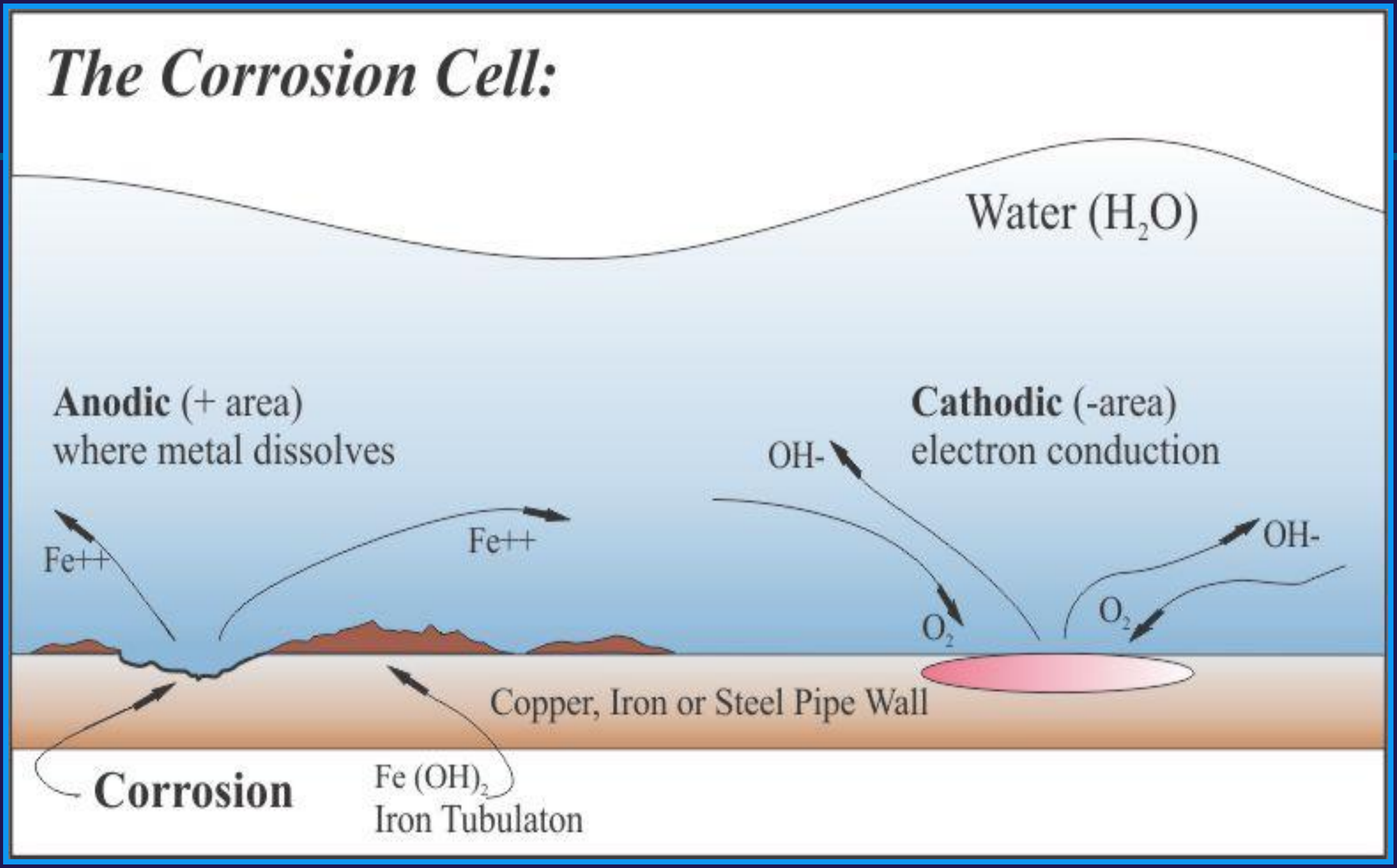
Fulfillment of the sixth semester

- Characterization of the formed layers by:
  - Electrochemical Impedance Spectroscopy (EIS)
  - Atomic force microscopy (AFM)
- Study the effect of:
  - Perchloride ions
  - Time of layer formation
  - Time of immersion in aggressive solution

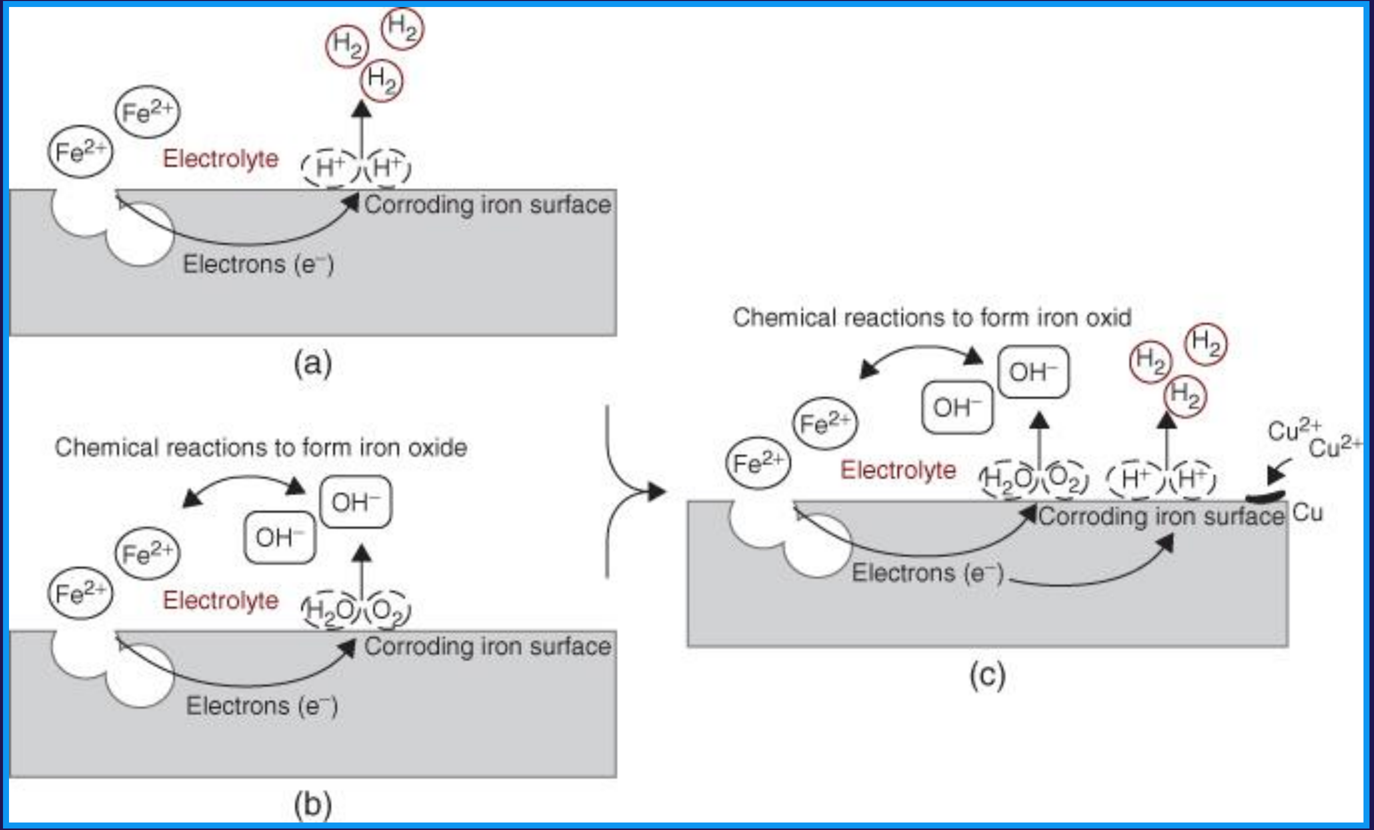
Publication on the sixth semesters

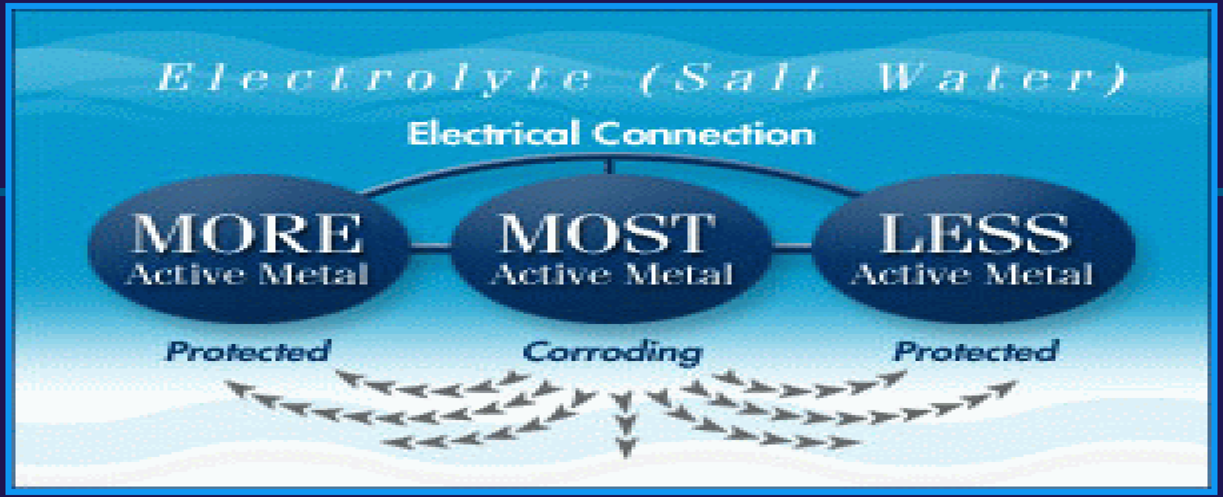
- A presentation "***Special phosphonic acid nanolayers for controlling corrosion processes***" Chemical Engineering day, 21- 23 April 2015, Veszprém,- Hungary
- A journal publication "***Corrosion protection of carbon steel by special phosphonic acid nanolayers***" Materials and Corrosion. (IF 2.3)
- A journal publication (in review) "***Corrosion processes controled by phosphonic acid nano- layers***" Periodica Polytechnica Chemical Engineering. (IF 0.3)

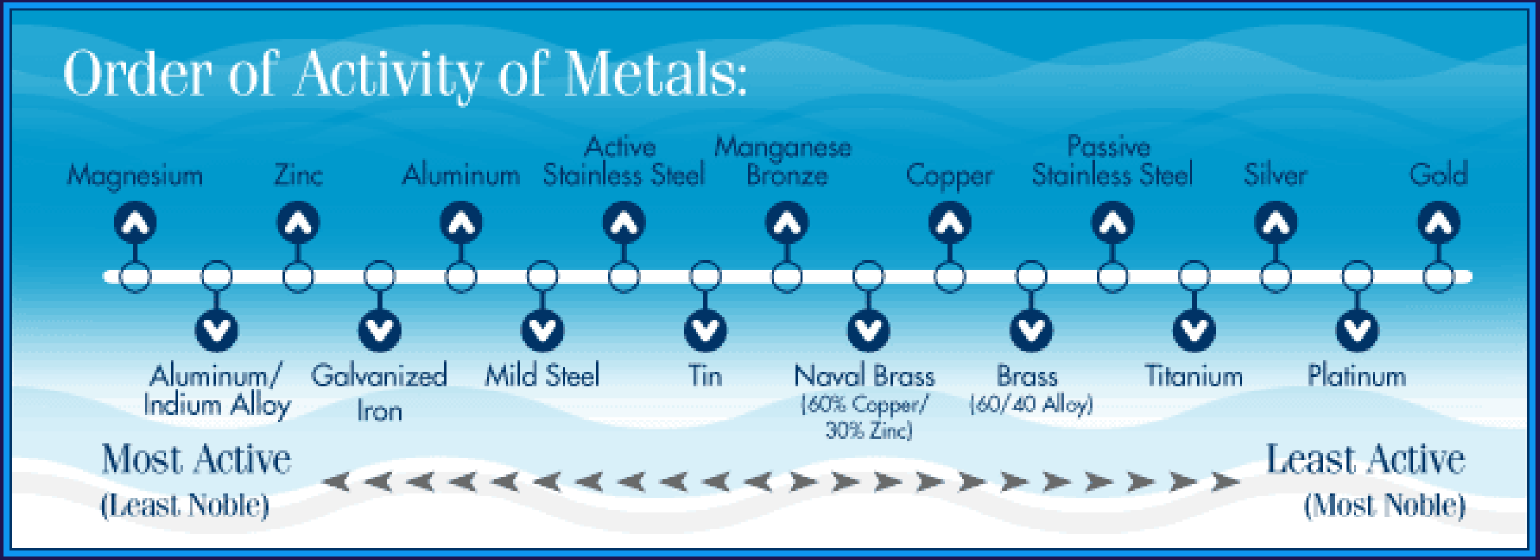
Test Methods

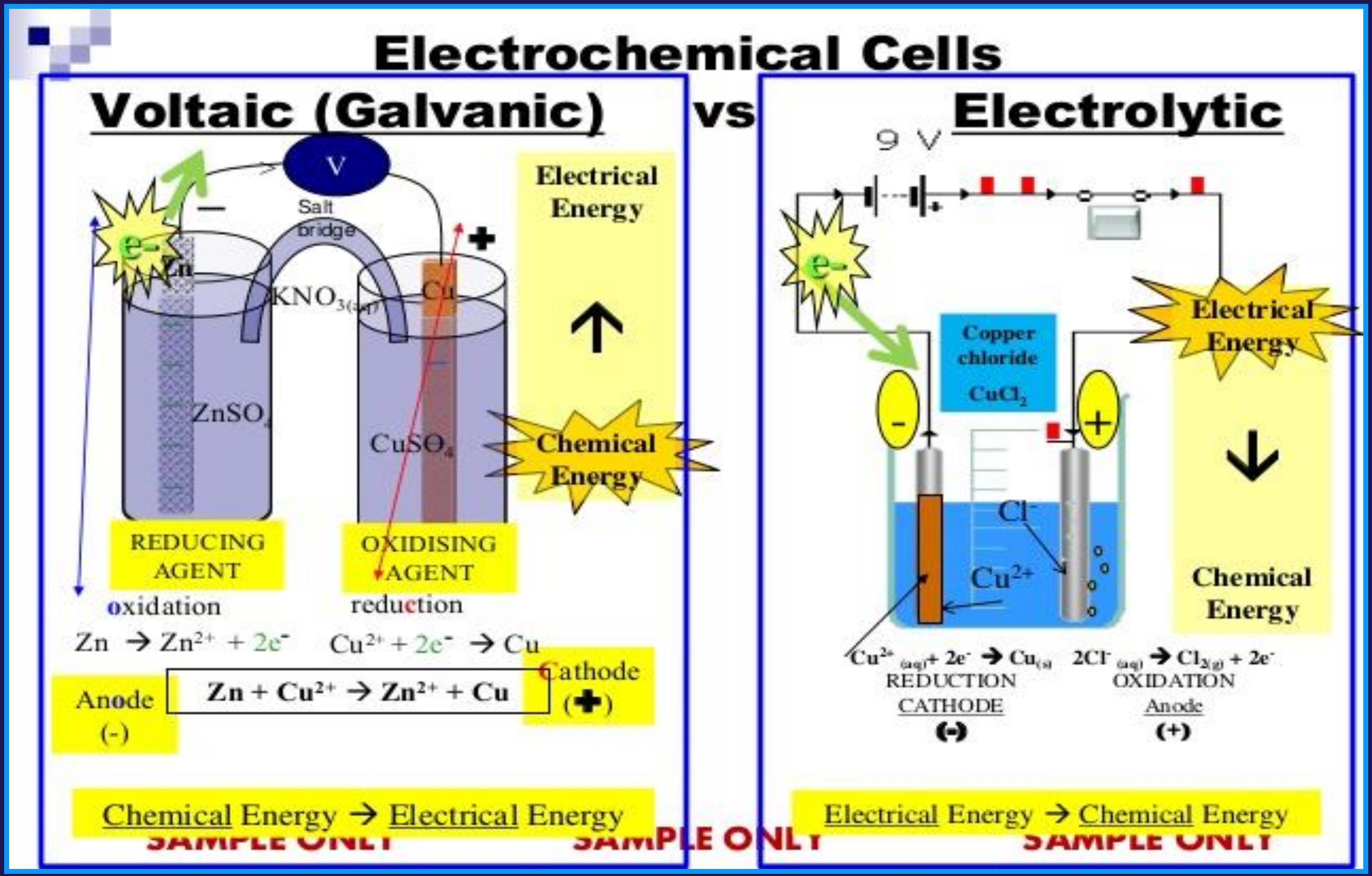

The Corrosion Cell:
Water (H_2O)
Anodic (+ area)
where metal dissolves
Cathodic (-area)
electron conduction
OH-
Fe++
Fe++
OH-
O_2
O_2
Copper, Iron or Steel Pipe Wall
Corrosion
Fe $(OH)_2$
Iron Tubulaton

➢Corrosion process

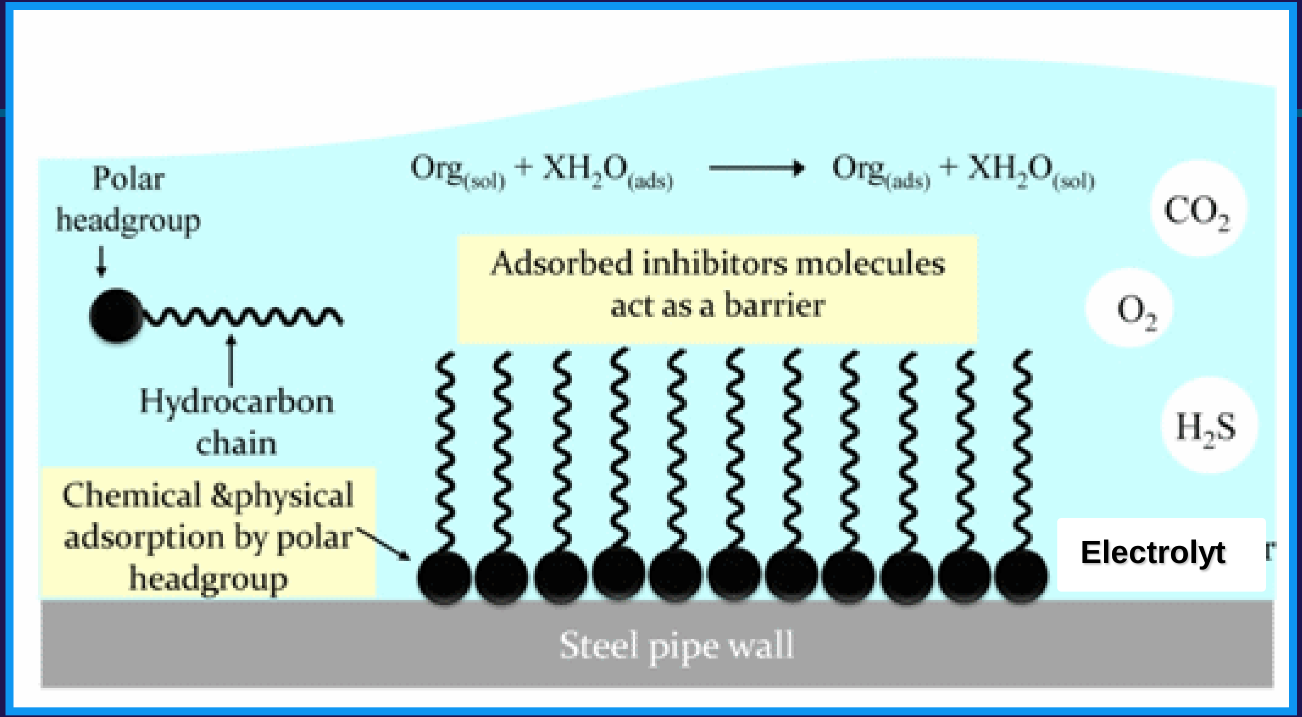


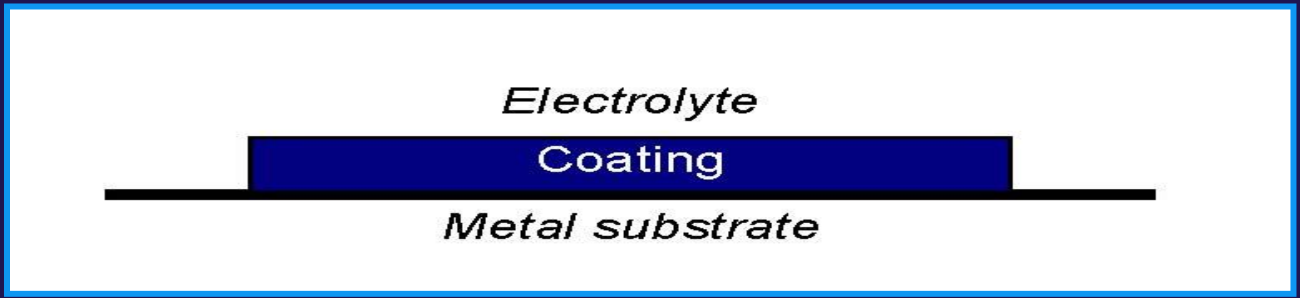

Electrolyte (Salt Water)
Electrical Connection
MORE
Active Metal
MOST
Active Metal
LESS
Active Metal
Protected
Corroding
Protected

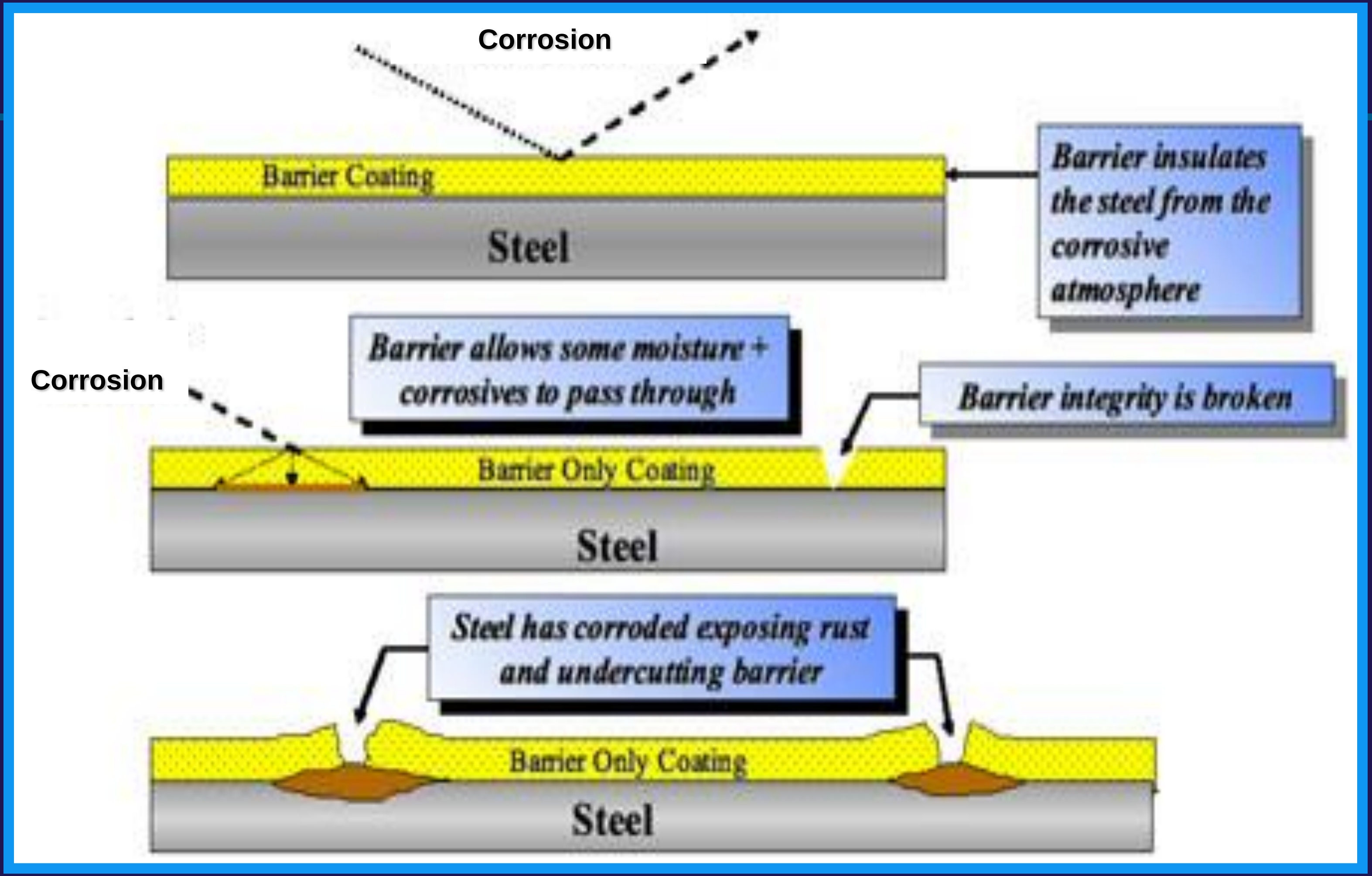

Order of Activity of Metals:
Magnesium
Zinc
Aluminum
Active Stainless Steel
Manganese Bronze
Copper
Passive Stainless Steel
Silver
Gold
Aluminum/ Indium Alloy
Galvanized Iron
Mild Steel
Tin
Naval Brass
(60% Copper/ 30% Zinc)
Brass
(60/40 Alloy)
Titanium
Platinum
Most Active
(Least Noble)
Least Active
(Most Noble)


Electrochemical Cells
Voltaic (Galvanic) vs Electrolytic
V
Salt bridge
e-
Zn
KNO3(aq)
Cu
ZnSO4
CuSO4
Electrical Energy
Chemical Energy
REDUCING AGENT
OXIDISING AGENT
oxidation
reduction
Zn → Zn2+ + 2e-
Cu2+ + 2e- → Cu
Anode (-)
Zn + Cu2+ → Zn2+ + Cu
Cathode (+)
Chemical Energy → Electrical Energy
9 V
Copper chloride CuCl2
-
+
Cl-
Cu2+
Electrical Energy
Chemical Energy
Cu2+ (aq) + 2e- → Cu(s)
REDUCTION
CATHODE
(-)
2Cl- (aq) → Cl2(g) + 2e-
OXIDATION
Anode
(+)
Electrical Energy → Chemical Energy
SAMPLE ONLY
SAMPLE ONLY
SAMPLE ONLY

Methods of corrosion control

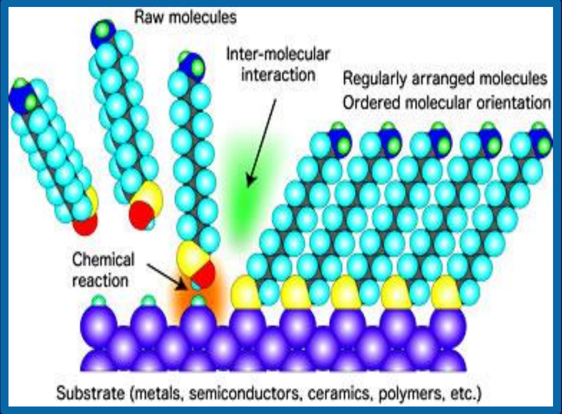

Polar headgroup
$Org_{(sol)} + XH_2O_{(ads)} \longrightarrow Org_{(ads)} + XH_2O_{(sol)}$
CO_2
Adsorbed inhibitors molecules act as a barrier
O_2
Hydrocarbon chain
H_2S
Chemical &physical adsorption by polar headgroup
Electrolyt
Steel pipe wall

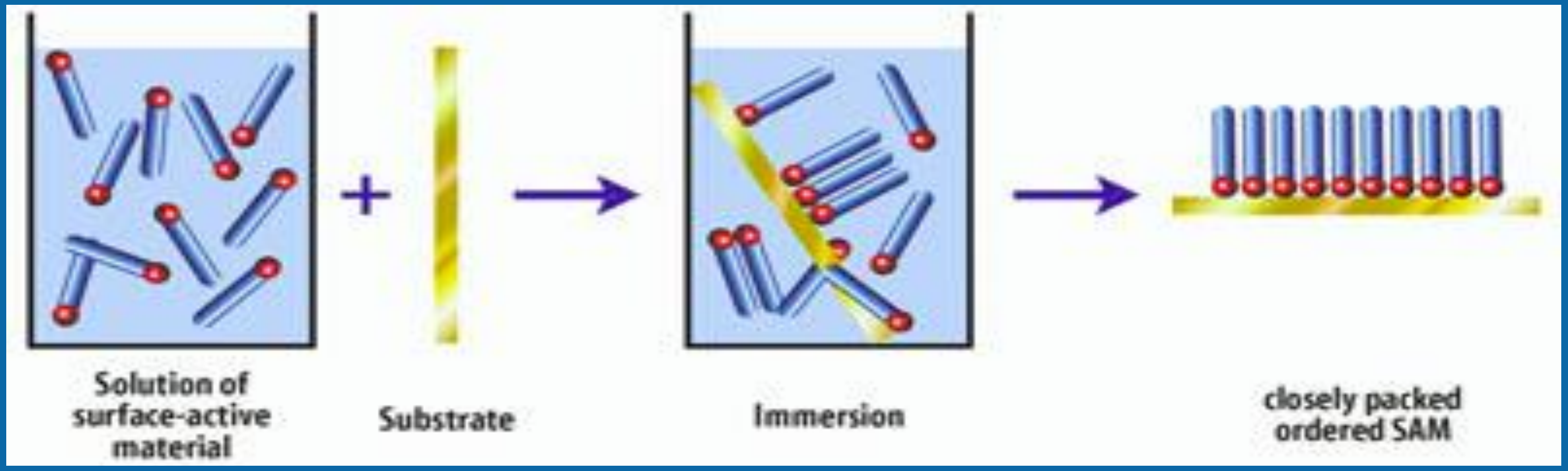

Electrolyte
Coating
Metal substrate


Corrosion
Barrier Coating
Steel
Barrier insulates the steel from the corrosive atmosphere
Corrosion
Barrier allows some moisture + corrosives to pass through
Barrier integrity is broken
Barrier Only Coating
Steel
Steel has corroded exposing rust and undercutting barrier
Barrier Only Coating
Steel

Introduction to the techniques

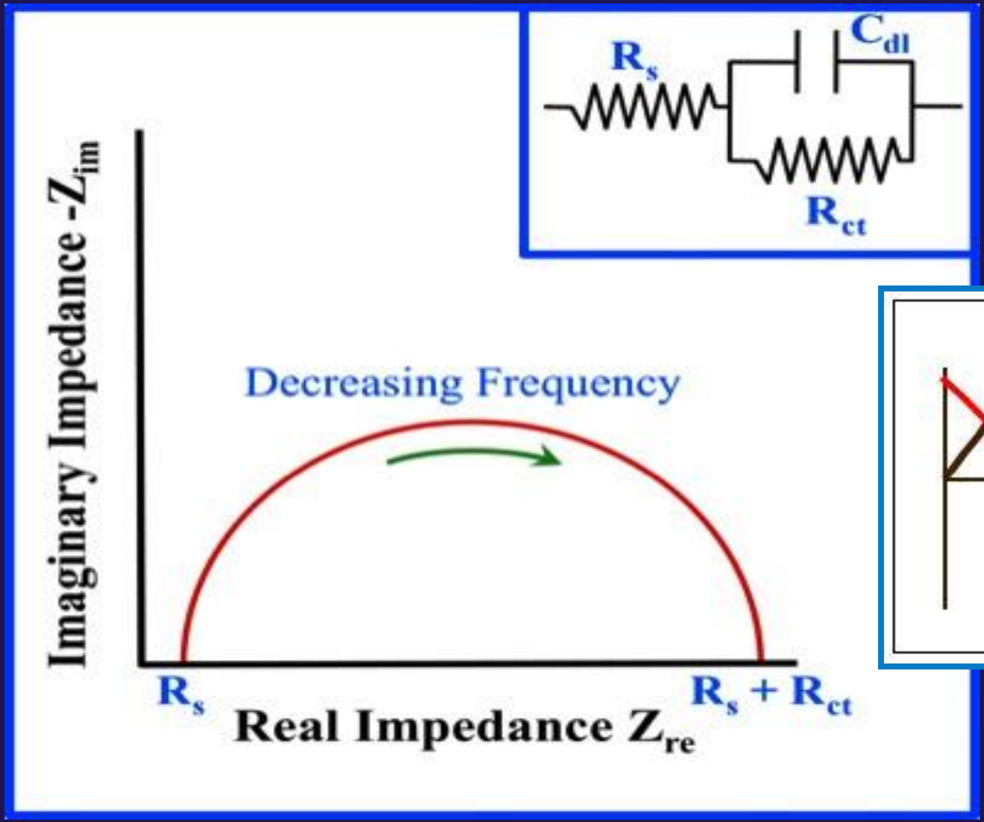
➢Self-assembled monolayers (SAM)

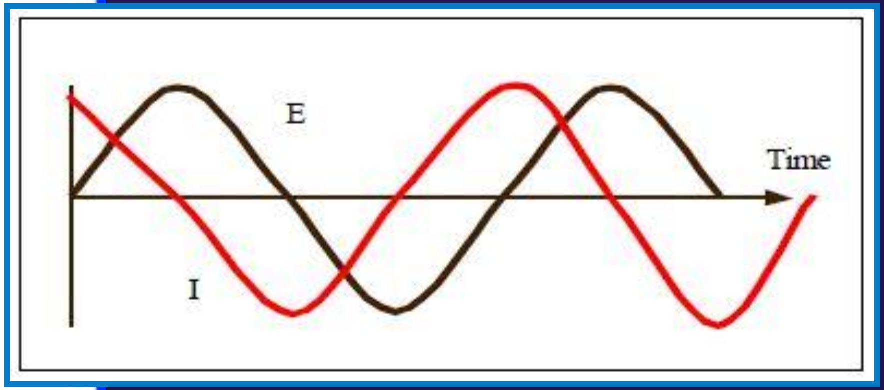


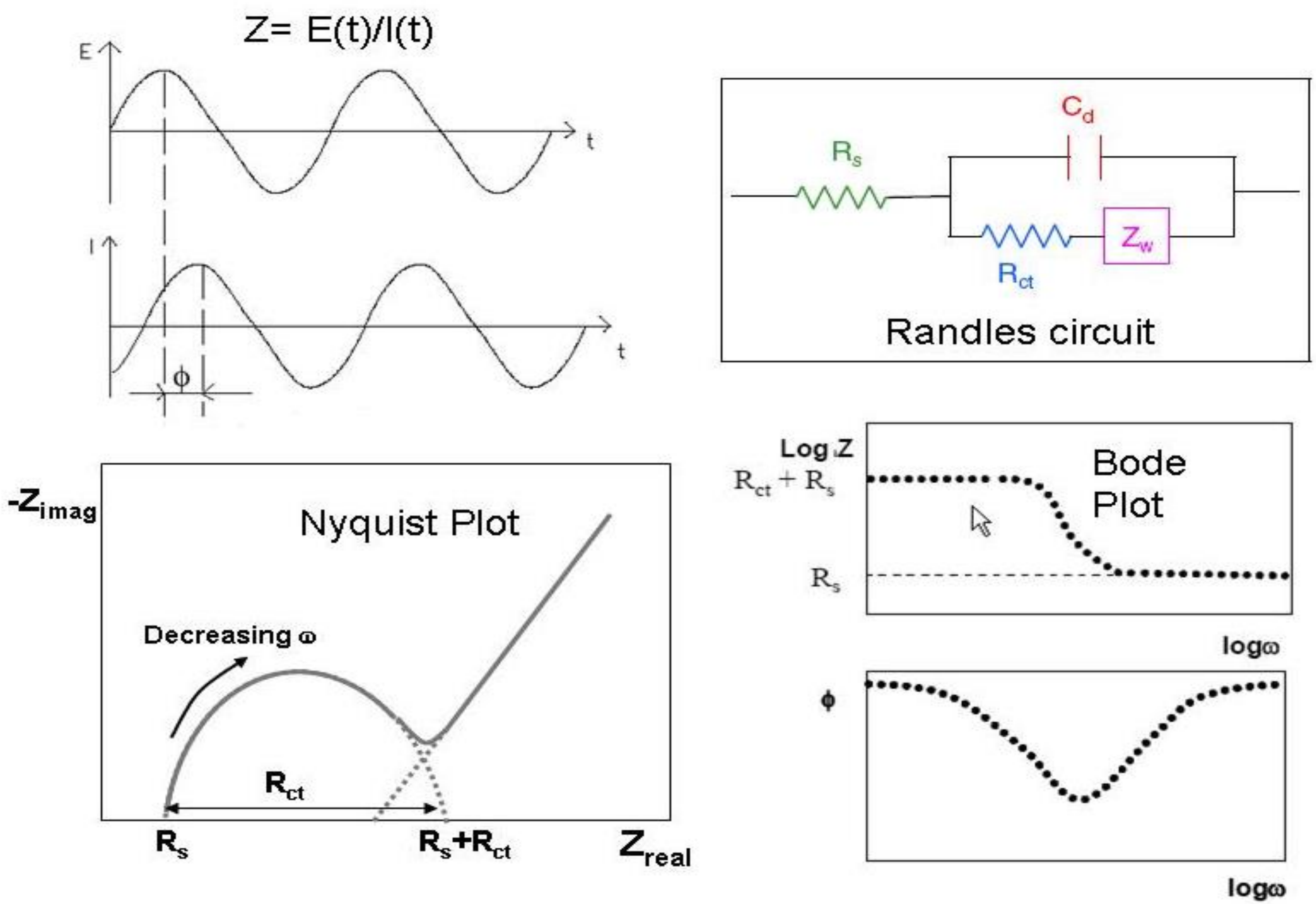


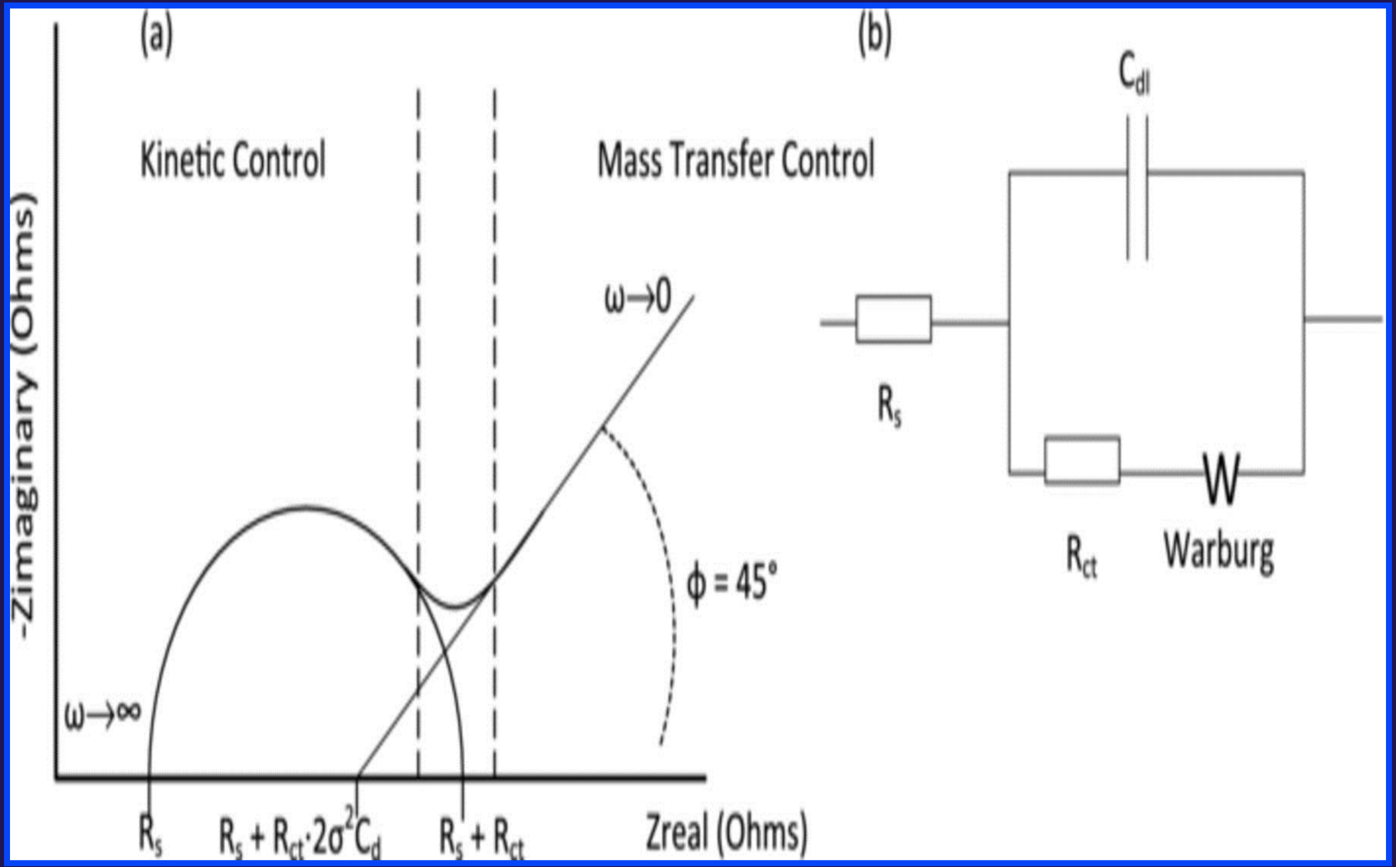
Representation of a SAM structure

➢ Electrochemical Impedance Spectroscopy (EIS)






Z= E(t)/I(t)
E
t
I
t
ϕ
C_d
R_s
Z_w
R_{ct}
Randles circuit
-Z_{imag}
Nyquist Plot
Decreasing ω
R_{ct}
R_s
R_s+R_{ct}
Z_{real}
Log Z
R_{ct} + R_s
Bode
Plot
R_s
logω
ϕ
logω


(a)
(b)
Kinetic Control
Mass Transfer Control
-Zimaginary (Ohms)
ω→0
ω→∞
ϕ = 45°
Rs
Rs + Rct·2σ2Cd
Rs + Rct
Zreal (Ohms)
Cdl
Rs
Rct
W
Warburg

Reference Electrodes

Reference Electrode	Component Composition	vs (SHE) Volts	vs SCE Volts	vs Ag/AgCl$^-$ Volts	vs Cu/$CuSO_4$ Volts
(SHE) Standard Hydrogen	(Pt) H_2/H^+	●	-0.241	-0.25	-0.30
(SCE) Saturated Calomel Electrode	Hg/Hg_2Cl_2/ sat KCl	+0.241	●	-0.009	-0.059
Silver/Silver Chloride (seawater)	Ag/AgCl/ 0.6 MCl$^-$	+0.25	+0.009	●	-0.05
Copper/ Copper Sulphate	$Cu/CuSO_4$ sat	+0.30	+0.059	+0.05	●

Conversion factors (to convert add the value indicated)

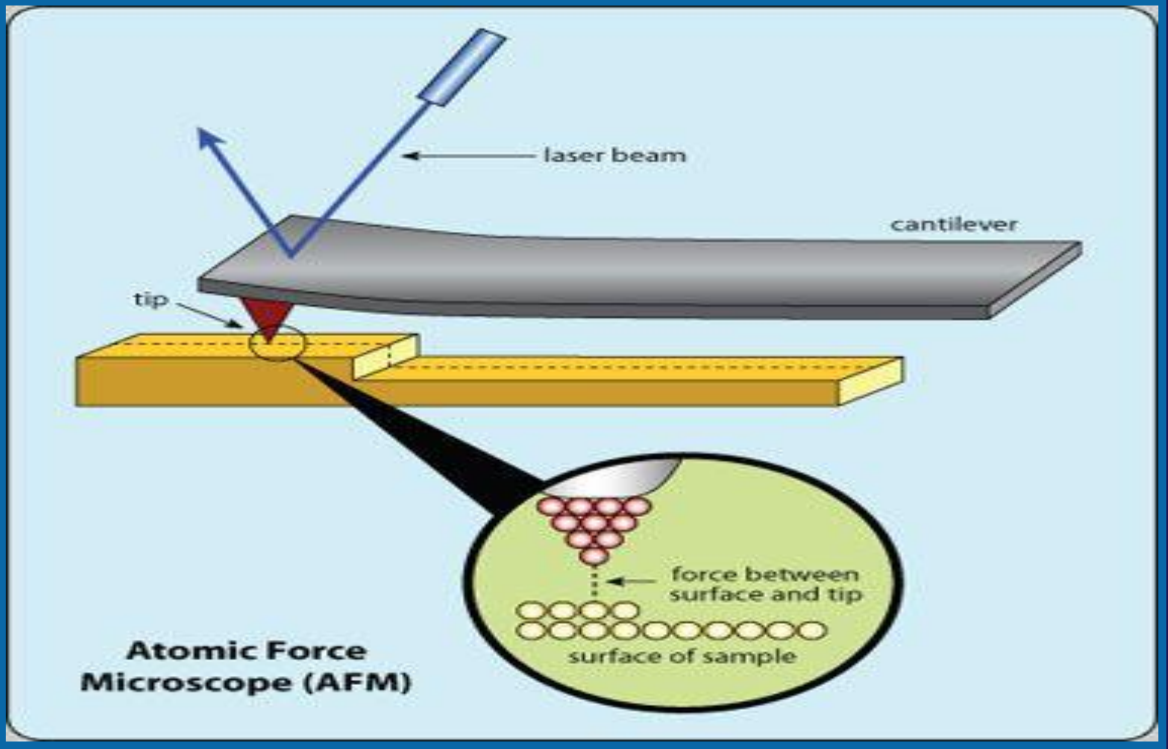
From E[1]	To SHE Scale	To SCE Scale
H_2/H^+ (SHE)		-0.241
Ag/AgCl sea water	+0.25	+0.047
Hg/Hg_2Cl_2/sat KCl (SCE)	+0.241	

Potentiodynamic curve
(SI1287 Sorltron/Electrochemical Interface(Potentiostat))

Electrochemical impedance spectroscopy (EIS)
(SI 1260 Impedance/ Gain- Phase analyzer)

Surface morphology

➢Atomic force microscopy (AFM)

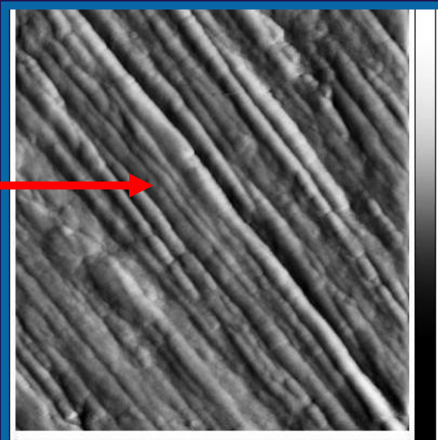


Test Results

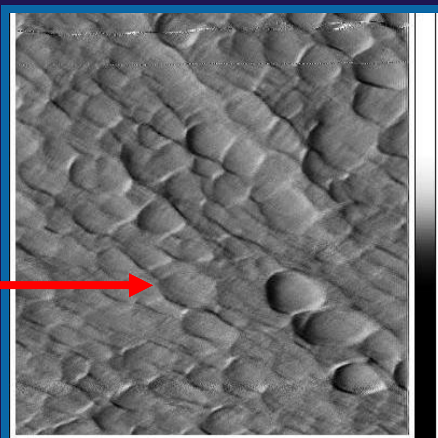
AFM result

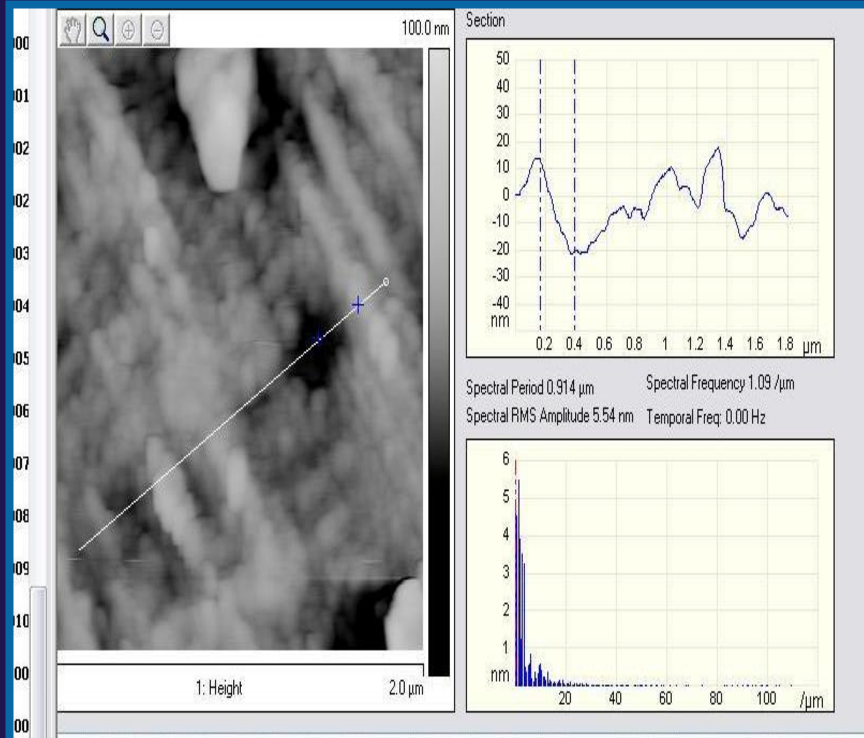
Udecenyl phosphonic acid

undecenyl phosphonic acid layer formed at 30min



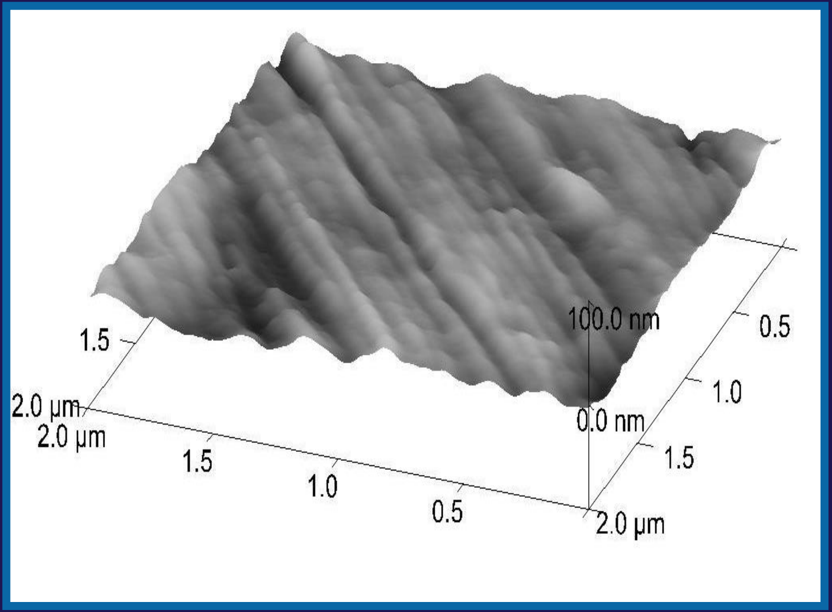
undecenyl phosphonic acid layer formed at 30min and treated with NaClO4 for 2hrs.



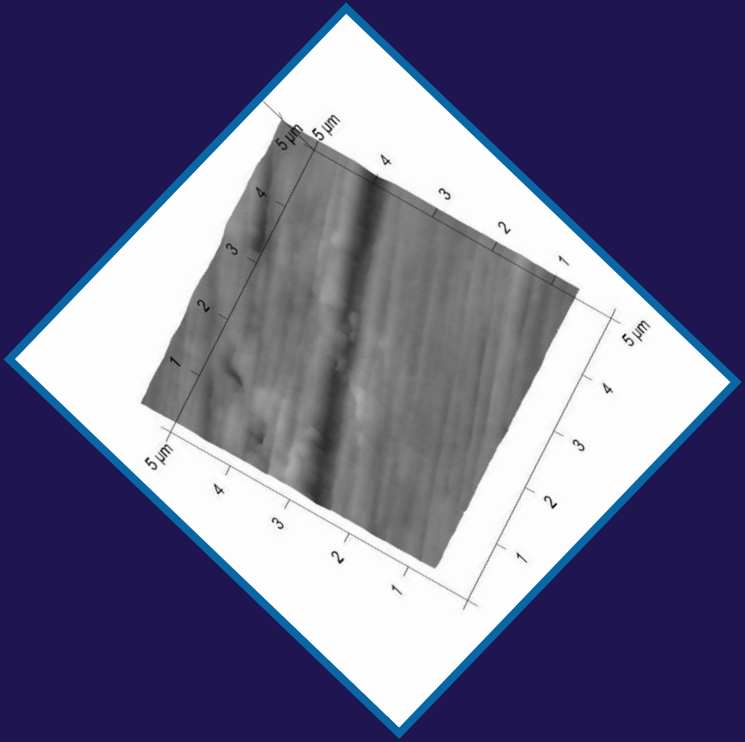


undecenyl phosphonic acid layer formed at 30min and treated with NaCl for 2hr.

Fluorophosphonic acid



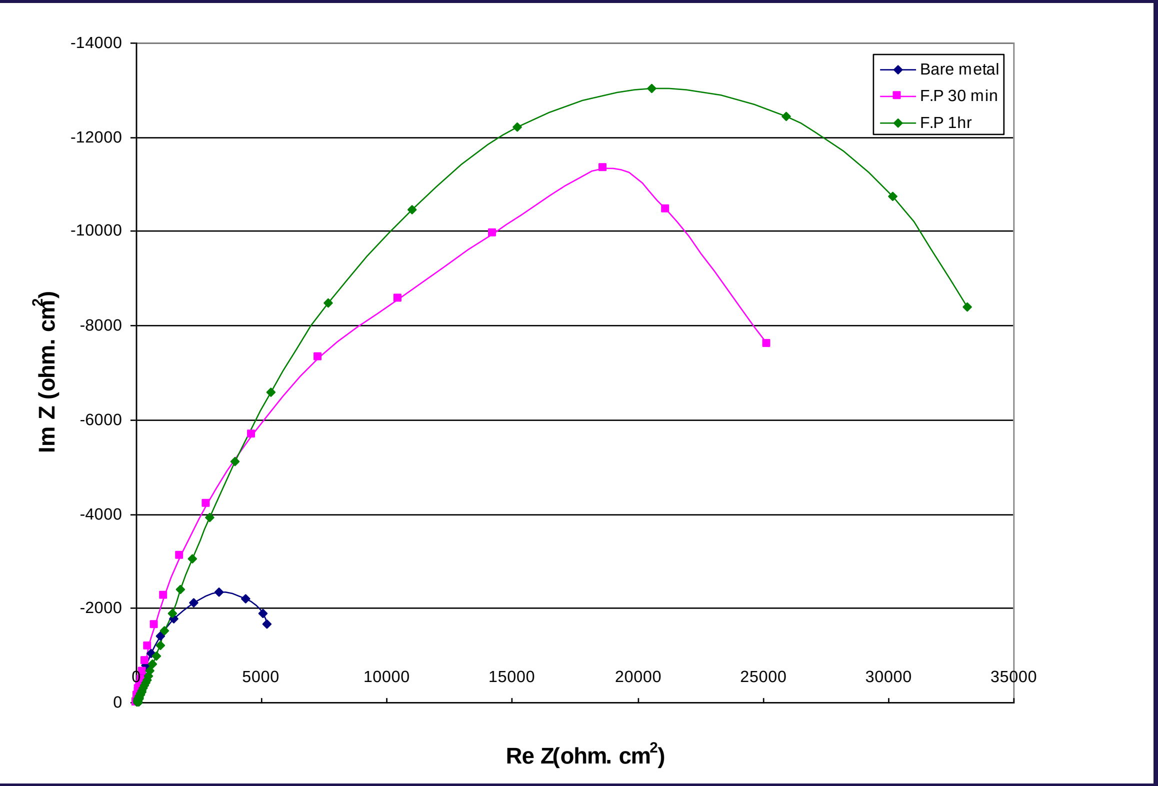
fluorophosphonic layer formed at 30min.



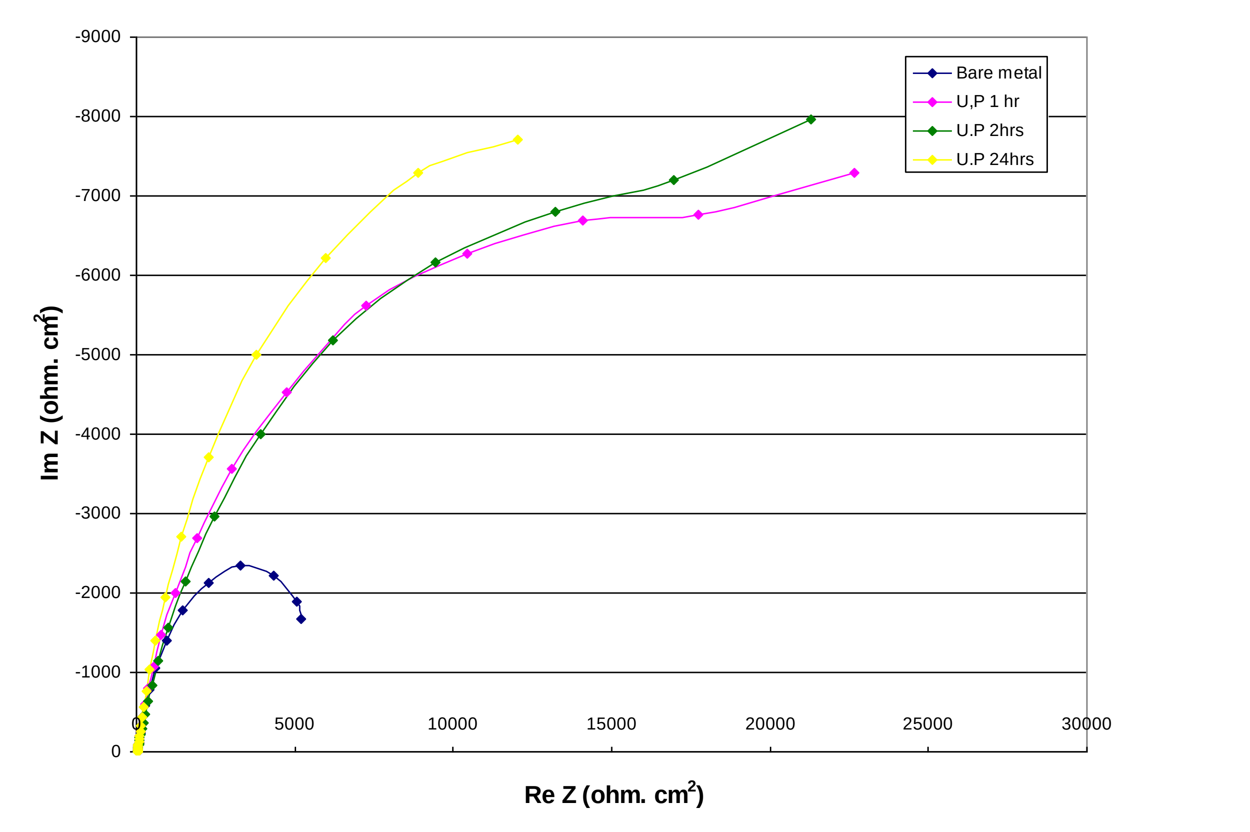
fluorophosphonic layer formed at 30min and treated with NaCl for 1hr.

EIS result

➢Effect of layer formation time

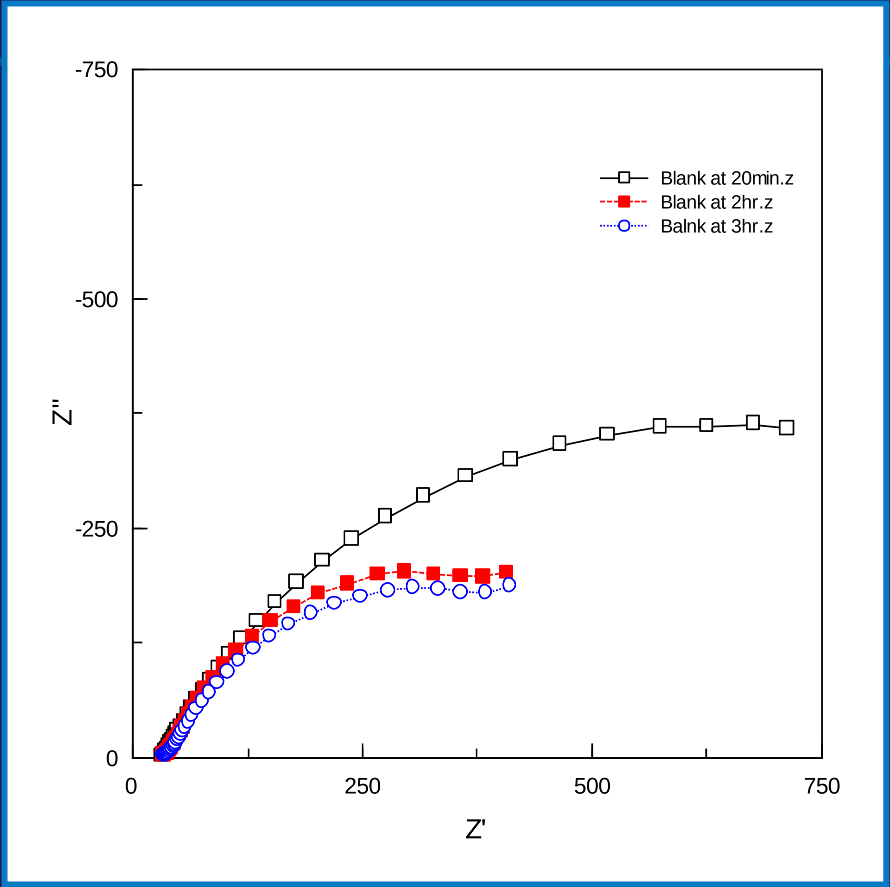


EIS measurements for fluorophosphonic acid layer at different formation time and tested in NaClO4 solution

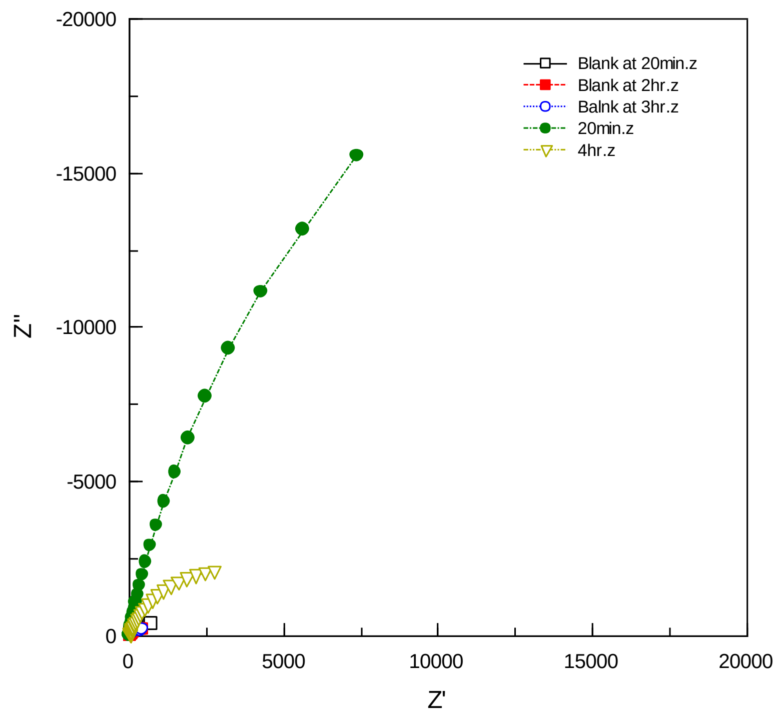


EIS measurements for undecenyl phosphonic acid layer at different formation time and tested in NaClO4 solution

➢ Effect of time immersion in aggressive solution

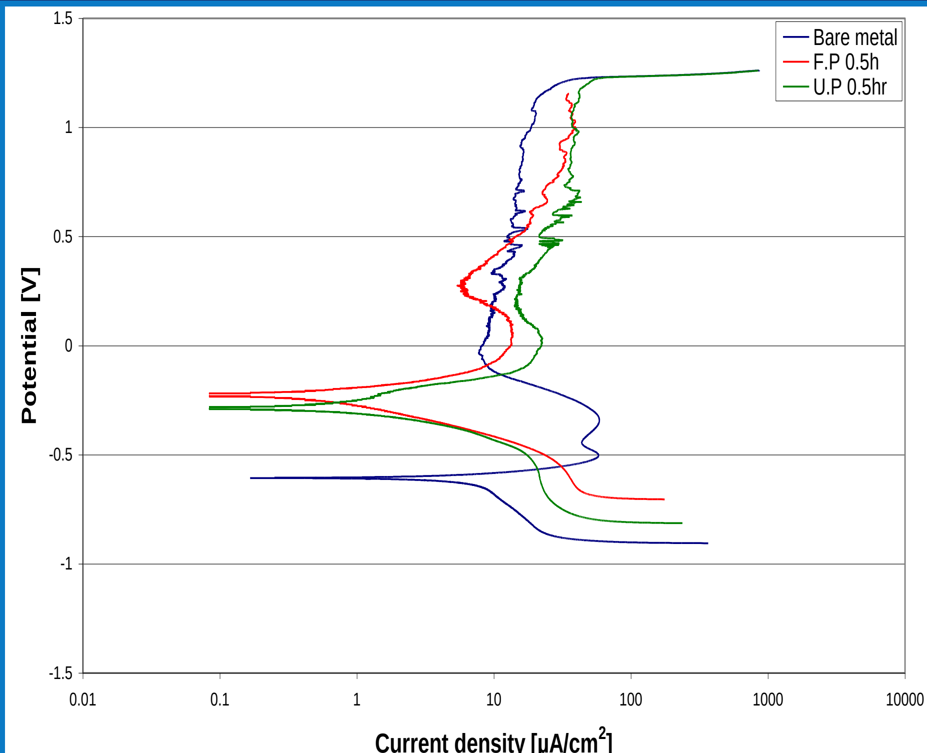


EIS measurements for fluorophosphonic acid layer (2hr) on carbon steel in $NaClO_4$ solution

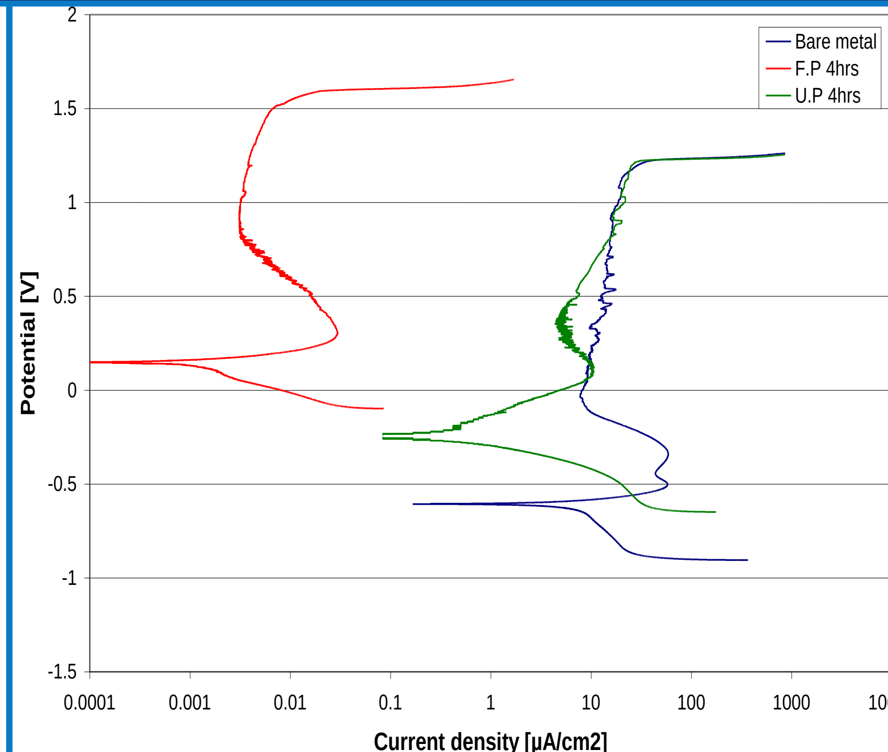


EIS measurements for undecenyl phosphonic acid layer (24hr) on carbon steel in $NaClO_4$ solution

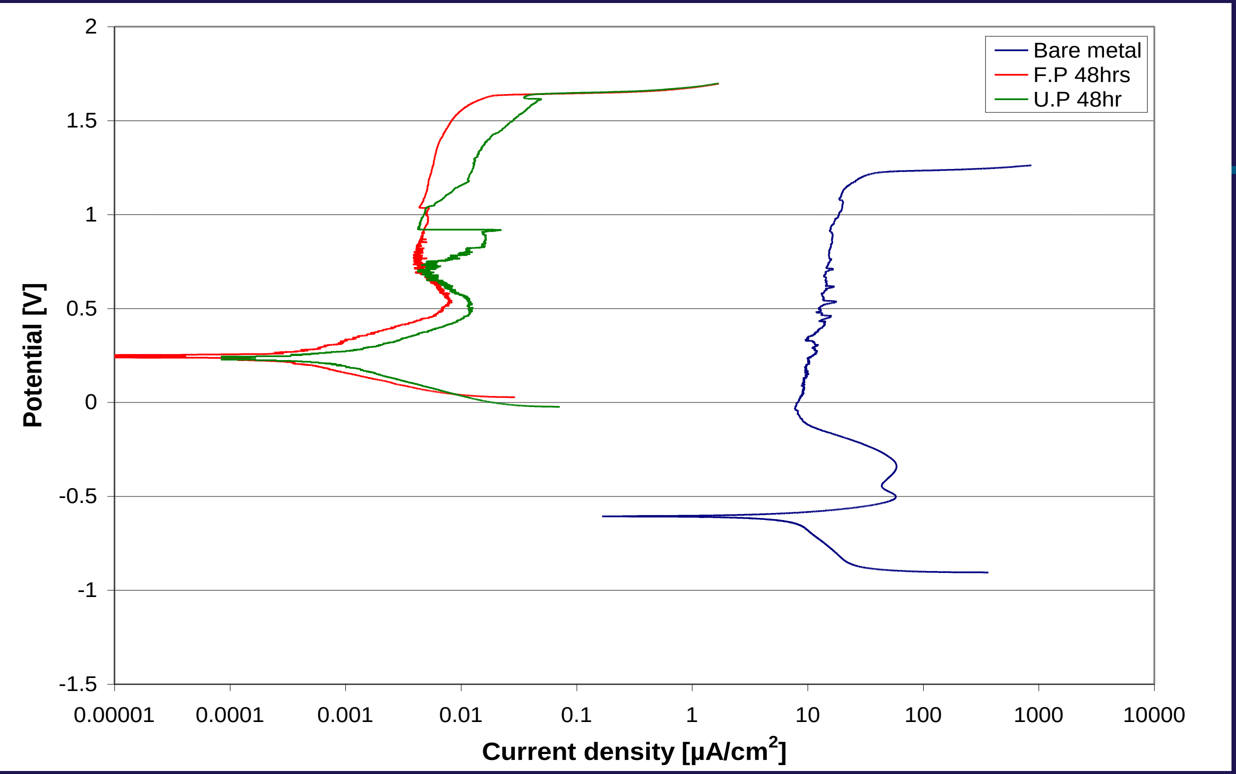
Potentiodynamic results



Potentiodynamic polarization curves for layers formed at 30min with different chemicals (undecenyl and flourophosphonic acid) ($NaClO_4$).



Potentiodynamic polarization curves for layers formed at 4hrs with different chemicals (undecenyl and flourophosphonic acid) ($NaClO_4$).



Potentiodynamic polarization curves for layers formed at 48hrs with different chemicals (undecenyl acid phosphonic and flourophosphonic acid) (NaClO4).

Conclusion

1. **The EIS results show** The undecenyl phosphonic acid and fluorophosphonic acid layers performded protection of the metal surface agains aggressive solution.

2. Potentiodynamic results showed that the undecenyl phosphonic acid and fluorophosphonic acid had the same performance for layers formed at 30min and 48 hrs although tre was a differnece with layers formed at 4hrs.

3. Undecenyl phosphonic acid resulted in excellent protective layers against corrosion although it decreased after 4hr.

4. In case of fluorophosphonic acid, increasing the layer formation time led to decreasing the corrosion rate.

5. AFM showed that the effect of sodium chloride was more savior than that of sodium perchloride where pitting corrosion occurred.

Thank you for your attention