WEB SEMINAR
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# Steel corrosion protection mechanism of PANI based coatings

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# Intrinsic Conductive Polymers (ICP) and metal corrosion protection

Materials

- Different Conductive Polymers:
  - Polyaniline (PANI)
  - Polypyrrole
  - Polythiophene

- Different substrates:
  - Stainless steel
  - Steel
  - Aluminum alloys
  - Magnesium alloys
  - Zinc
  - Copper alloys

Every combination of polymer and substrate has a different corrosion protection mechanism

Starting Point

# PANI and Steel

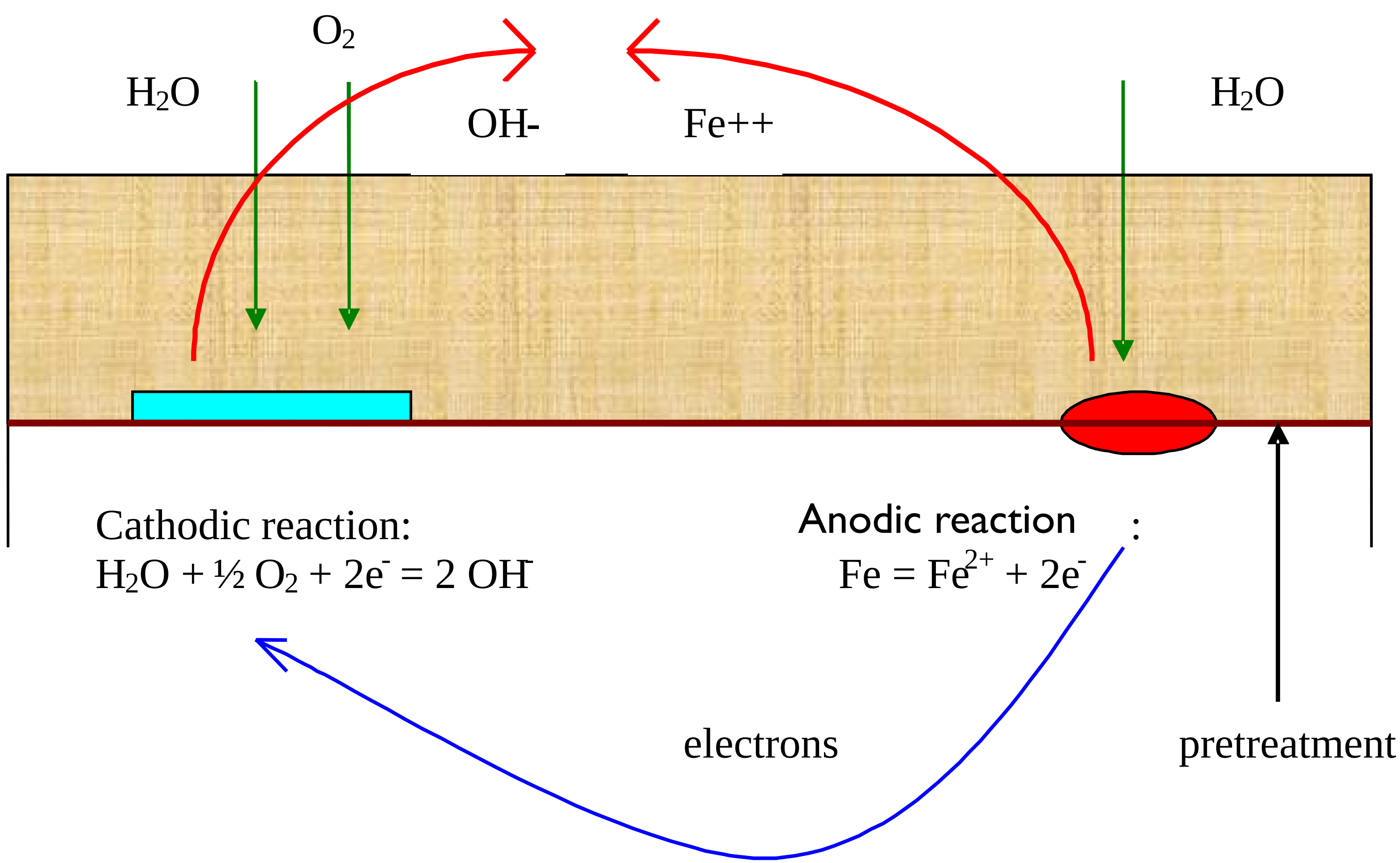
- The mechanism of corrosion protection of steel by PANI is still a controversial issue.
- Many research studies with the wide variations of experimental procedures used:
  - Coating deposition method
  - Surface preparation
  - Environment
  - Test method
  - ……

# Classes of possible mechanisms of corrosion protection of PANI on Steel

Classification

- Barrier properties
  - physical action
- Corrosion inhibition
  - chemical action
- **<u>Anodic protection</u>**
  - electrochemical action

# Barrier properties (general)




Physical action

# Barrier properties (PANI)

- Water permeability:
  - Similar to commercial epoxy coatings
- Oxygen permeability
  - Dependent on the oxidation state
- Ion diffusion
  - Depending on PANI state (not higher than normal coatings)

Results on scratched samples lead to conclude that the barrier effect is not the dominant mechanism

Chemical action

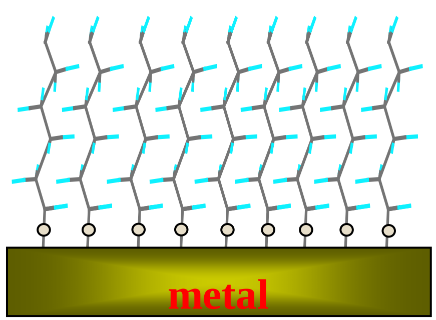
# Corrosion inhibitors (general)

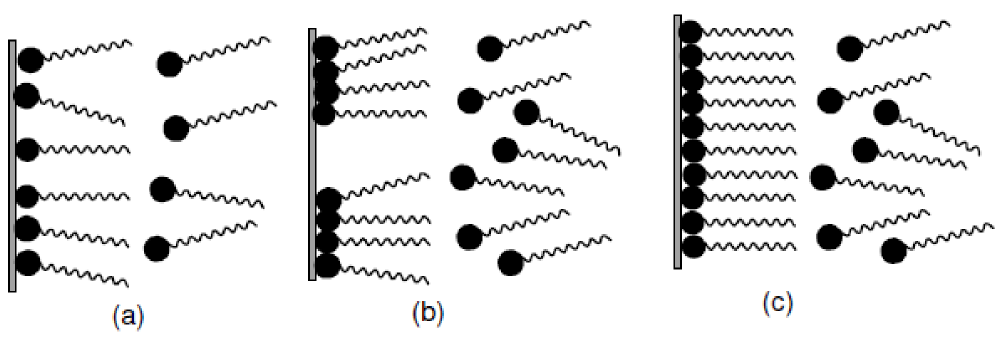
- Both anodic and cathodic effects are sometimes observed in the presence of organic inhibitors, but as general rule, organic inhibitors effect the entire surface of corroding metal present in sufficient concentration.
- Organic inhibitors, usually designated as film forming, protect the metal by forming hydrophobic film on the metal surface. Their effectiveness depends on the chemical composition, their molecular structures, and their affinities for the metal surface. Because film formation is an adsorption process, the temperature and pressure in the system is the important factors.
- Organic inhibitors will adsorbed according to the ionic charge of inhibitors and the charge of the surface. The strength of adsorption bond is the dominant factor for soluble organic inhibitors.

# Corrosion inhibitors (general)

Chemical action

- Organic inhibitors build up a protective film of adsorbed molecules on the metal surface, which provides a barrier to the dissolution of the metal in the electrolyte. Because the metal surface covered is proportional to the inhibitors concentration, the concentration of inhibitor in the medium is critical. For any specific inhibitor in any given medium there is an optimal concentration.



# Corrosion inhibitors (PANI)

Chemical action

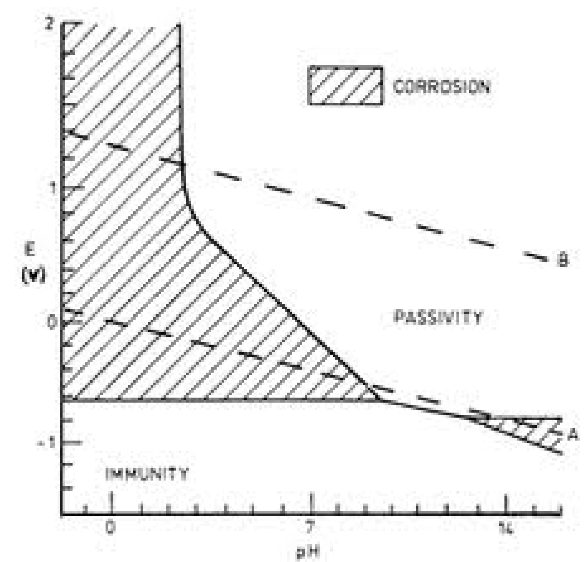
- Monomeric aniline has been proved to act as an organic inhibitor:
  - Acid environments and chlorides
- The mechanism is an strong adsorption of aniline forming a hydrophobic surface layer

The adsorption could promote, in the case of PANI a good adhesion with the steel surface

# Anodic protection (general)

Corrosion protection strategy based on an anodic polarisation controlling the potential in a zone where the metal tends to be passive.

It can be used for materials having any passivation possibility. Iron (steel) can passivate.




Pb? PANI stabilty as a function of the pH

Electrochemical action

# Anodic protection (CP)

$$1/n\ M + 1/m\ CP^{m+} + y/n\ H_2O \Rightarrow 1/n\ M(OH)_y^{(n-y)+} + 1/m\ CP^0 + y/n\ H^+$$

Where M is the metal (Steel) and CP an electroactive conductive polymer

$$m/4\ O_2 + m/2\ H_2O + CP^0 \Rightarrow CP^{m+} + mOH^-$$

How to prove it ?:

By electrochemical method (Open Circuit Potential OCP)

By surface analysis (oxide layer)

By analysis of the CP electrochemical state

# Anodic protection (CP and steel)

Passivation region (V vs SCE) for mild steel in 1 M of sulfuric acid (indicative values)

Between + 0.5 and about 1 V

However the passivation potential is in general dependent on the local environment (pH, oxygen concentration, chlorides, etc.) normally unknown close to the corroding area.

Many Authors reported an increases of the OCP (moving to anodic direction) of steel coated with CP in comparison with bare steel (ennobling).

This is a necessary condition for anodic protection, but it **is not sufficient**, being the OCP of a coated steel often increased also for barrier coatings because of the different corrosion conditions (concentrations and ohmic drop).

# Anodic protection (PANI and steel)

Many Authors reported an ennobling OCP (moving to anodic direction) of steel and stainless steel coated. The amount of anodic shift depends very much on the experimental conditions.

Local electrochemical study of OCP (scanning reference electrode):

Controversial results, but in general agreement with an ennobling process.

General difficulties to prove the anodic protection just with OCP measurements.

Electrochemical action

# Anodic protection (PANI and steel):
## surface analysis

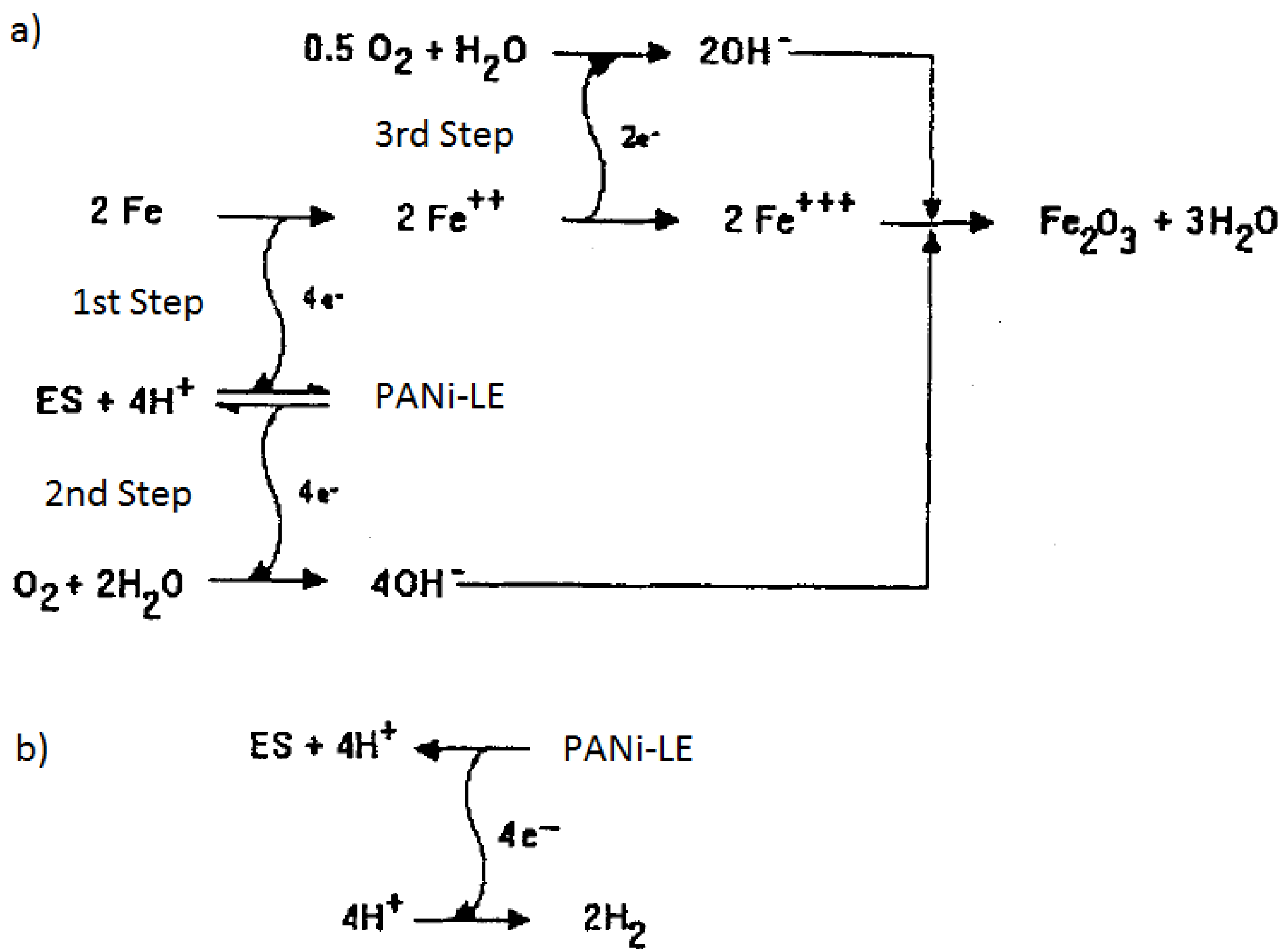
It has been proved that PANI can modify the steel surface conditions (electrochemical studies of bare steel and bare steel obtained after removal of the PANI layer exposed to the electrolyte).

Impedance measurements (charge transfer resistance)
Visual observation (change of color)
XPS analysis (formation of $Fe_2O_3$, $Fe_3O_4$)
Mass spectroscopy

Surface conditions dependent on PANI form:
EB (emeraldine base) or ES (emeraldine salt).

# Anodic protection (PANI and steel):
## proposed passivation scheme (Wesseling)

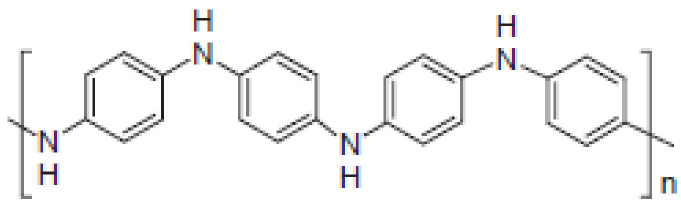
Electrochemical action



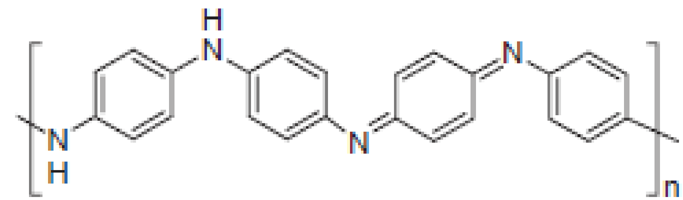
Electrochemical action

# Anodic protection (PANI and steel):

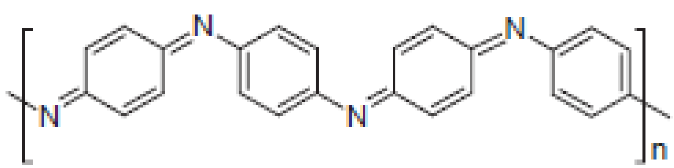
## redox and proton exchange reactions



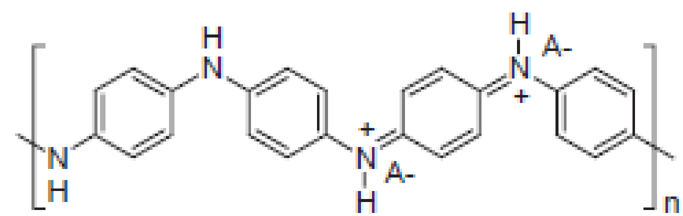
Leucoemeraldine form



Emeraldine base, intermediate form



Pernigraniline form



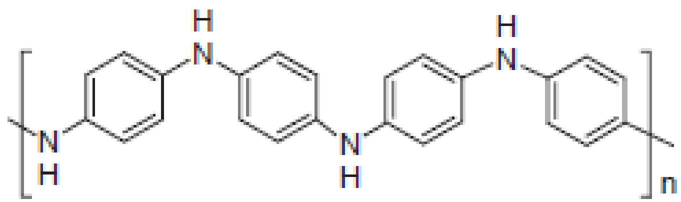
Emeraldine salt, conducting form

Oxidation state LE (reduced form)< EB < PG (fully oxidised)

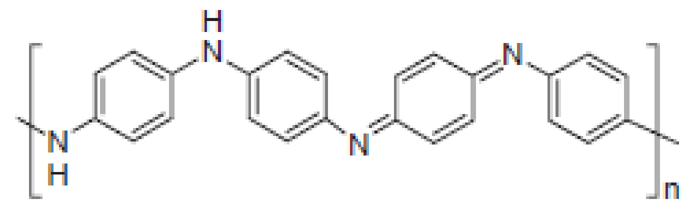
PANI ES is the only really conductive form. Anions are necessary for balancing the charge of salts.

Electrochemical action

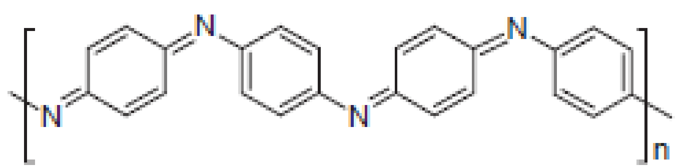
# Anodic protection (PANI and steel): **redox** and proton exchange reactions



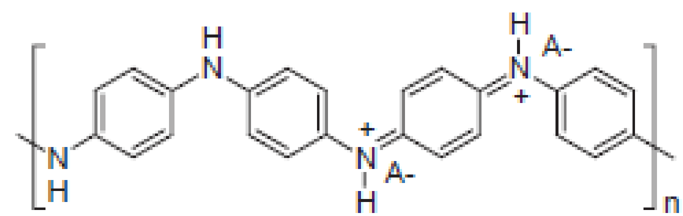

Leucoemeraldine form




Emeraldine base, intermediate form




Pernigraniline form




Emeraldine salt, conducting form

Oxidation state LE (reduced form)< EB < PG (fully oxidised)

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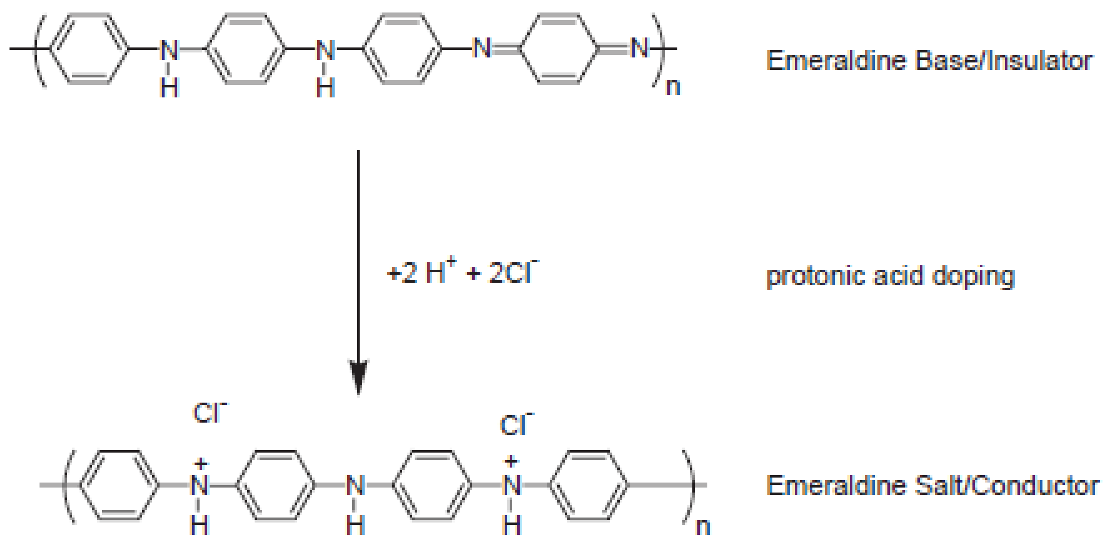
# Anodic protection (PANI and steel):

## redox and **proton exchange reactions**




Anions are necessary (not necessary $Cl^-$ ) for balancing the charge of salts.
The ES is often called doped PANI (while EB undoped PANI).

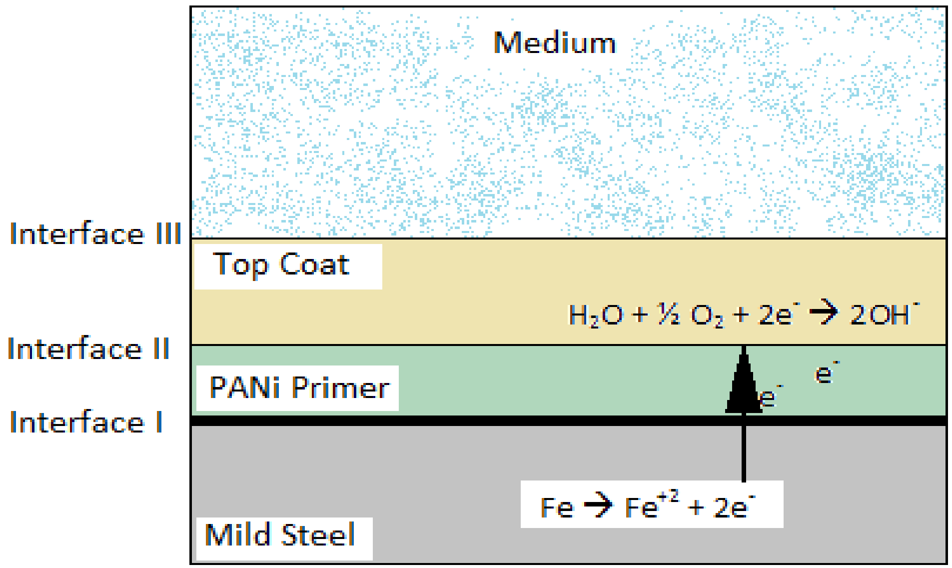
# Anodic protection (PANI and steel):

## PANI redox state analysis

XPS analysis proved the reduction of PANI from EB (or ES) to LE (supposing to oxidize steel). If the substrate is inert, this change is not measured.

However, again the results are controversial and very dependent on the testing environment.

# Electrochemical action (PANI - steel):
## shift of the cathodic interface (Schauer)




The cathodic reaction can be the PANI reduction, followed by re-oxidation.
PANI and iron ions form complex able to increases the kinetics of oxygen reduction.

# Electrochemical action (PANI - steel):

## shift of the cathodic interface (Schauer)

Prevention of high pH at the metal surface:

•Stabilize the surface oxides

•Reduce cathodic disbonding.

?? High pH promote passivation
?? Emeraldine state is quickly reduce to LE not conductive
?? Is it still possible for EB (undoped PANI)?

Mechanism non yet completely understood

**Open problem: role and properties of the top coat**

# Electrochemical action (PANI - steel):
## emeraldine salts ES vs emeraldine base EB
## role of the counter anions

Difficult comparison ES EB (dynamic equilibrium).

- No significant differences proved in anodic protection
- Higher barrier properties for EB (lower ions mobility)
- Conductivity role?

Counter ions could play a role in ES PANI

- Affecting corrosion rate (promoting corrosion)
- Complessing Fe (or other ions - Ce?) ions and causing a precipitation of insoluble salts (pseudo-passivation).
- Actual inhibition (proposed for Al where anodic protection is difficult to justify)

# Corrosion protection: PANI – steel

Comments

Probably more than one mechanism can be active in the same system (anodic protection, cathodic interface shift)

- Both for anodic protection (passivation) and cathodic interface shift,  a critical role is played by the metal surface conditions (pre-passivation, pre-treatments, etc) and the barrier properties of top-coat.
- The electrical conductivity of PANI and the contact of the PANI layer with the substrate is critical for any active corrosion protection function.
- Synergistic (or negative?) role of PANI with the electrochemically action ("passivation") of other possible ingredients of the coating (Ce??).