The University of Manchester

Corrosion Inhibition: Separating Fact from Fiction

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CORROSION @Manchester

CI's: Applications

(Source: www/wahchang.com)

(Source: www.clevelandart.org)

Historical Note

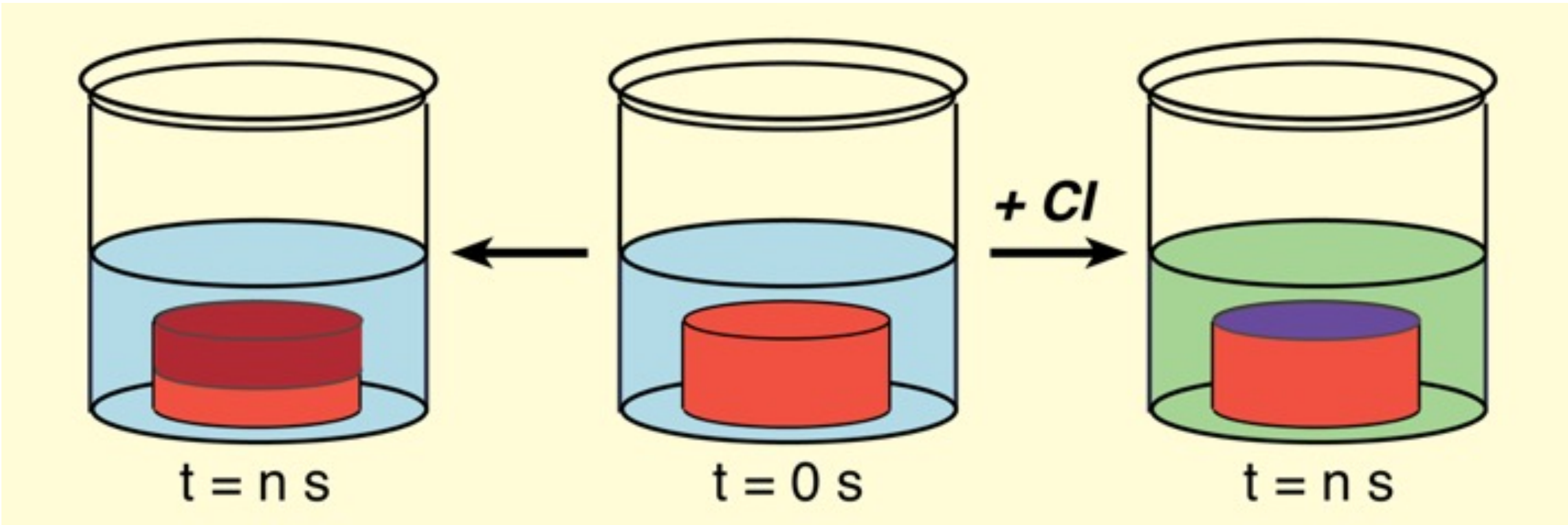
116 ABSTRACTS OF CHEMICAL PAPERS.
On the Influence of certain Liquids in Retarding or Arresting the Action of Acids upon Metals.
By C. MARANGONI and P. STEFANELLI (IL Nuovo Cimento [2],iv, 373-389).

The evolution of hydrogen from dilute sulphuric acid by the action of zinc, is quickly arrested on adding a small quantity of an essential oil, such as oil of myrtle, thyme, lavender, turpentine, or cherry-laurel, and agitating briskly with a glass rod, but recommences, though less strongly, on addition of a certain quantity of alcohol. Fixed oils like-wise arrest the action completely, but less quickly than essential oils ; ether, naphtha, benzene, and nitrobenzene have but little effect, the evolution of hydrogen being merely retarded by them while the agita-tion continues, and recommencing soon after the liquid is left at rest.

J. Chem. Soc. 25 (1872)

Definition

A corrosion inhibitor is a substance that, when added in small quantity to a normally corrosive environment, reduces the corrosion rate by bringing about a change at or near the metal surface, without significantly changing the concentration of corrosive species.



CI Efficiency

Figure of merit for CI performance

$$\eta\% = \frac{(U - I)}{U} \times 100$$

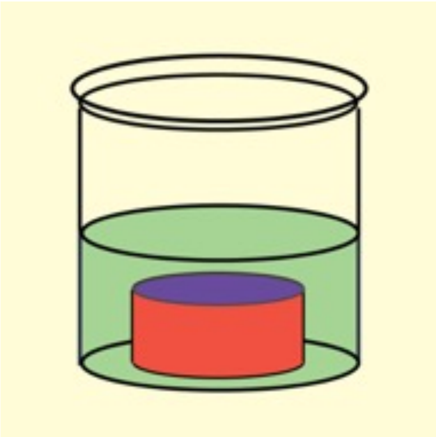
- *U: Uninhibited CR*
- *I: Inhibited CR*

A good inhibitor will have an efficiency of over 95% (i.e. inhibited corrosion rate is less than one twentieth of rate without inhibitor.)

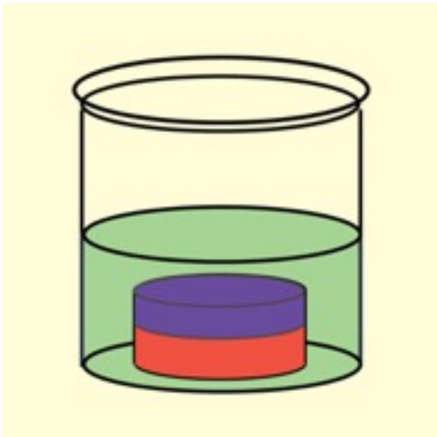
CI Classification

- *2D/3D film forming*
- *Organic/Inorganic*
- *Anodic/Cathodic/Mixed*
- *Oxidising/Non-oxidizing*
- *Safe/Dangerous*

Nature of Surface Film

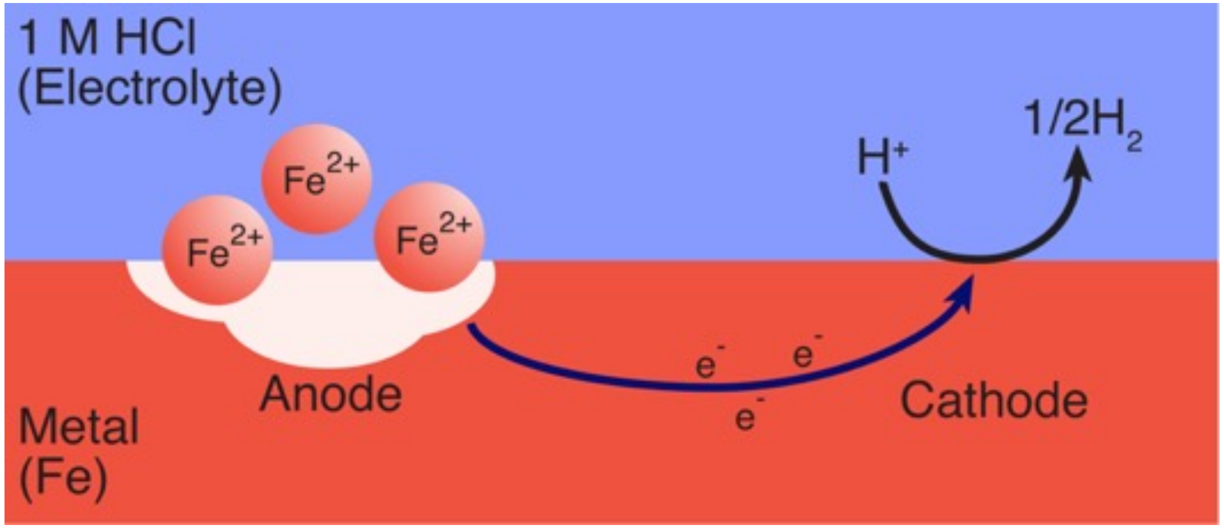


- *2D adsorbed film*
  More typical in acidic solution



- *3D film*
  More typical in aerated near-neutral solution

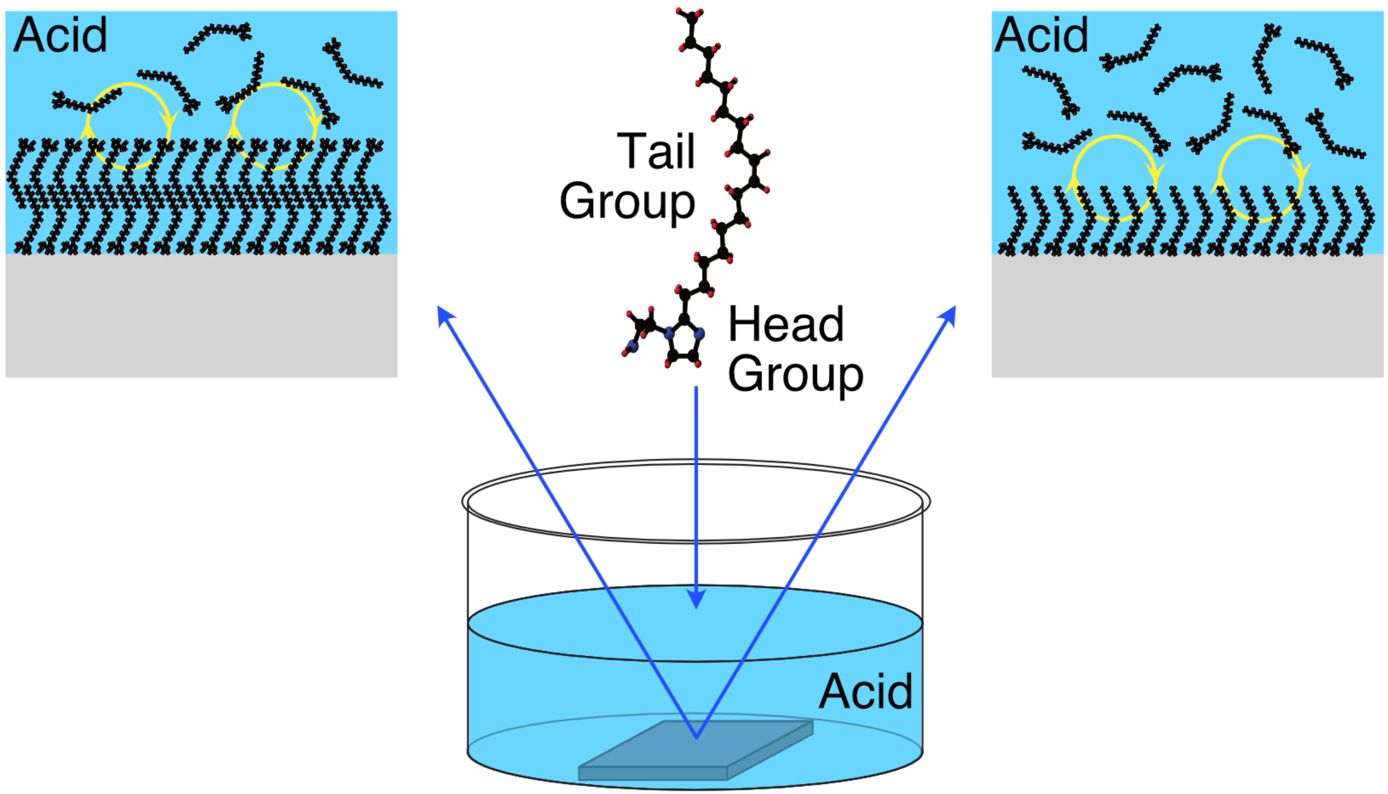
Acidic Environment



$Fe \rightarrow Fe^{2+} + 2e^-$ (Anodic Reaction; Oxid.)

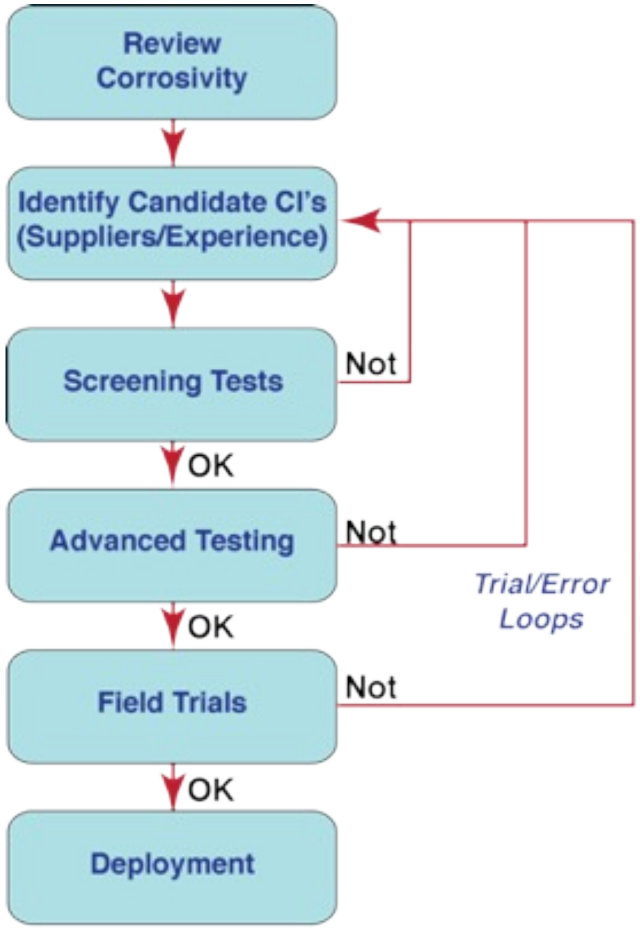
$2H^+ + 2e^- \rightarrow H_2$ (Cathodic Reaction; Red.)

CI: Acidic Environment



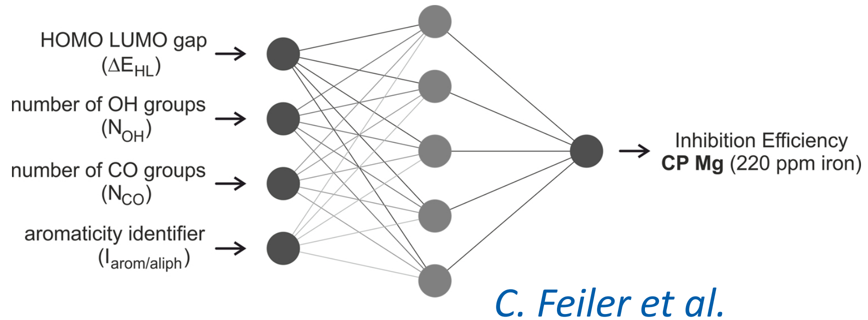
CI: Practical Selection

- *Essentially Empirical*
- *Trial & Error*



Current Research Effort

- *Adsorption Thermodynamics*
- *Machine Learning*



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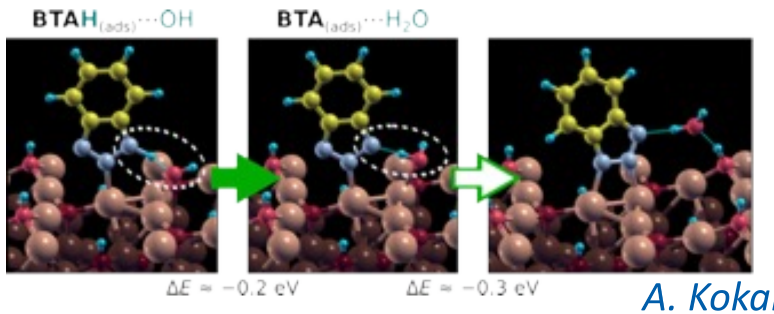
- *Interface Characterisation*
- *Green CI's*



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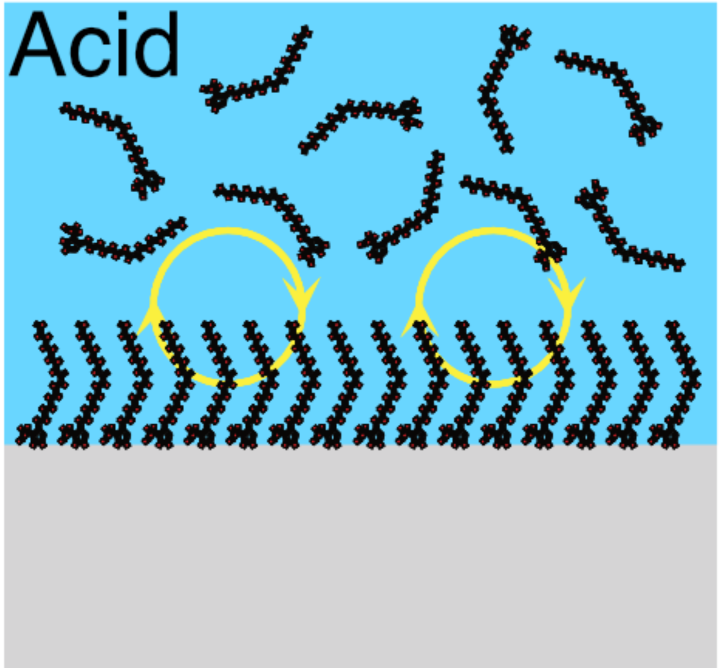
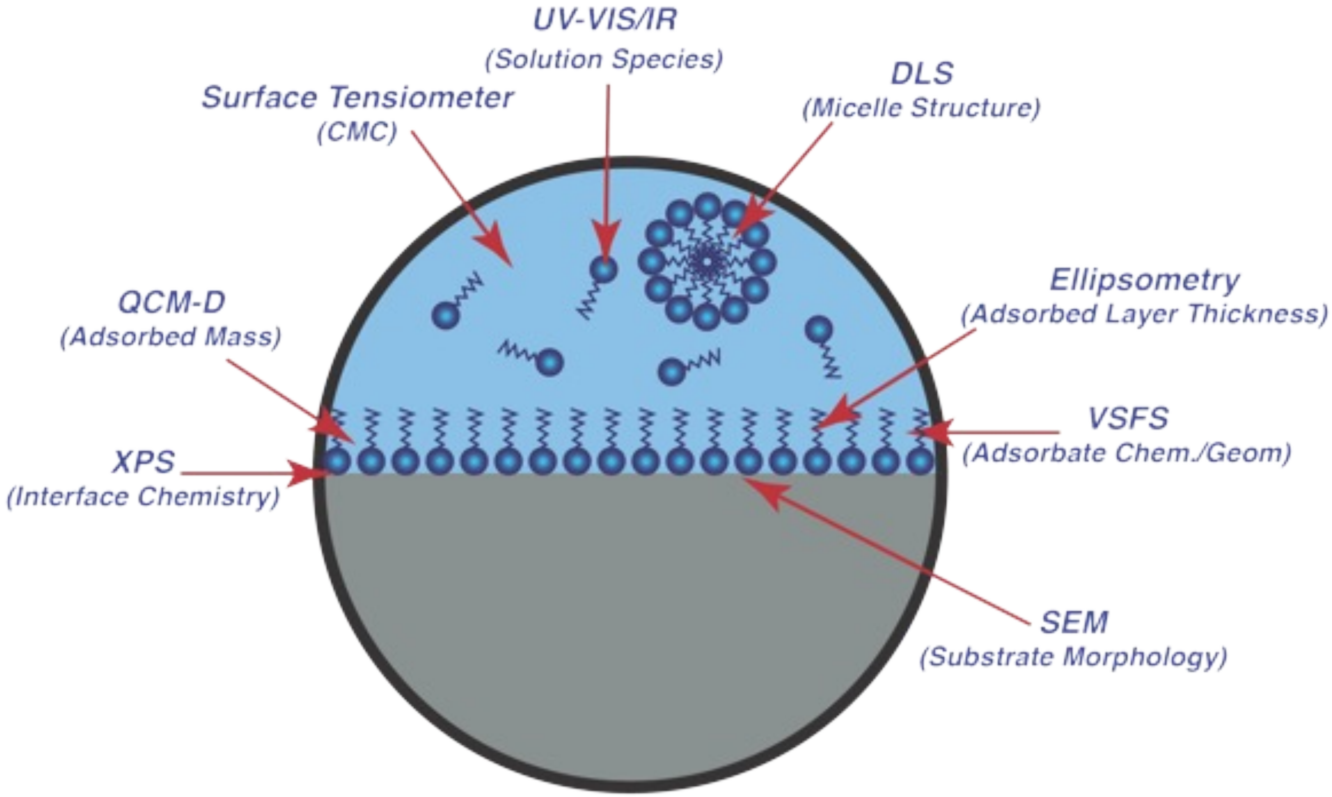
Research Goal



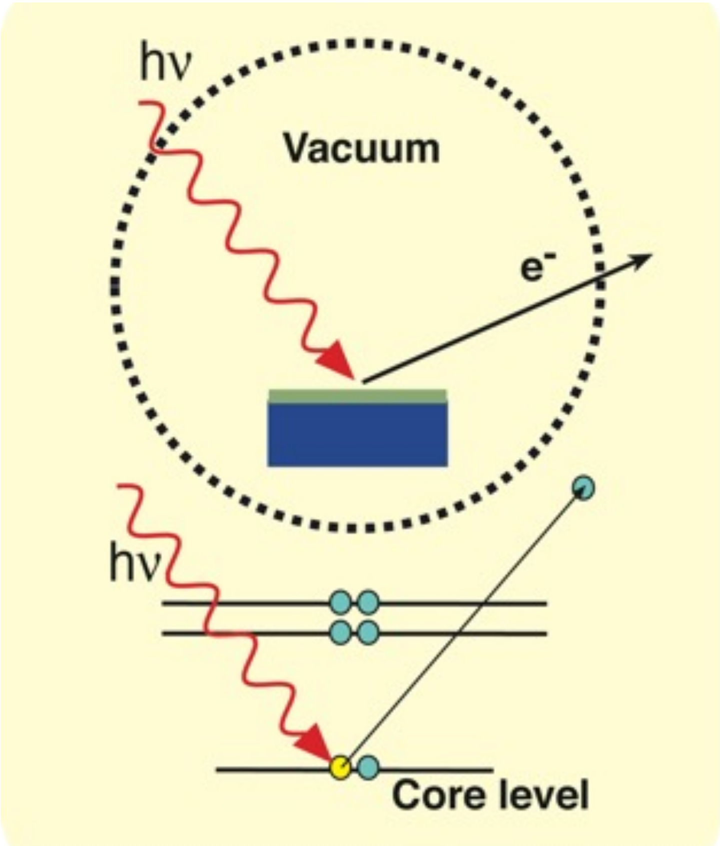
Cartoon or Reality?

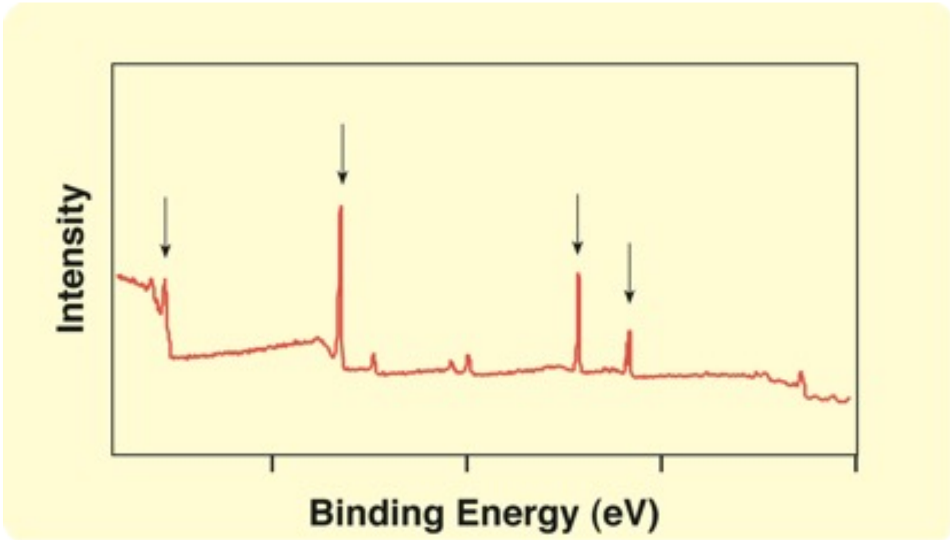
Our Experimental Toolbox



Corrosion Rate: LPR/PDP + Weight Loss

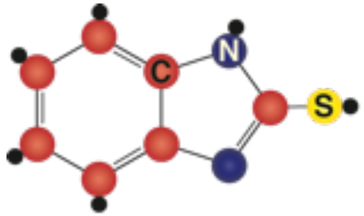
XPS: Basics

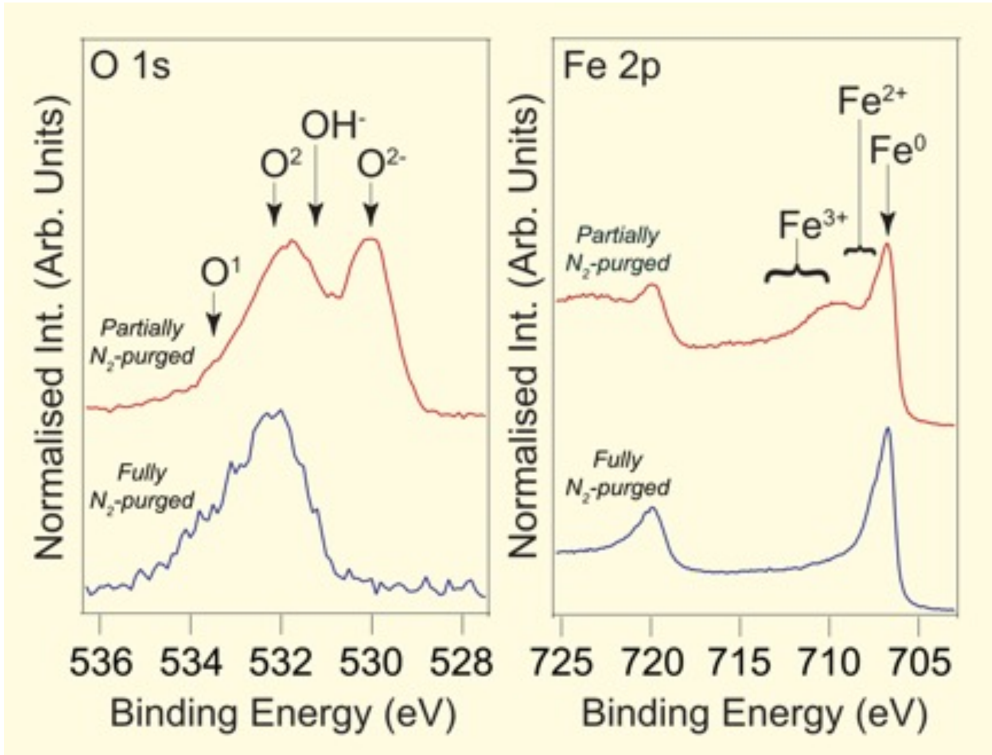




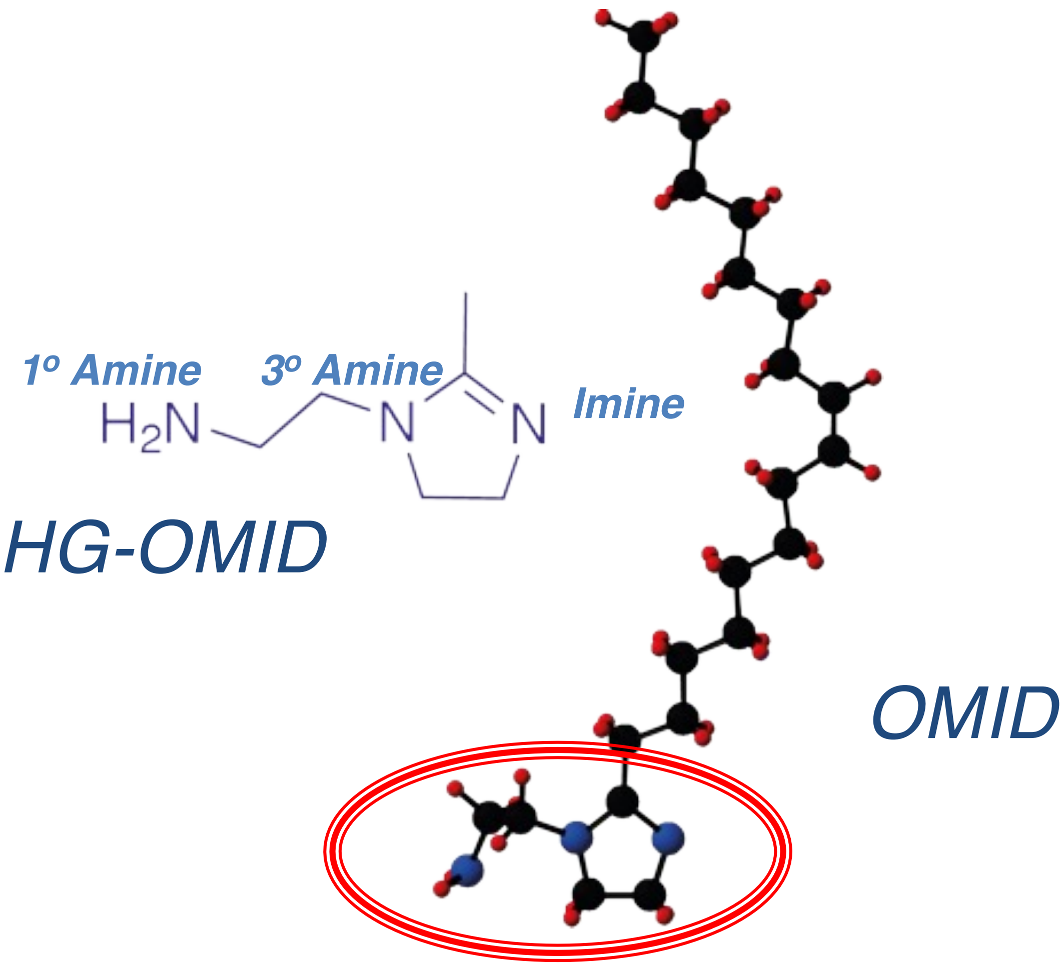
- *Surface Sensitive*
- *Elemental/Chemical Composition*

XPS: Methodology

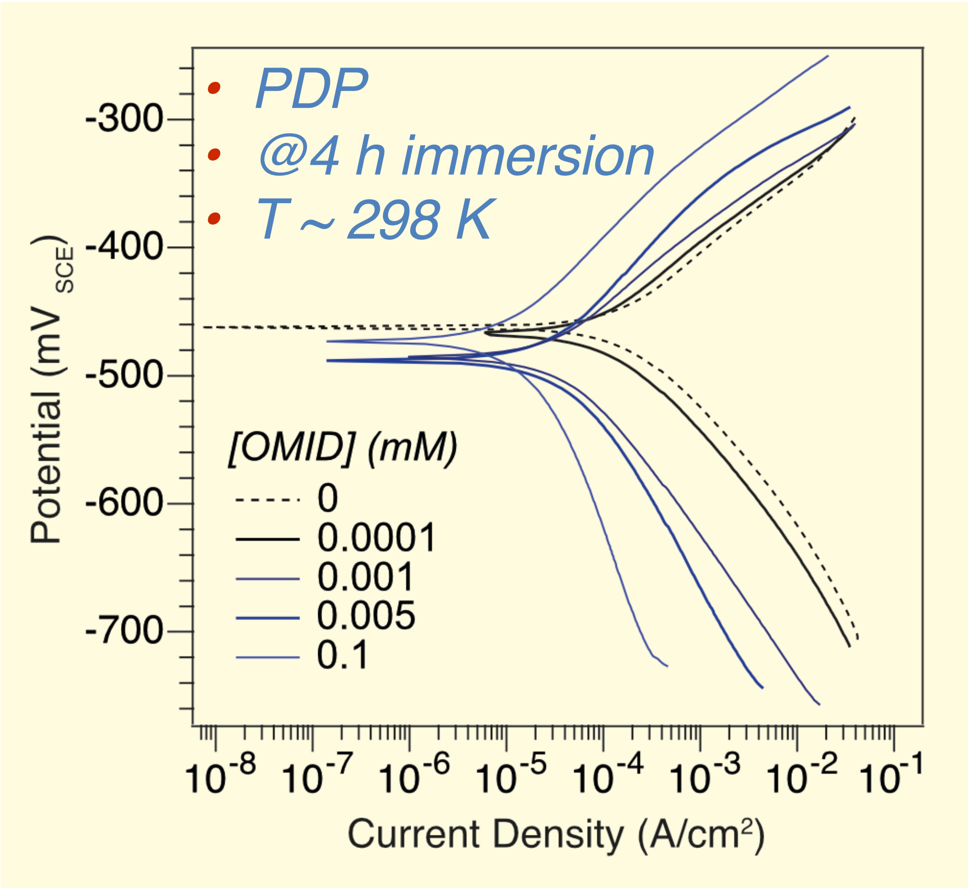




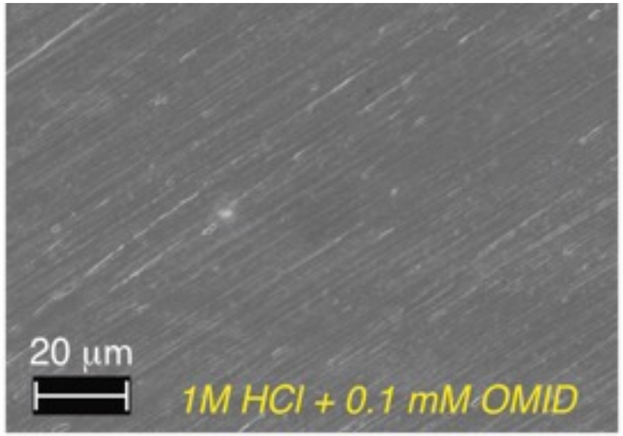
System of Interest: c-steel + OMID

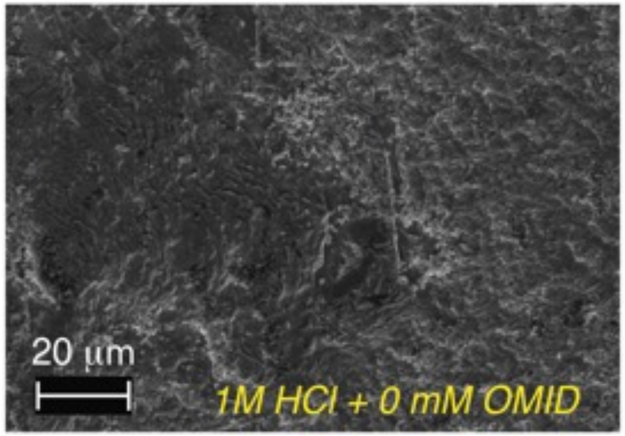


C-Steel/1 M HCl + OMID: Performance



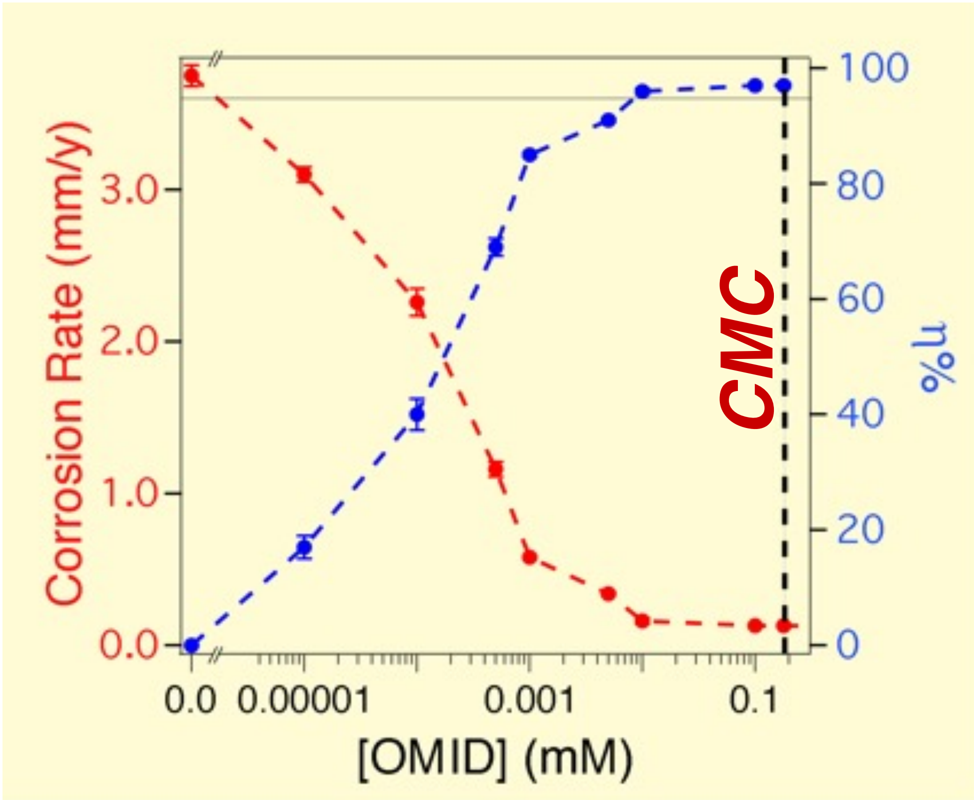
CMC = 0.18 ± 0.03 mM





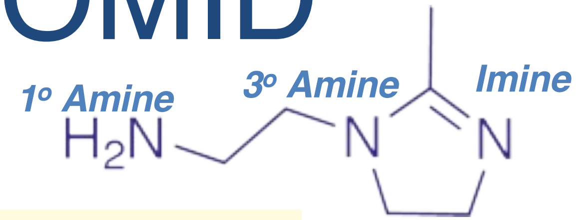
C-Steel/1 M HCl + OMID: CR/η%

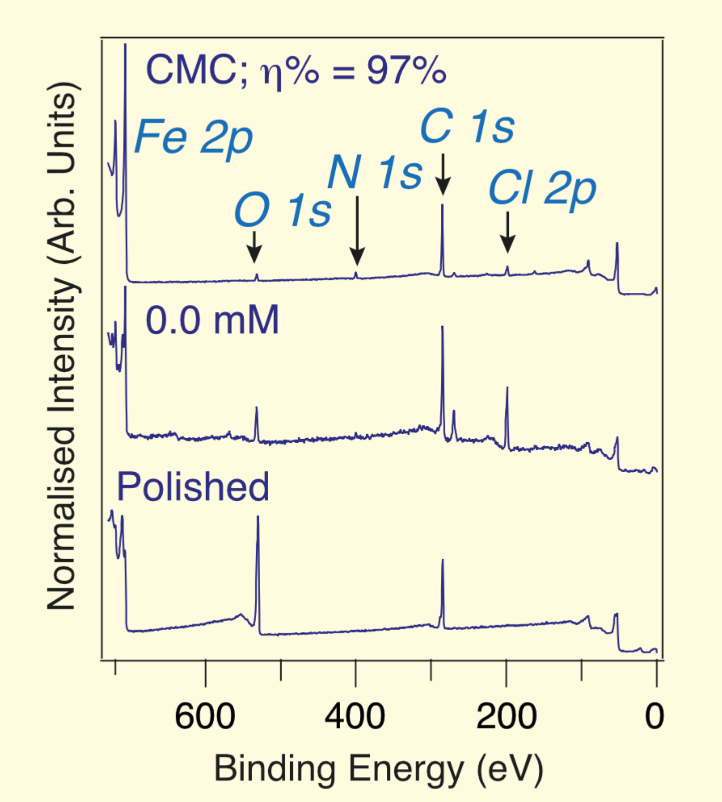
$$\eta\% = \frac{(U - I)}{U} \times 100$$

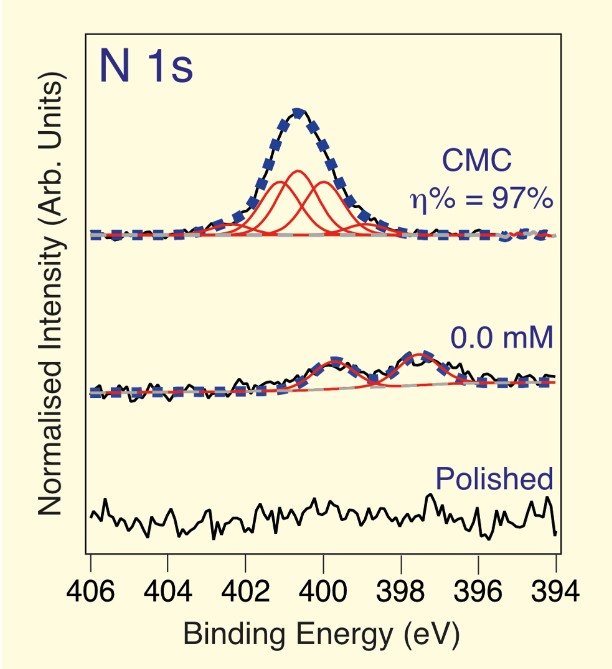


- *CR from LPR*
- *@4 h immersion*
- *T ~ 298 K*

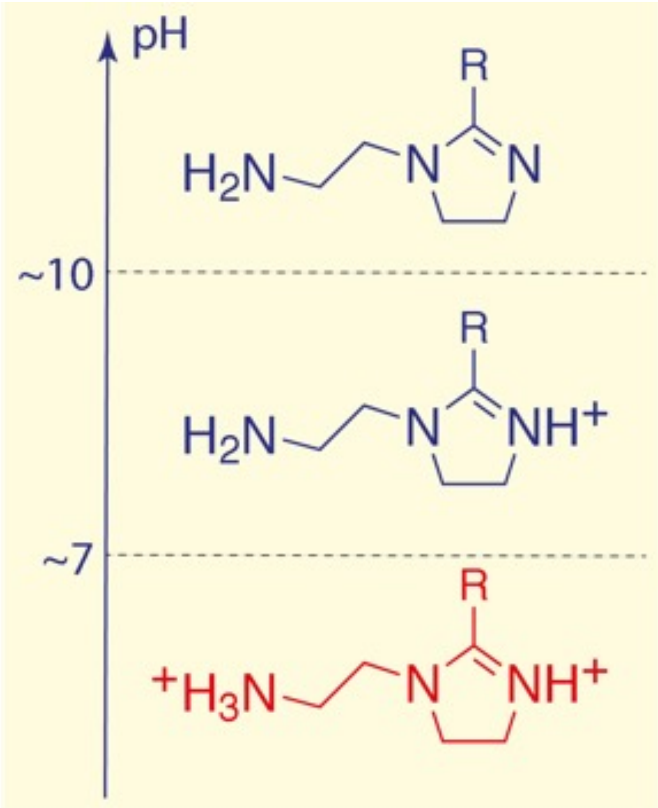
XPS: C-Steel/1 M HCl + OMID







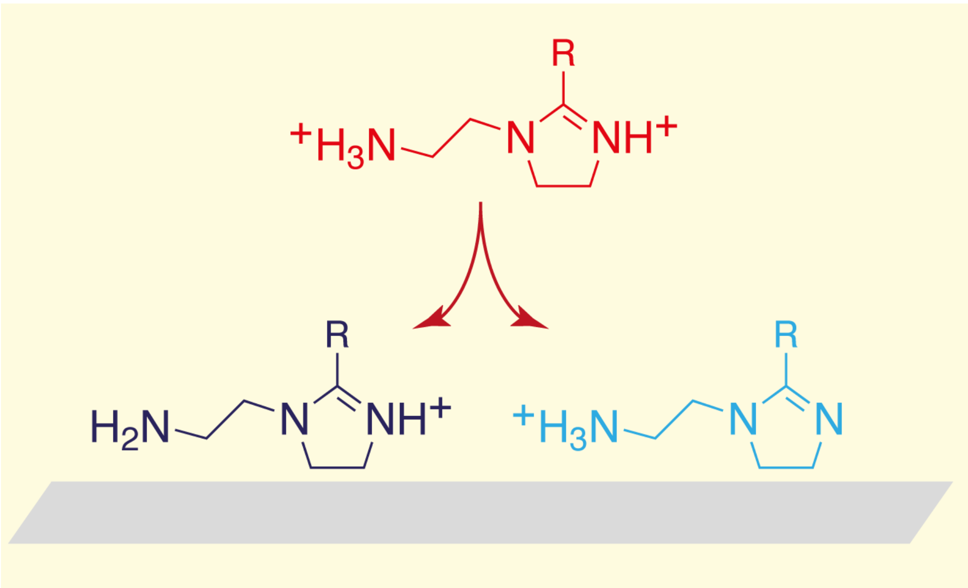
N 1s Profile: Protonation?

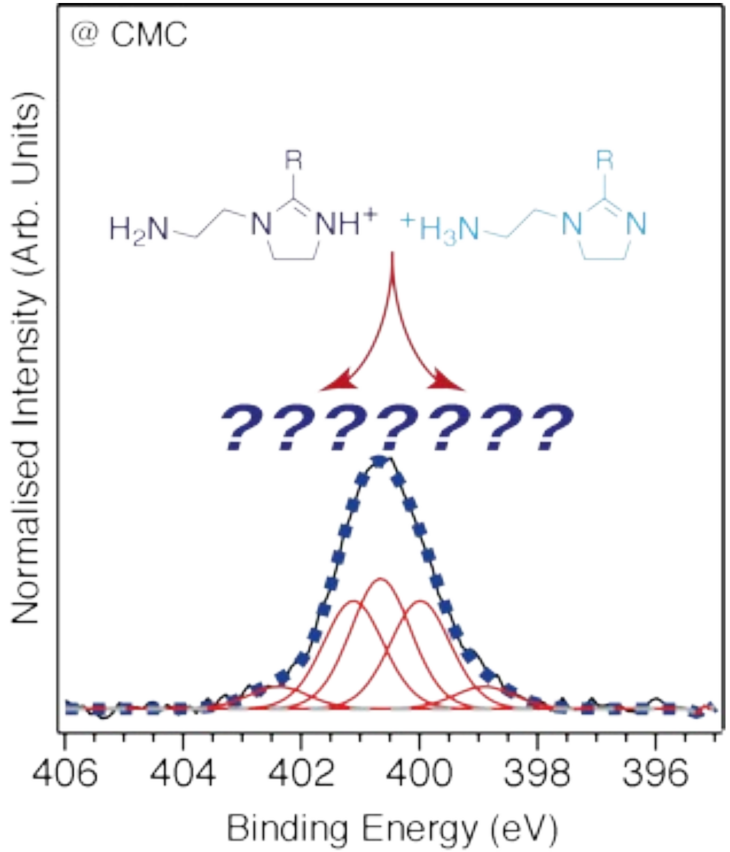


- *Online Software (Chemicalize, Chemaxon)*

OMID: Double Protonation in 1 M HCl

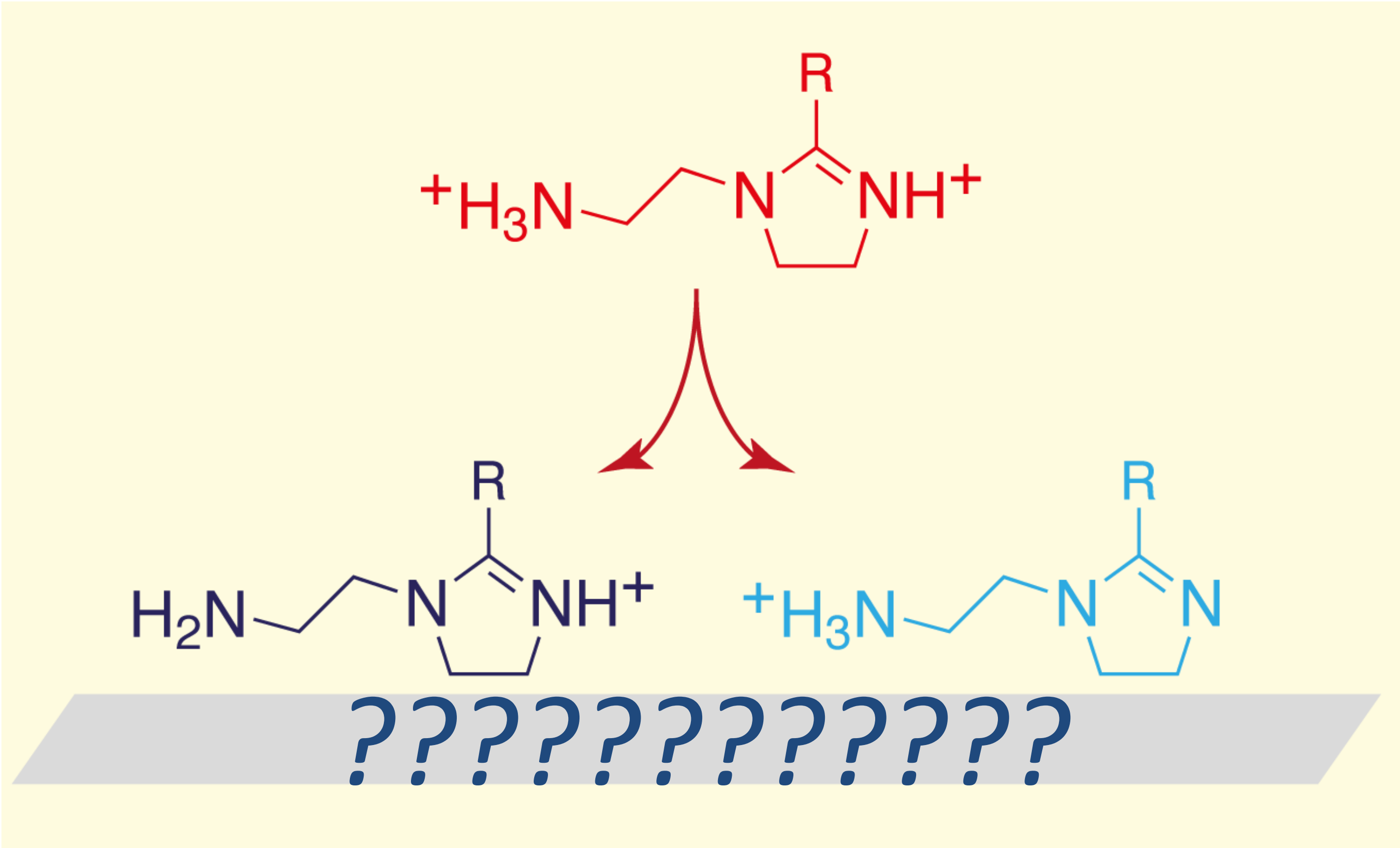
N 1s Profile: Interpretation



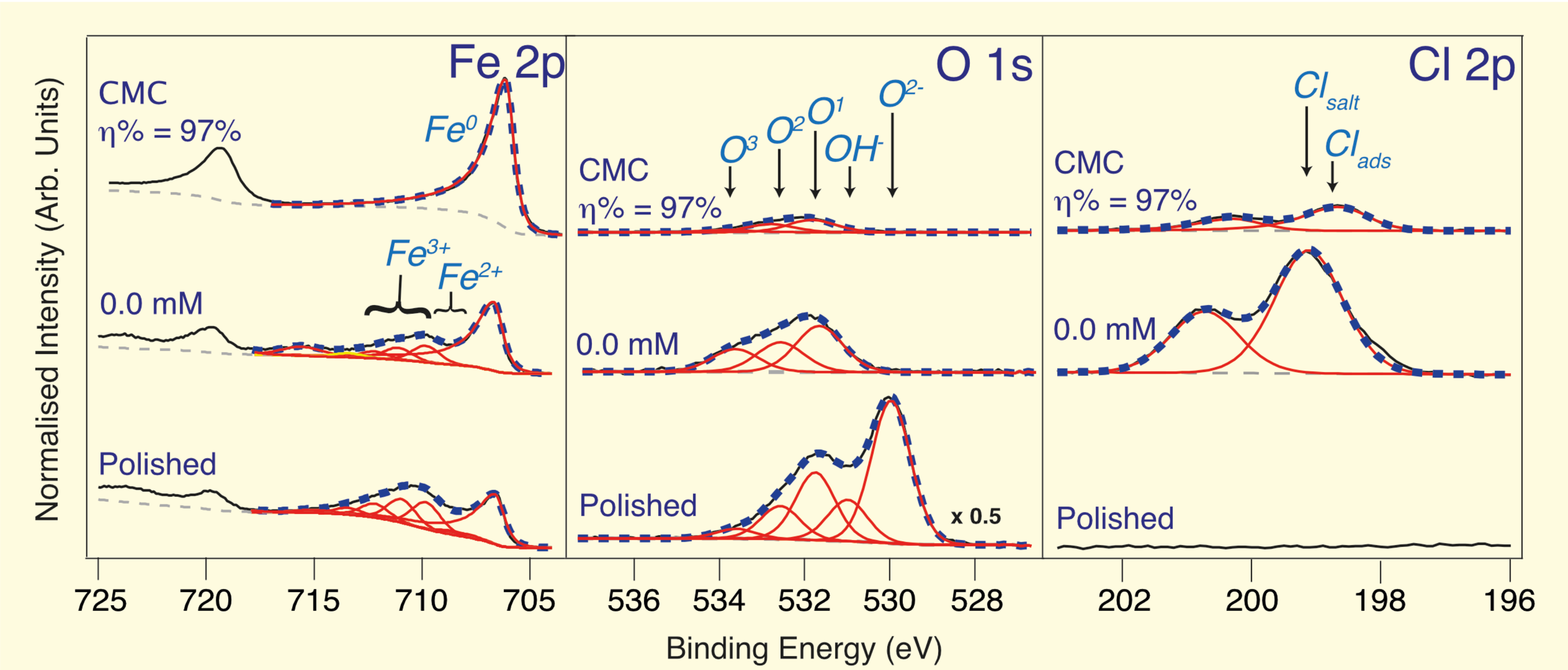


Adsorbed OMID: 2x Singly Protonated

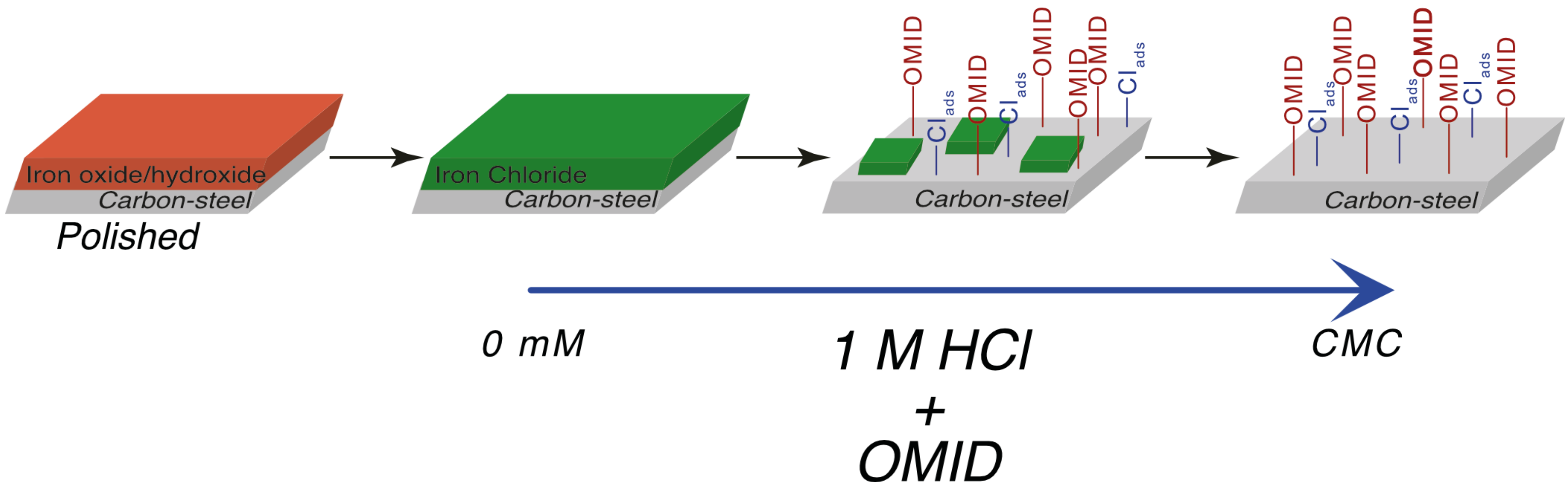
OMID: Adsorbed State



Fe 2p, O 1s, Cl 2p Profiles

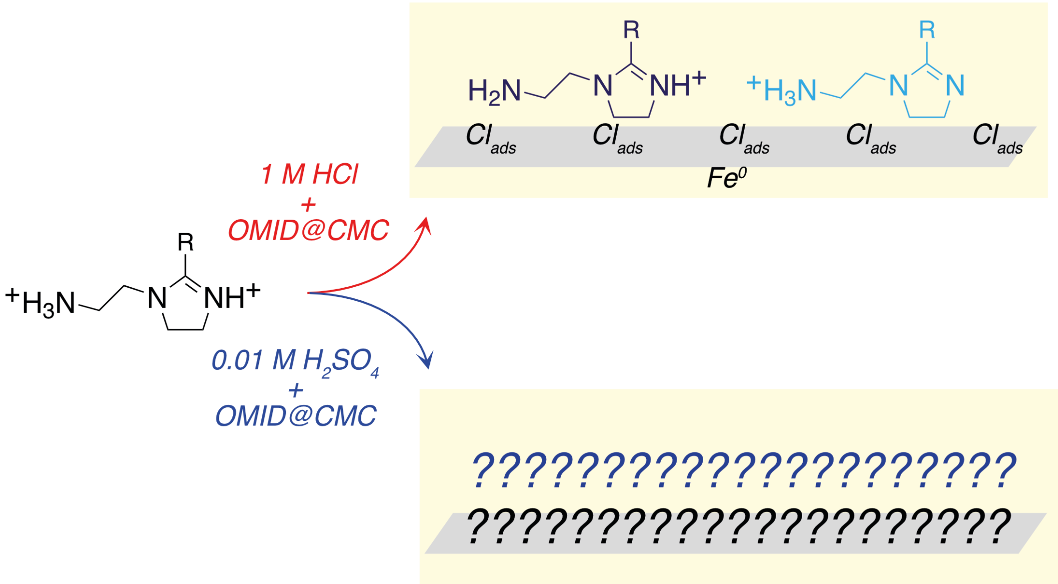


Interface Evolution: 1 M HCl + OMID

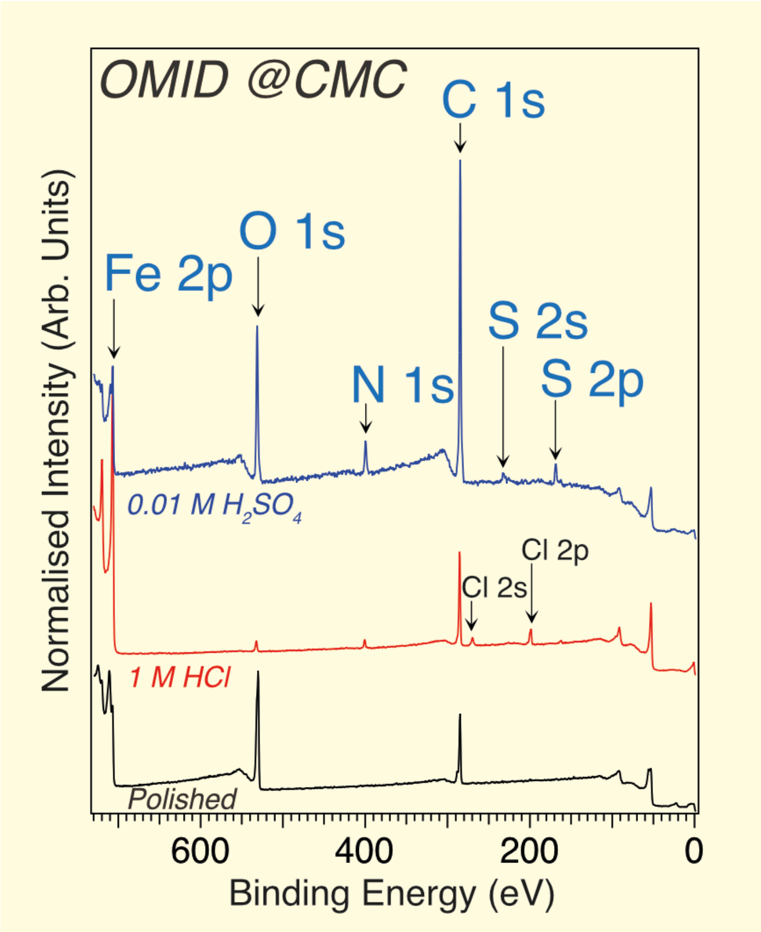


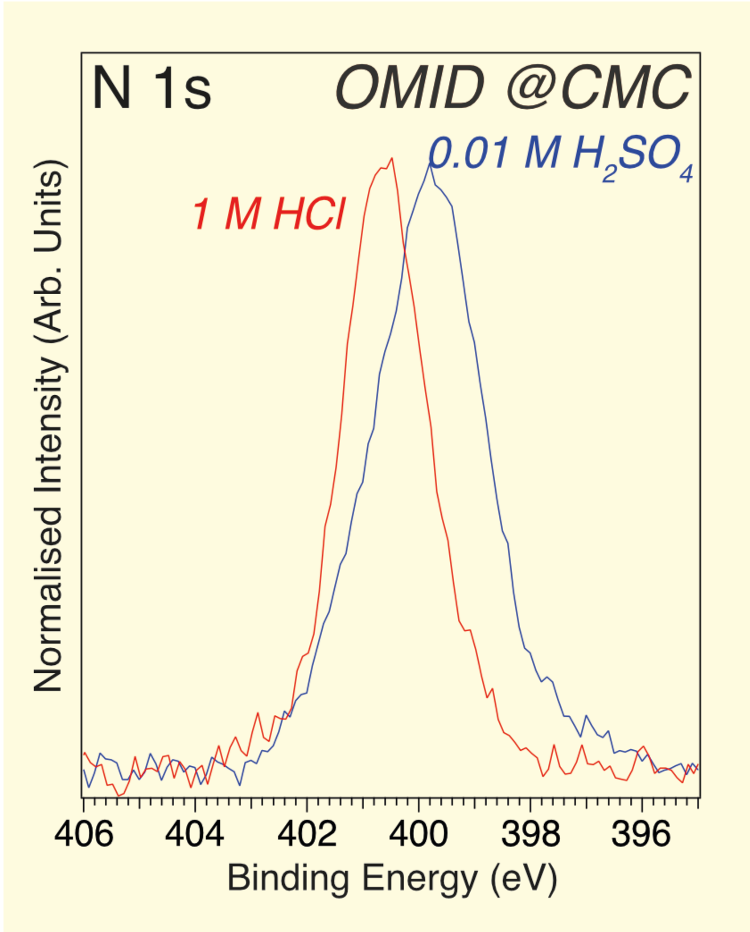
Acid Solution: HCl to H_2SO_4

Solution	CR 0 mM [OMID] (mm y^{-1})	CR CMC [OMID] (mm y^{-1})	η% (%)
1 M HCl	3.75 ± 0.07	0.11 ± 0.01	97.1 ± 0.3
0.01 M HCl	1.96 ± 0.12	0.28 ± 0.03	85.7 ± 1.8
1 M H_2SO_4	52.71 ± 0.80	1.09 ± 0.07	97.9 ± 0.1
0.01 M H_2SO_4	4.43 ± 0.70	0.20 ± 0.01	95.5 ± 0.8

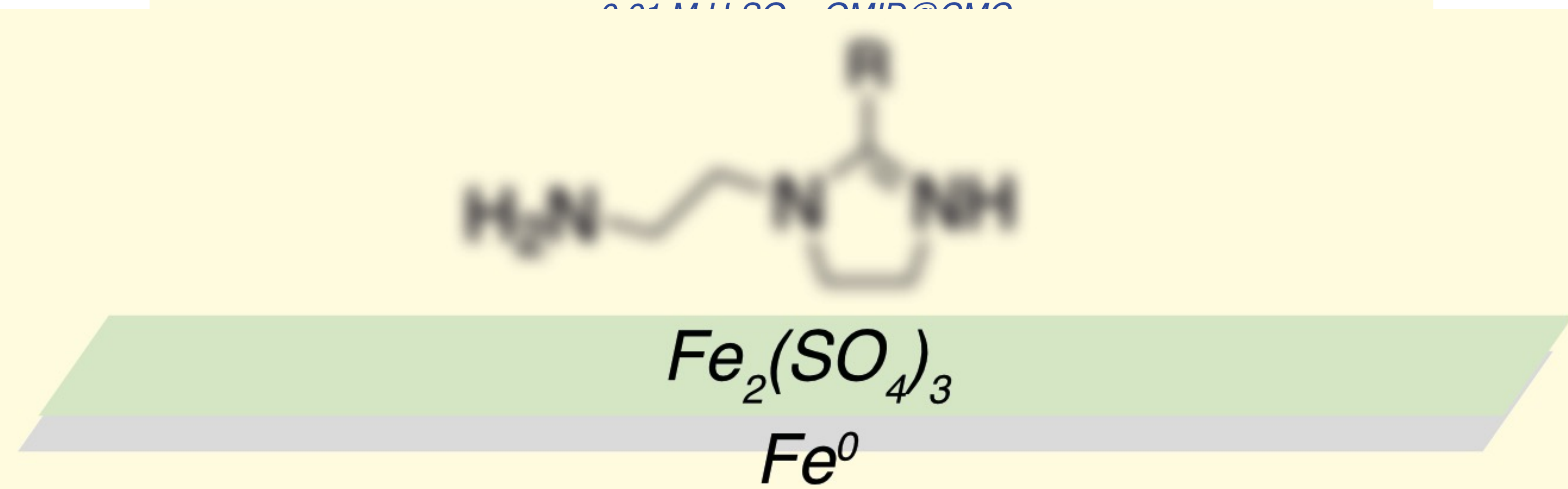


XPS: HCl vs H_2SO_4

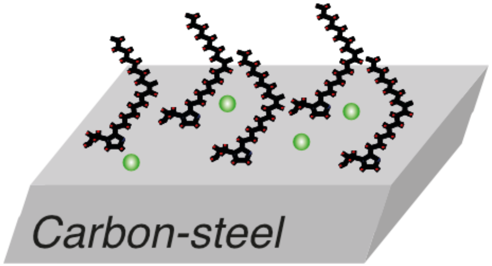




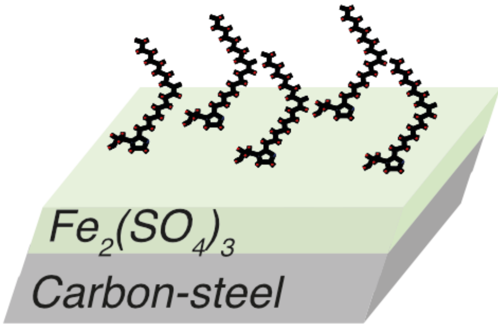
Fe 2p, O 1s, S 2p, Cl 2p Profiles



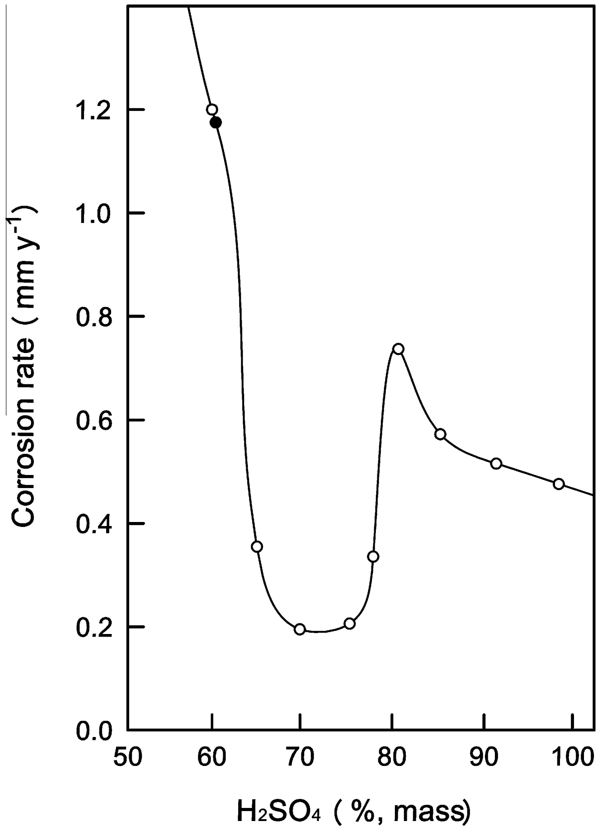
$H_2SO_4 \neq HCl$: Why?



1 M HCl + OMID



0.01 M H_2SO_4 + OMID

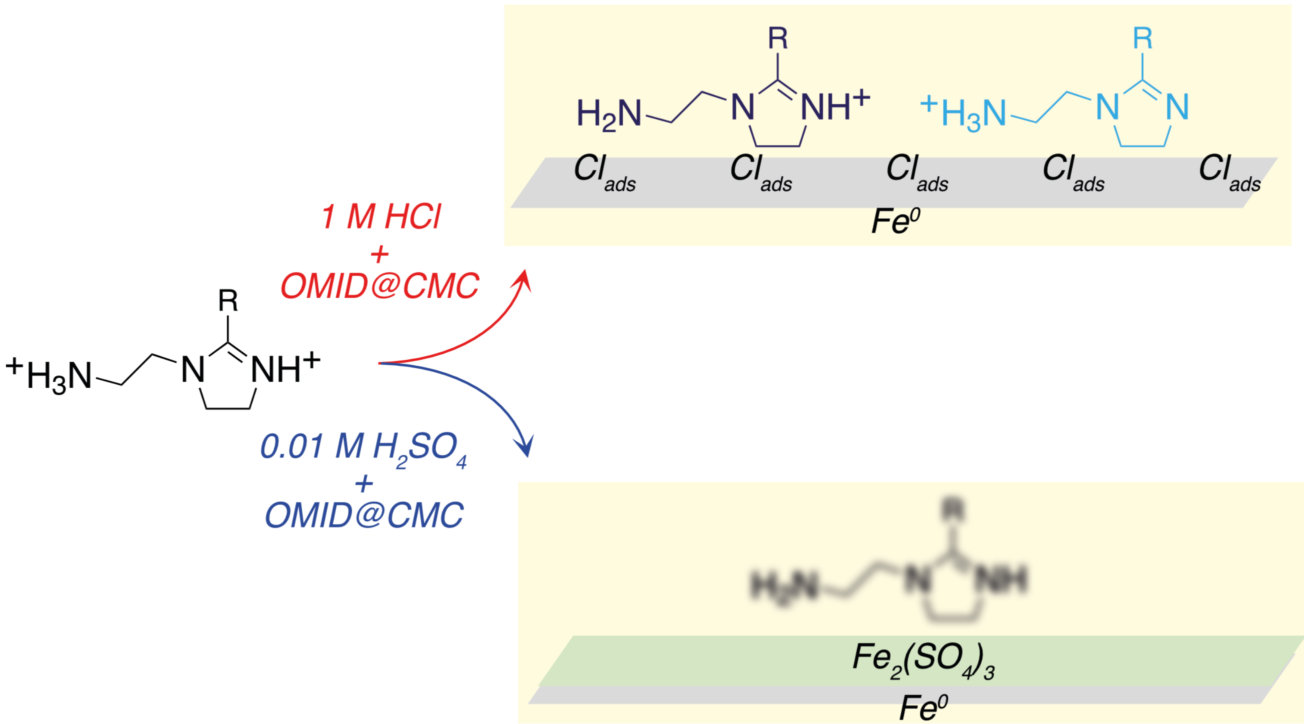


Hines et al, Corros. Sci. (1964).

Summary

Acid dependency:

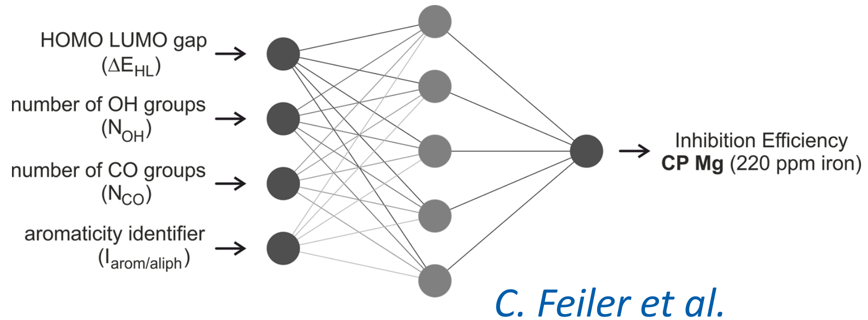
- *Adsorbed OMID*
- *Substrate termination*



Key information for knowledge-based development of next generation corrosion inhibitors

Current Research Effort

- *Adsorption Thermodynamics*
- *Machine Learning*
- *Interface Characterisation*
- *Green CI's*



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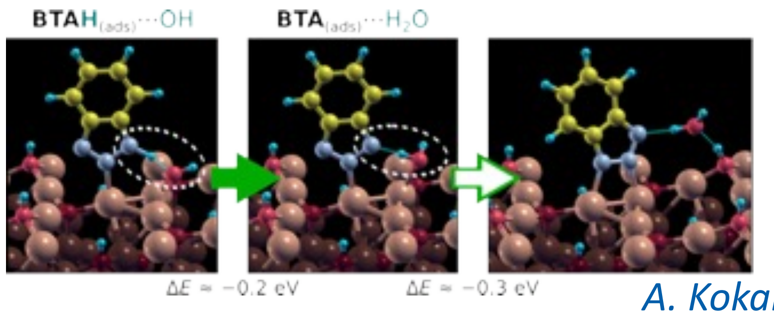

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$\eta\%$ to ΔG^o_{ads}

Select optimum CI's from thermodynamics

$$\eta\% = \frac{(U - I)}{U} \times 100$$

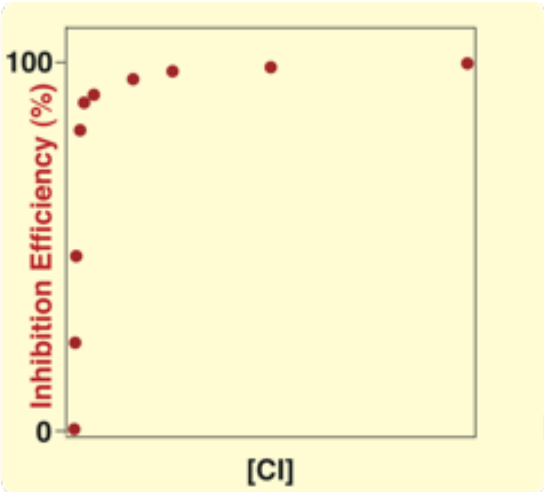
$$\eta\% = 100 \times \theta$$

$$\theta = \frac{K_{eq}[CI]}{(1 + K_{eq}[CI])}$$

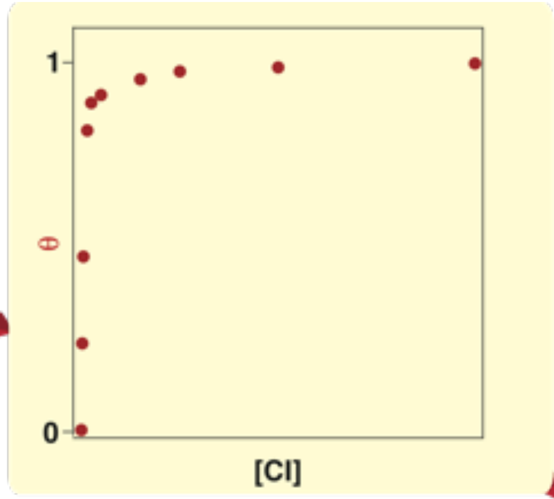
$$\Delta G^o_{ads} = -RT \ln K_{eq}$$

Significant Number of Publications

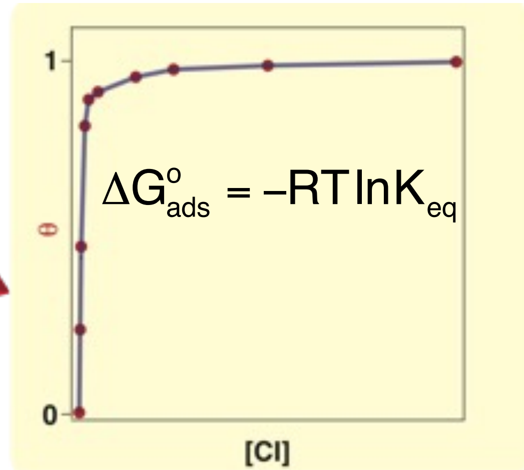
Methodology



$$\eta\% = 100 \times \theta$$

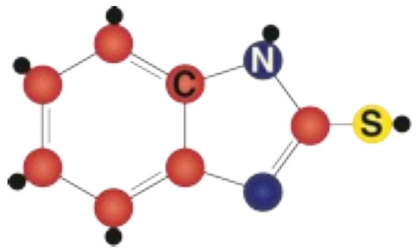


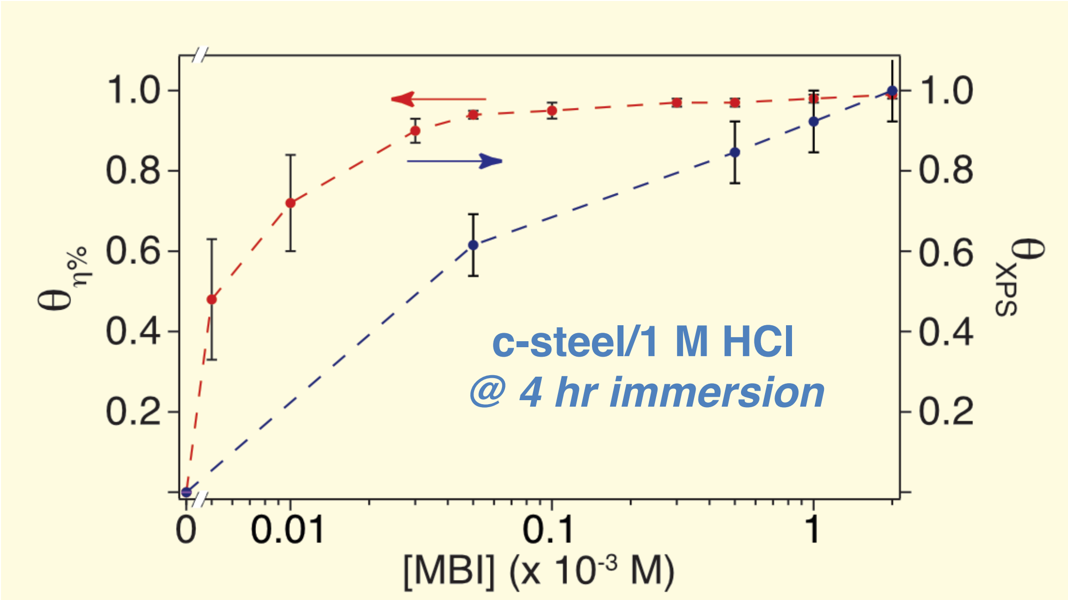
$$\theta = \frac{K_{eq}[CI]}{(1 + K_{eq}[CI])}$$



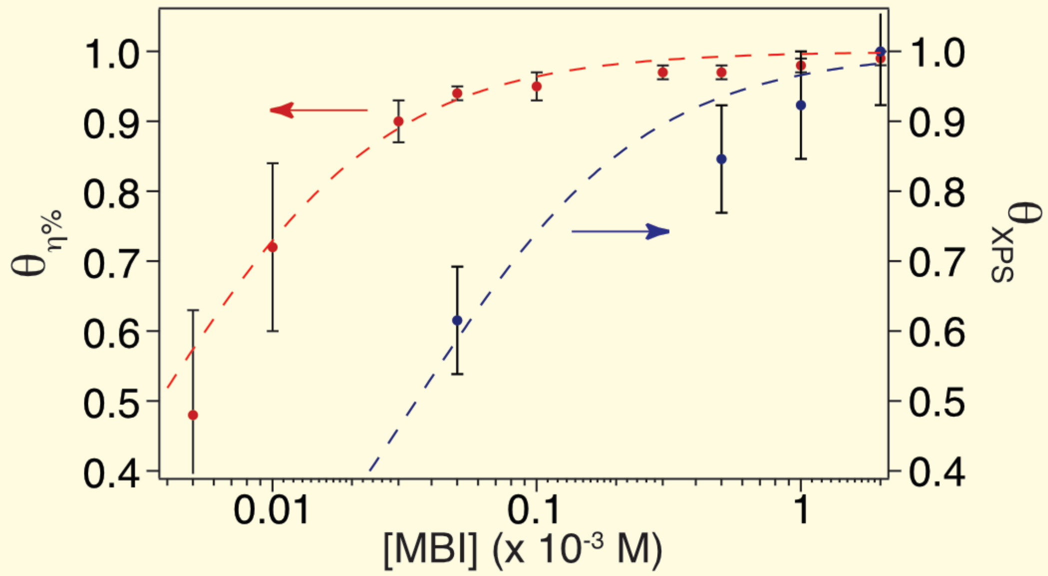
$$\Delta G^{o}_{ads} = -RT\ln K_{eq}$$

$\theta_{\eta\%}$ versus θ_{XPS}





$\theta_{\eta\%}/\theta_{XPS}$: Impact on $K_{eq}/\Delta G^o_{ads}$



$\theta_{\eta\%}$

$K_{eq} = 2.7 \times 10^5 \pm 3 \times 10^4\ M^{-1}$

$\Delta G^o_{ads} = -\ 31.0 \pm 0.3\ kJmol^{-1}$

θ_{XPS}

$K_{eq} = 2.9 \times 10^4 \pm 9 \times 10^3\ M^{-1}$

$\Delta G^o_{ads} = -\ 25.5 \pm 0.8\ kJmol^{-1}$

Significantly different values

….and using θ_{XPS}?

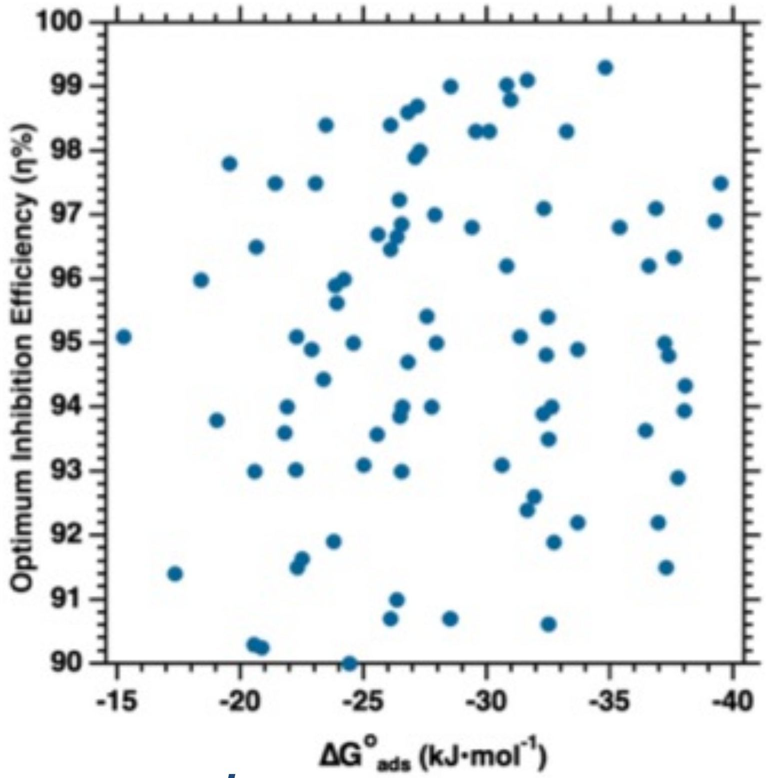
$$\theta = \frac{K_{eq}[Cl]}{(1+K_{eq}[Cl])}$$

MUST STILL demonstrate adherence to following criteria for application of Langmuir Isotherm:

(i) Maximum adsorbate coverage is a monolayer;
(ii) A dynamic equilibrium state has been achieved;
(iii) All adsorption sites are equivalent;
(iv) No adsorbate-adsorbate interactions perturb adsorption behavior.

Summary

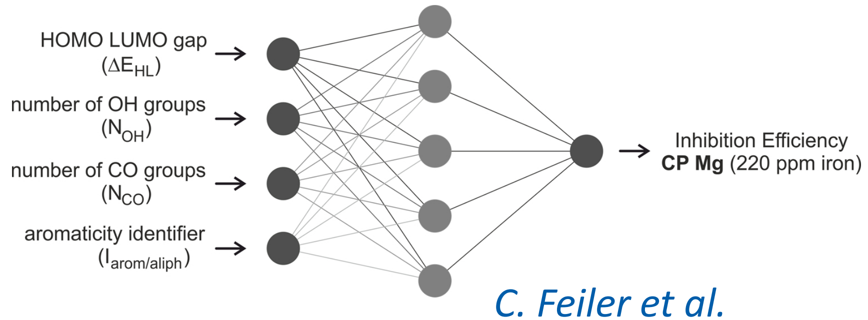
- *Validity of $\eta\% \propto \theta$ is not guaranteed*
- *Accuracy of ΔG^{o}_{ads} is questionable*



Question utility of this approach for advancing CI selection

Current Research Effort

- *Adsorption Thermodynamics*
- *Machine Learning*
- *Interface Characterisation*
- *Green CI's*



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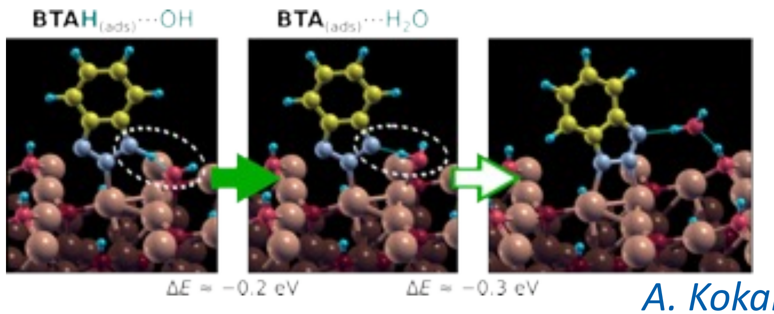

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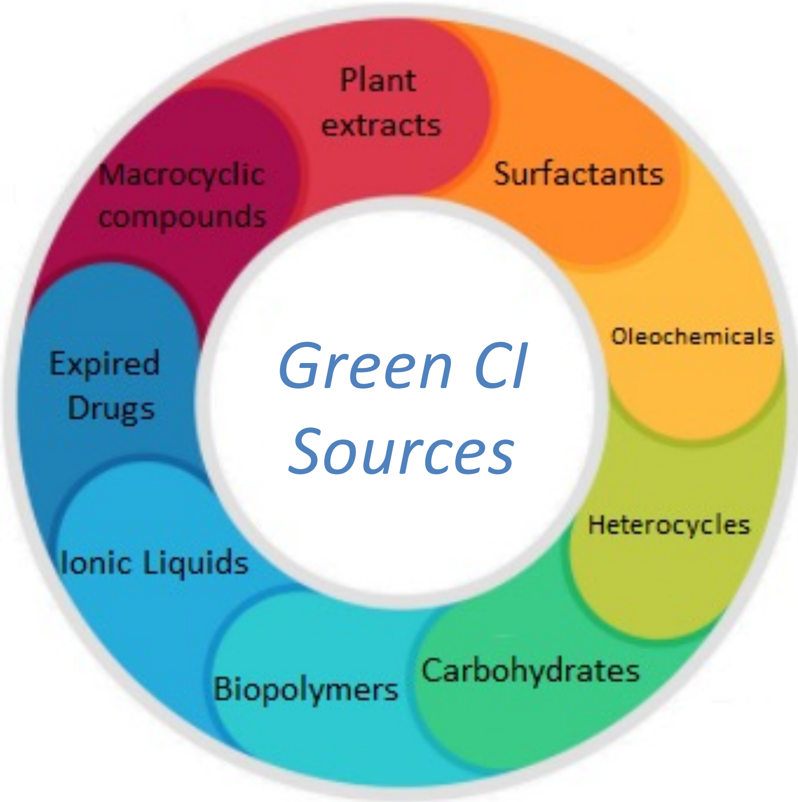
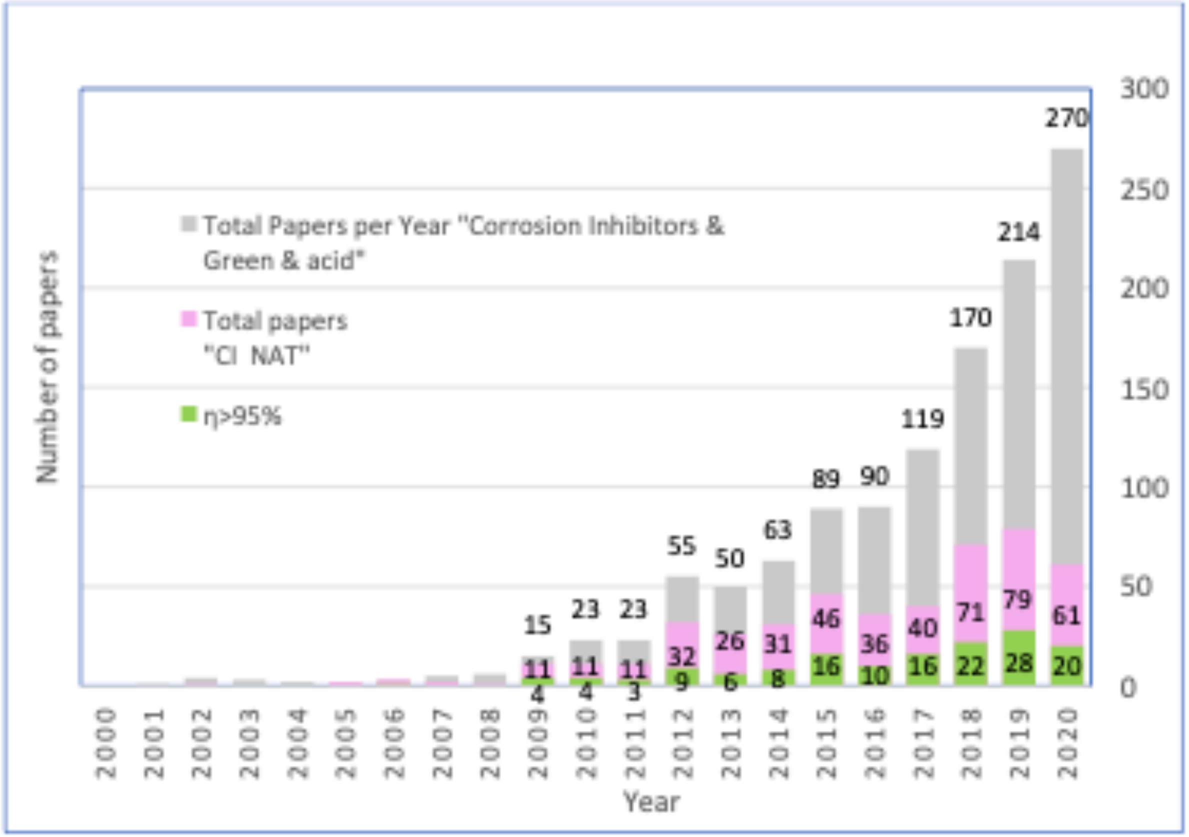
Green CI: Definition

More sustainable/environmentally friendly??



Literature Search: CI_{Nat}



- *Acidic Solution*
- *C-steel/Iron*

Ana Moreno (MSc thesis, 2021)

Other Commercialisation Barriers

- *Mass Production*
- *Production Cost/Profit*
- *Toxicity/Biodegradability*
- *Regulatory*
- *Life-cycle 'greenness'*

Ana Moreno (MSc thesis, 2021)

Summary

CI_{NAT}:

- *Not much progress/success to date*
- *Think beyond laboratory testing*
- *More systematic selection of candidates*

Take Home Mesages

- *Interface Characterisation*
- *Adsorption Thermodynamics*
- *Green CI's*

Acknowledgements

- *AkzoNobel & Nouryon for funding project through UoM collaboration*

- *M4DE CDT (EPSRC) for studentships for Kiran and Michael*