

LAB T4B. Corrosão e Protecção Catódica

Introdução à corrosão electroquímica e protecção de metais

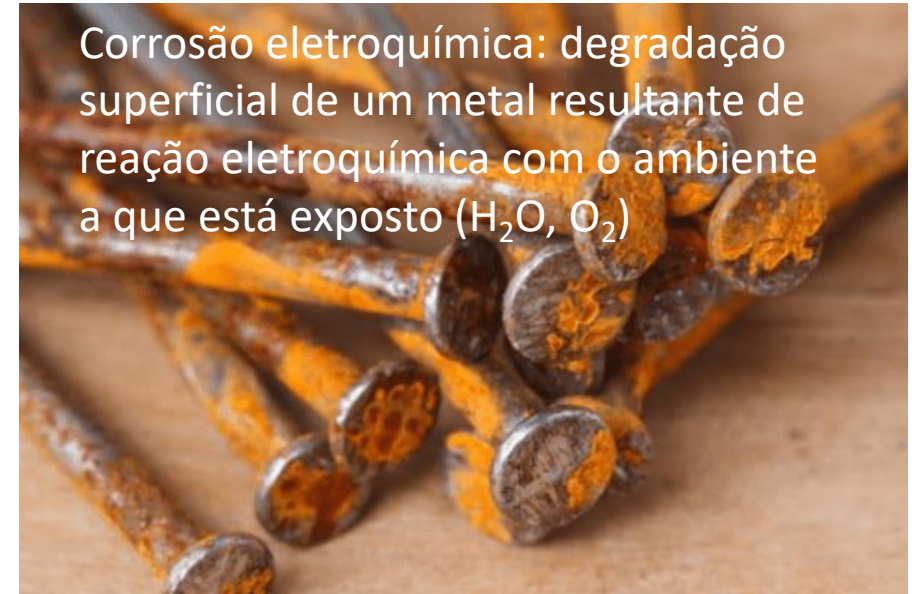
Identificação das zonas catódica e anódica no processo de corrosão de pregos de ferro

Ilustração de diversos tipos de corrosão:

- Pilha de composição
- Pilha de concentração
- Pilha de deformação

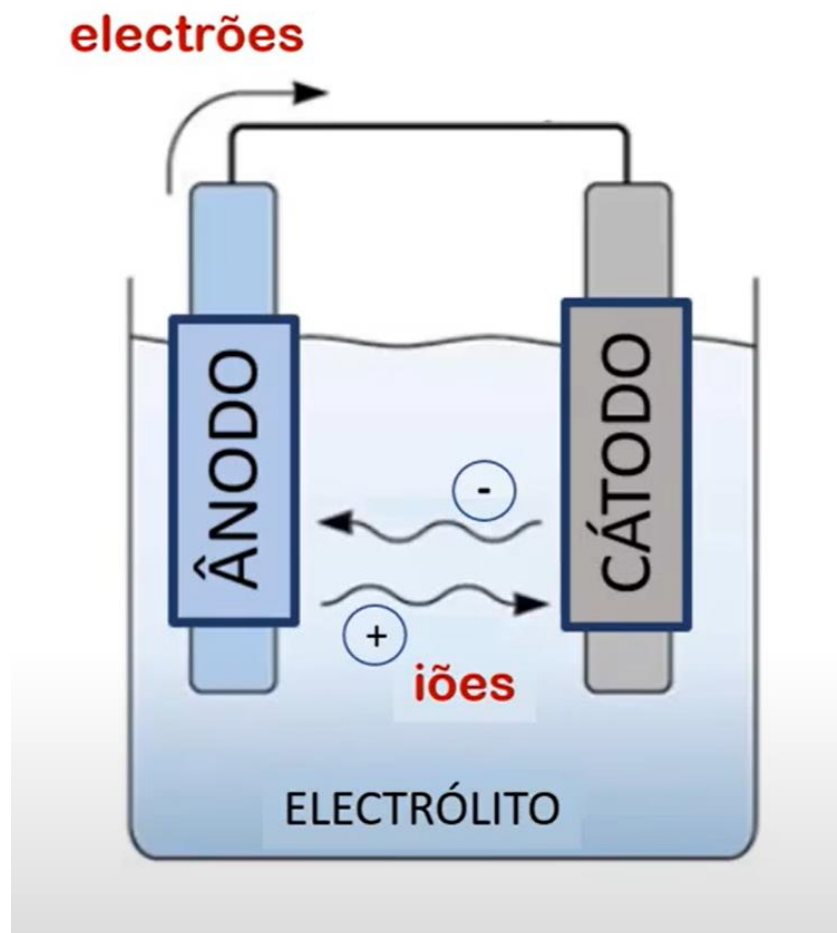
Ilustração dos principais processos de protecção catódica

- Por ânodo sacrificial
- Por potencial imposto



Célula eletroquímica

Oxidação
(perda de e^-)
 \uparrow nº ox



Redução
(ganho de e^-)
 \downarrow nº ox

Termodinâmica da Corrosão:

Para uma reação de eletrodo:

$$\Delta G = -nFE$$

E , potencial de eletrodo (referido ao $E^\circ(\text{H}^+/\text{H}_2) = 0 \text{ V}$)

n , número de moles de electrões transferidos

F , constante de Faraday (96485 C mol^{-1})

$$E = E^0 - \frac{RT}{nF} \ln Q = E^0 - \frac{0,0592}{n} \log Q$$

Para reação global:

$$\Delta G = -nF\Delta E \quad \text{Corrosão espontânea se } \Delta G < 0, \text{ i.e. } \Delta E > 0$$

$$\Delta E = E_{\text{cátodo}} - E_{\text{ânodo}}$$

Série Eletroquímica

$E^\circ(\text{M}^{n+}/\text{M}^0)$ [] = 1 M
P = 1 bar

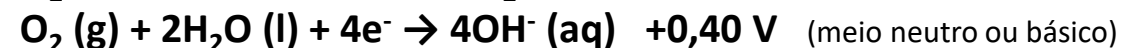
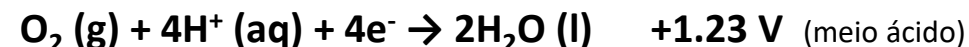
↑ tendência
a oxidar-se



Potenciais de oxidação (E°_{ox}), em volt		Potenciais de redução (E°_{red}), em volt
+ 3,04	$\text{Li}^+ + 1\text{e} \rightleftharpoons \text{Li}^\circ$	-3,04
+ 2,87	$\text{Ca}^{2+} + 2\text{e} \rightleftharpoons \text{Ca}^\circ$	-2,87
+ 2,71	$\text{Na}^+ + 1\text{e} \rightleftharpoons \text{Na}^\circ$	-2,71
+ 2,36	$\text{Mg}^{2+} + 2\text{e} \rightleftharpoons \text{Mg}^\circ$	-2,36
+ 1,66	$\text{Al}^{3+} + 3\text{e} \rightleftharpoons \text{Al}^\circ$	-1,66
+ 0,76	$\text{Zn}^{2+} + 2\text{e} \rightleftharpoons \text{Zn}^\circ$	-0,76
+ 0,44	$\text{Fe}^{2+} + 2\text{e} \rightleftharpoons \text{Fe}^\circ$	-0,44
+ 0,28	$\text{Co}^{2+} + 2\text{e} \rightleftharpoons \text{Co}^\circ$	-0,28
+ 0,25	$\text{Ni}^{2+} + 2\text{e} \rightleftharpoons \text{Ni}^\circ$	-0,25
+ 0,14	$\text{Sn}^{2+} + 2\text{e} \rightleftharpoons \text{Sn}^\circ$	-0,14
+ 0,13	$\text{Pb}^{2+} + 2\text{e} \rightleftharpoons \text{Pb}^\circ$	-0,13
0,00	$2\text{H}^+ + 2\text{e} \rightleftharpoons \text{H}_2$	0,00
-0,34	$\text{Cu}^{2+} + 2\text{e} \rightleftharpoons \text{Cu}^\circ$	+0,34
-0,80	$\text{Ag}^+ + \text{e} \rightleftharpoons \text{Ag}^\circ$	+0,80
-0,85	$\text{Hg}^{2+} + 2\text{e} \rightleftharpoons \text{Hg}^\circ$	+0,85
-1,07	$\text{Br}_2 + 2\text{e} \rightleftharpoons 2\text{Br}^-$	+1,07
-1,36	$\text{Cl}_2 + 2\text{e} \rightleftharpoons 2\text{Cl}^-$	+1,36
-1,50	$\text{Au}^{3+} + 3\text{e} \rightleftharpoons \text{Au}^\circ$	+1,50
-2,87	$\text{F}_2 + 2\text{e} \rightleftharpoons 2\text{F}^-$	+2,87



↑ tendência
a reduzir-se

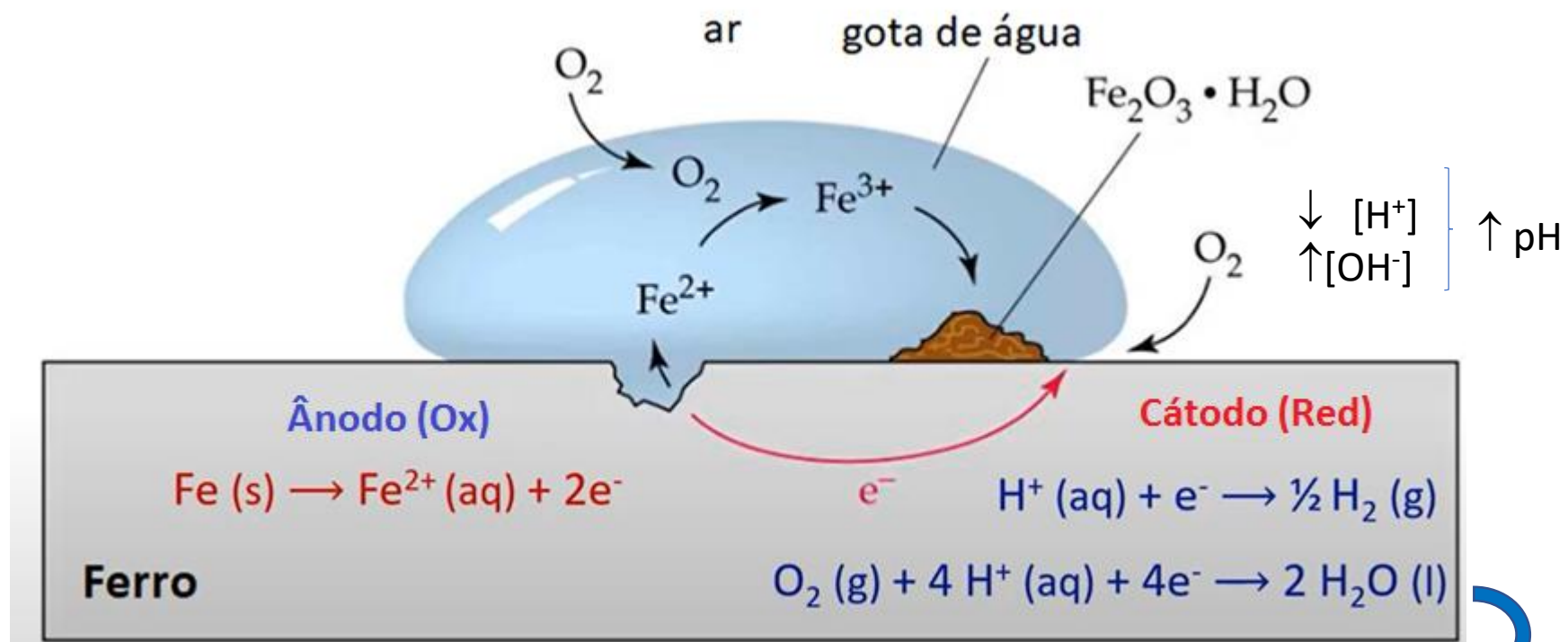


I. Pilha de composição (ex: peça de ferro em contacto com humidade, pH ácido)

$$E^0(\text{Fe}^{2+}/\text{Fe}^0) = -0.44 \text{ V}$$

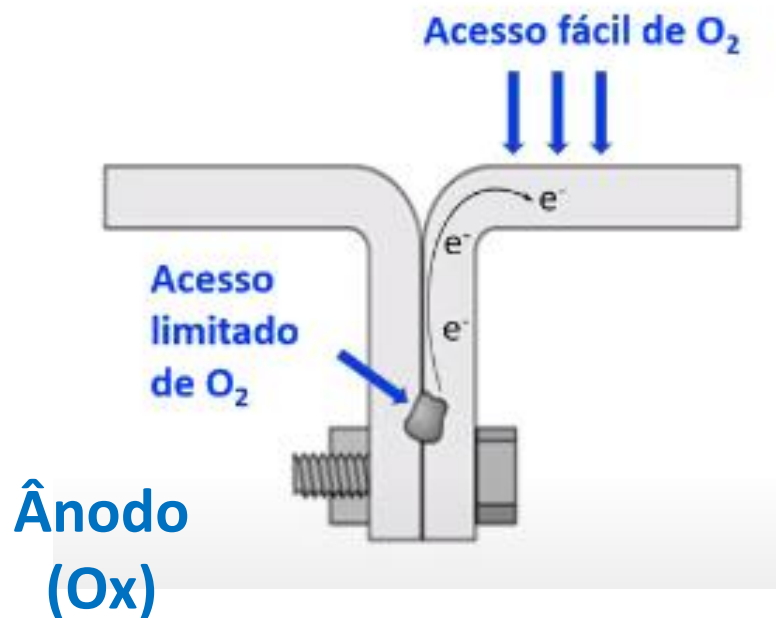
$$E^0(\text{H}^+/\text{H}_2) = 0.00 \text{ V}$$

$$E^0(\text{O}_2, \text{H}^+/\text{H}_2\text{O}) = 1.23 \text{ V}$$

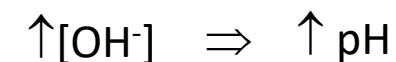
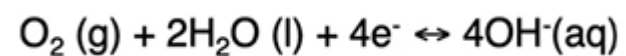


Processo catódico mais importante se existir oxigénio dissolvido

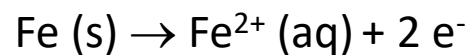
II. Pilha de concentração (corrosão por arejamento diferencial)



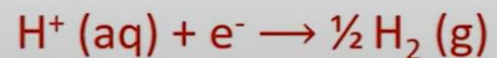
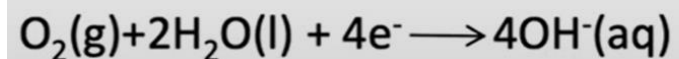
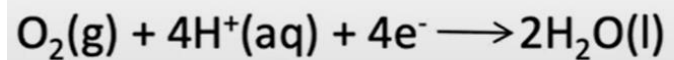
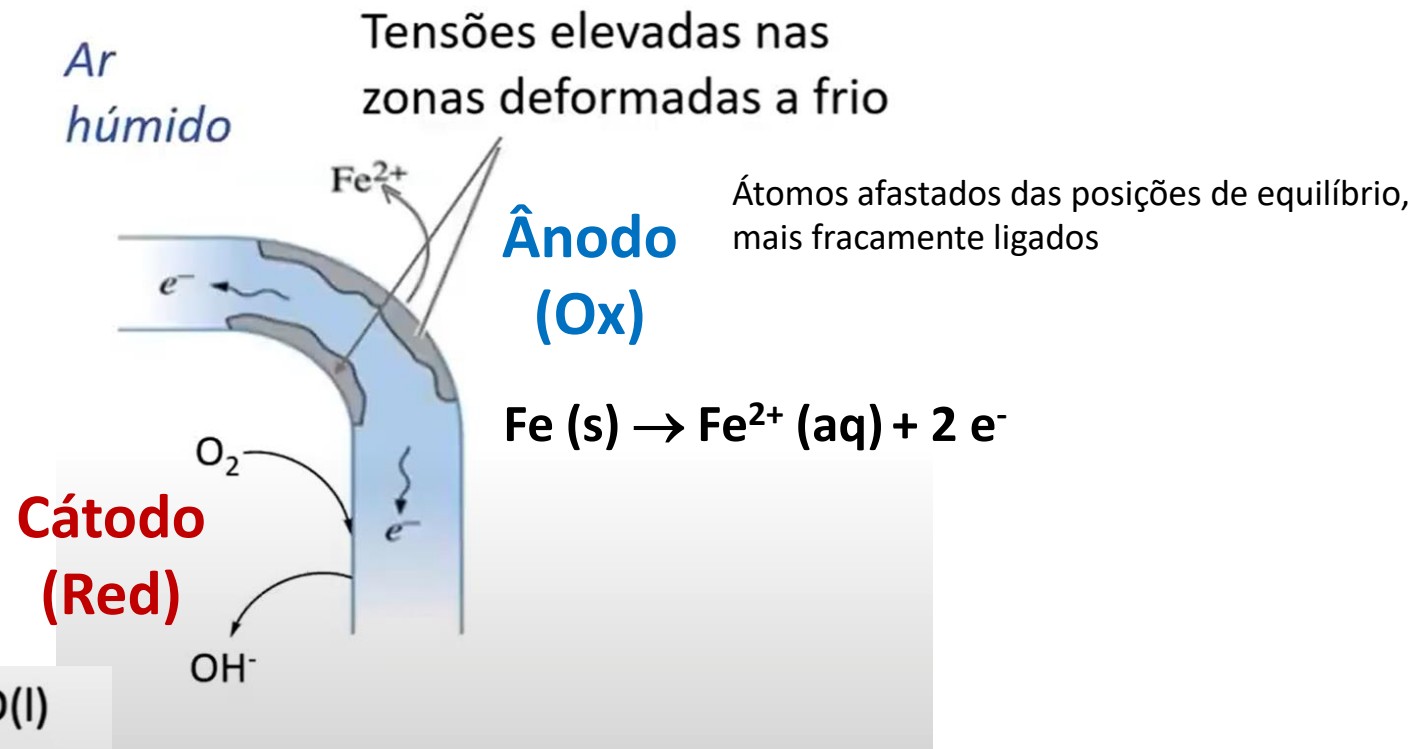
**Cátodo
(Red)**



$$E_{\text{O}_2/\text{OH}^-} = E_{\text{O}_2/\text{OH}^-}^0 - \frac{0.059}{4} \log \frac{[\text{OH}^-]^4}{p_{\text{O}_2}}$$



III. Pilha de deformação (peça metálica deformada a frio)



Proteção catódica: ânodo de sacrifício

Reacção de Redução	E^0 (V)
$\text{Li}^+ + \text{e}^- \leftrightarrow \text{Li}$	- 3.045
$\text{Mg}^{2+} + 2 \text{e}^- \leftrightarrow \text{Mg}$	- 2.37
$\text{Zn}^{2+} + 2 \text{e}^- \leftrightarrow \text{Zn}$	- 0.763
$\text{Cr}^{3+} + 2 \text{e}^- \leftrightarrow \text{Cr}$	- 0.74
$\text{Fe}^{2+} + 2 \text{e}^- \leftrightarrow \text{Fe}$	- 0.440
$\text{Cd}^{2+} + 2 \text{e}^- \leftrightarrow \text{Cd}$	- 0.403
$\text{Ni}^{2+} + 2 \text{e}^- \leftrightarrow \text{Ni}$	- 0.250

↑ tendência a oxidar-se

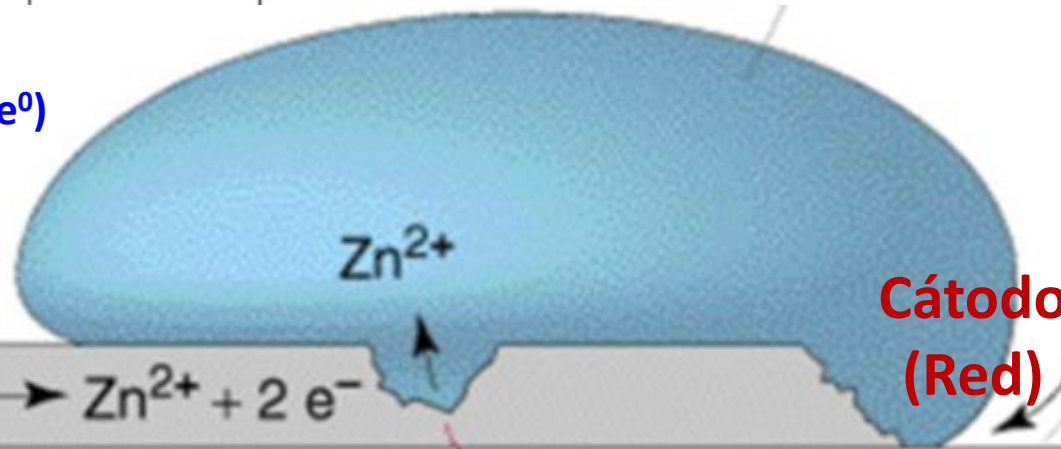


Gota de água



$$E^0(\text{Zn}^{2+}/\text{Zn}^0) < E^0(\text{Fe}^{2+}/\text{Fe}^0)$$

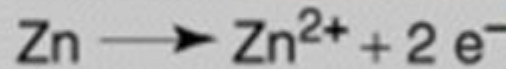
**Ânodo
(Ox)**



**Cátodo
(Red)**

fissura na camada de zinco

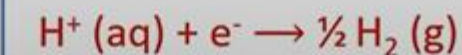
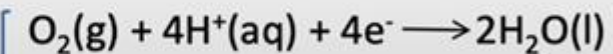
Zinco



Zinco

À superfície do ferro ocorre a redução do O_2 dissolvido e do H^+ da água.

Ferro

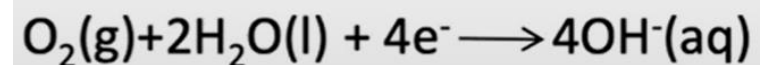
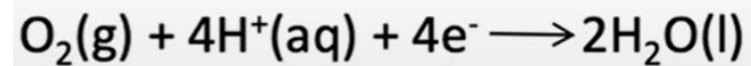
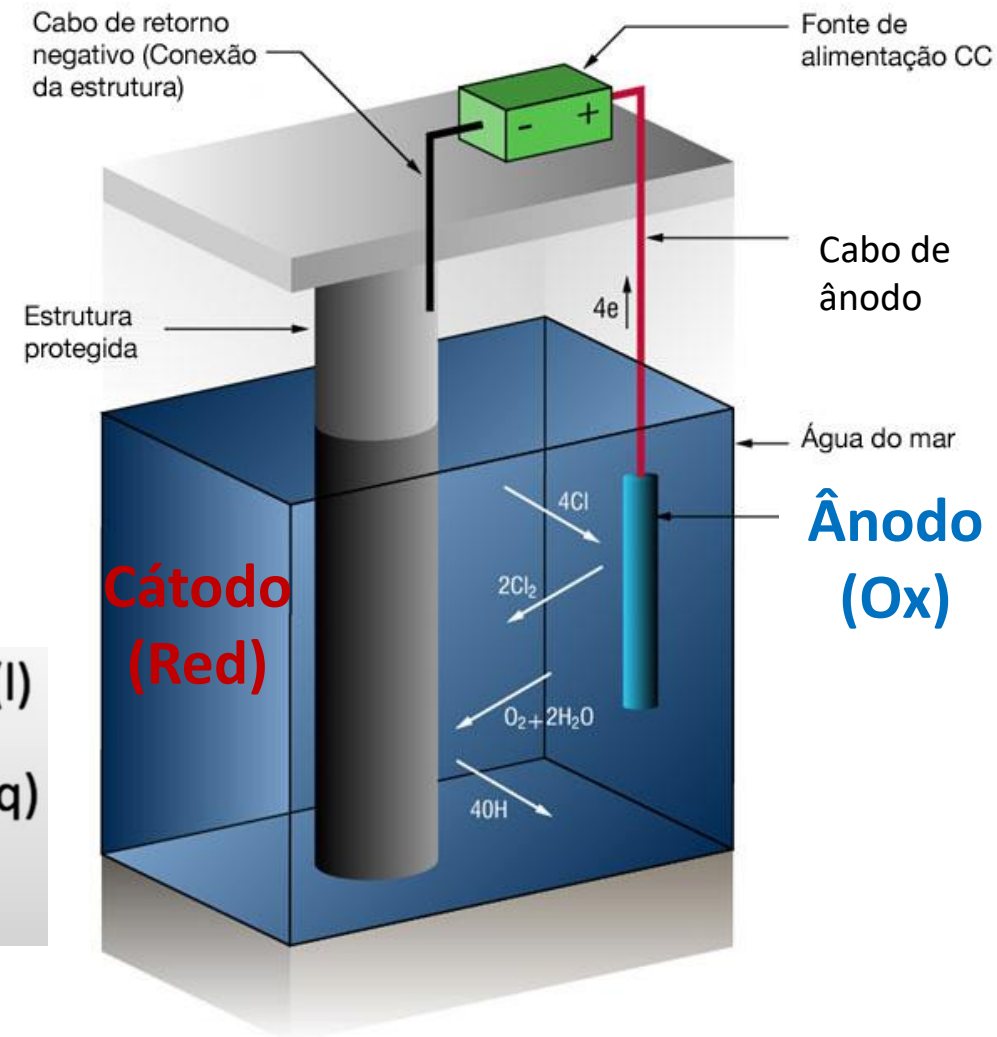


Fe não se reduz

E^0 + altos
↑ tendência a reduzir-se

Proteção catódica: potencial imposto

(Imposição de sobretensão exterior: metal a proteger ligado a terminal negativo de pilha exterior)



Trabalho experimental

1. Preparação do eletrólito (gel)

200 mL água



1.5 g agar-agar

(gelificante)



2.0 g NaCl

(eletrólito)



pH > 9.8

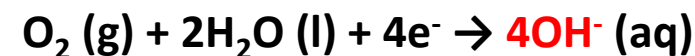
pH < 8.2

HCl diluído

(descoloração
fenolftaleína)

2 mL fenolftaleína

(indicador ácido-base)



2 mL solução de $\text{K}_3[\text{Fe}(\text{CN})_6]$

(indicador Fe^{2+} e Zn^{2+})



2. Preparação dos pregos e placa de zinco

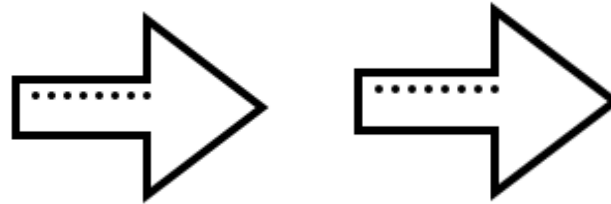
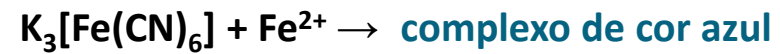
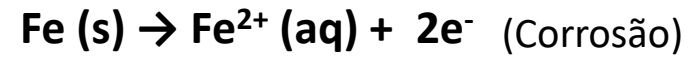


BANHO DE GELO

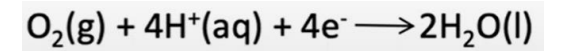


Polir com lixa, lavar e secar

Experiência 1. Pilha de deformação

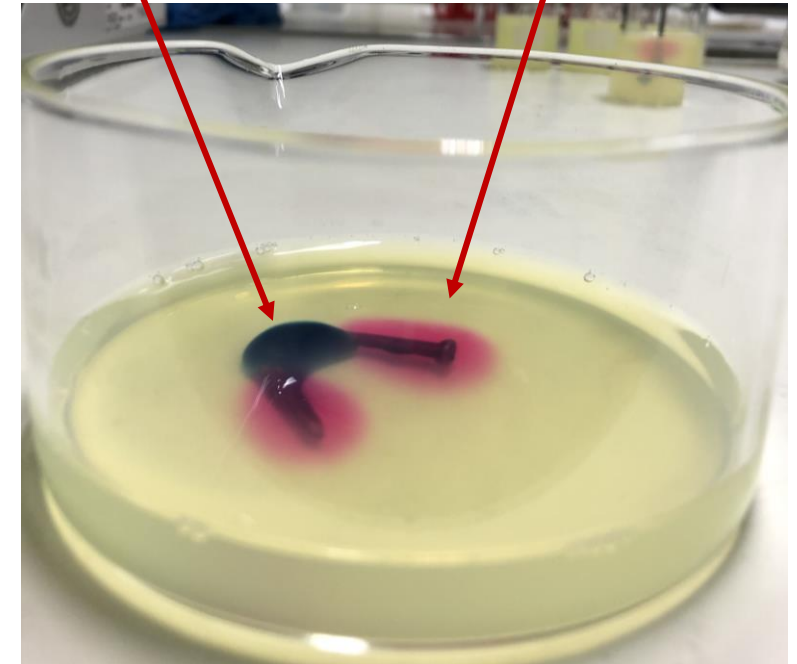


ARREFECIMENTO

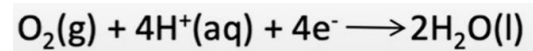
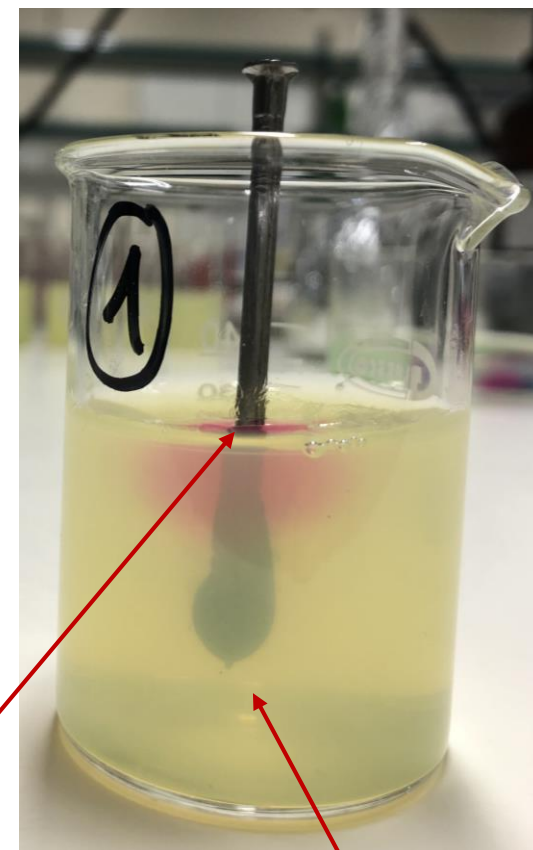
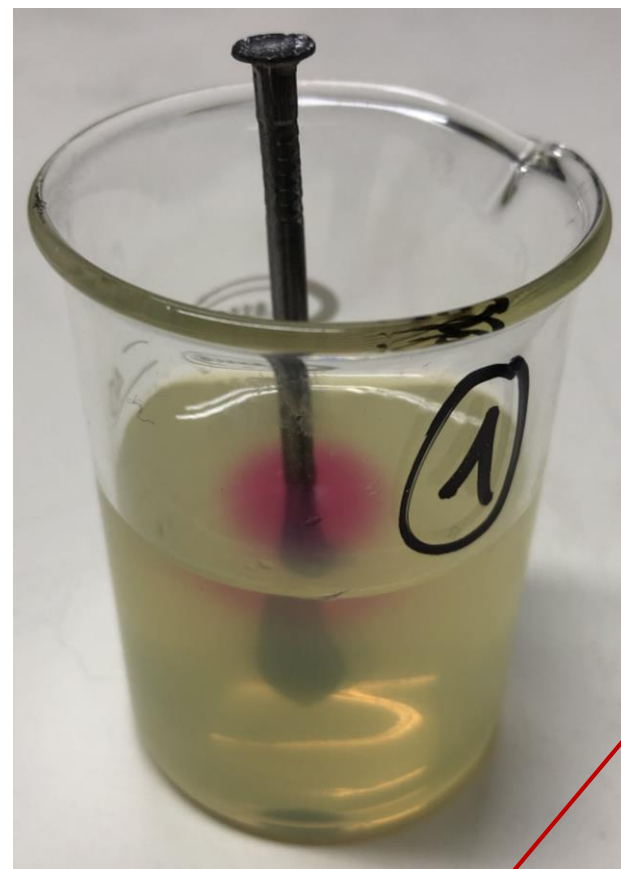
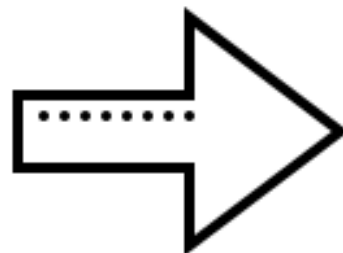
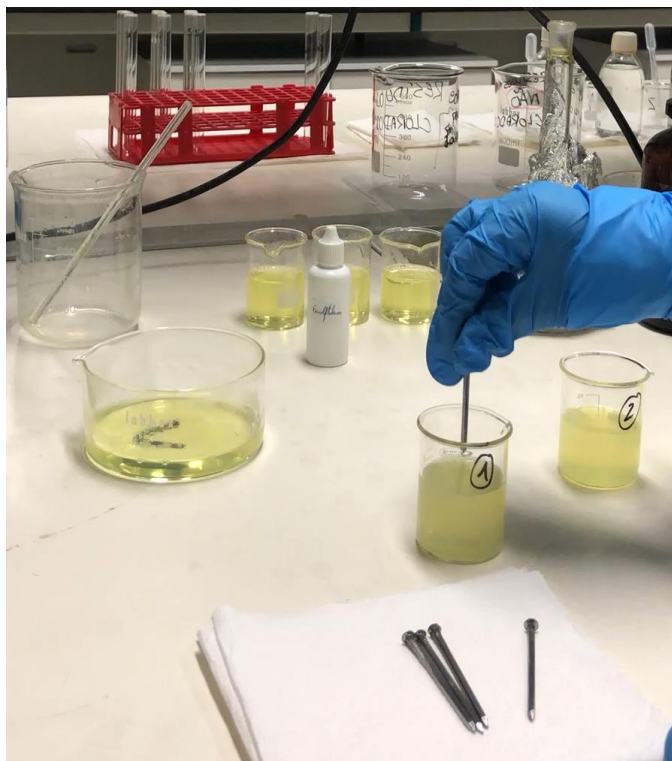


Ânodo
(Ox)

Cátodo
(Red)

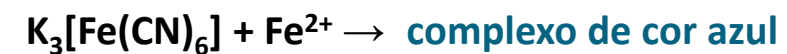
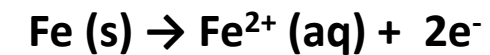


Experiência 2. Pilha de concentração

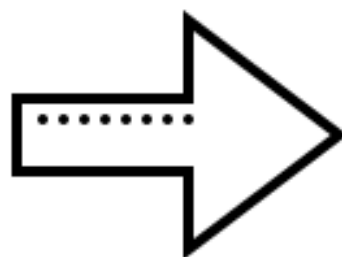


**Cátodo
(Red)**

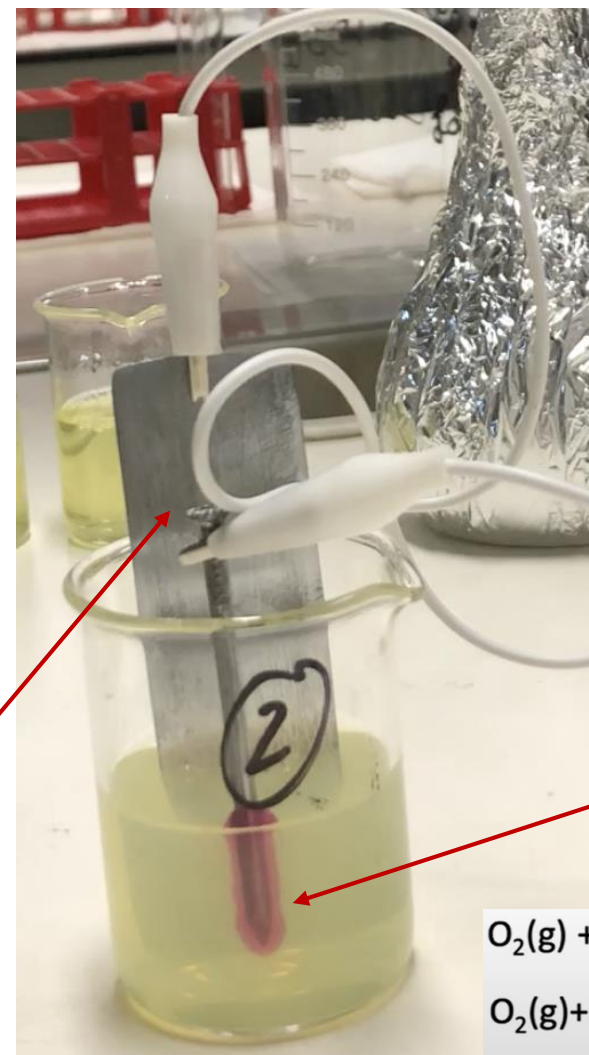
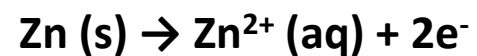
**Ânodo
(Ox)**



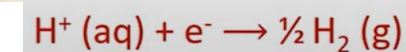
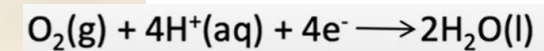
Experiência 3. Proteção por ânodo sacrificial



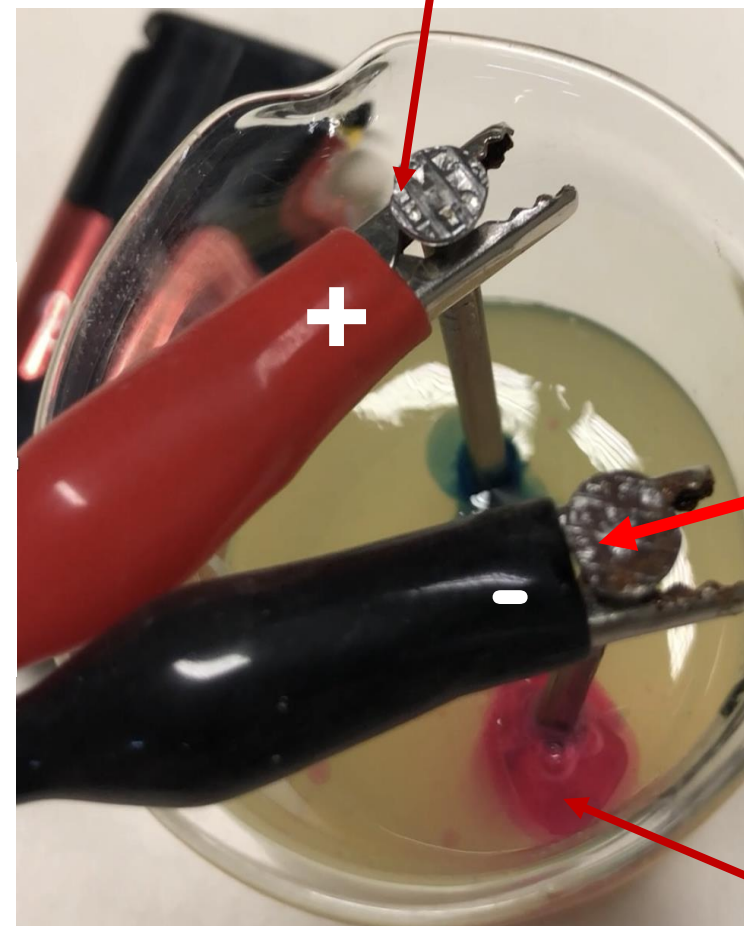
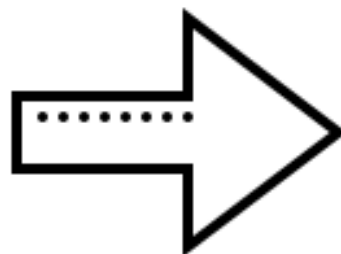
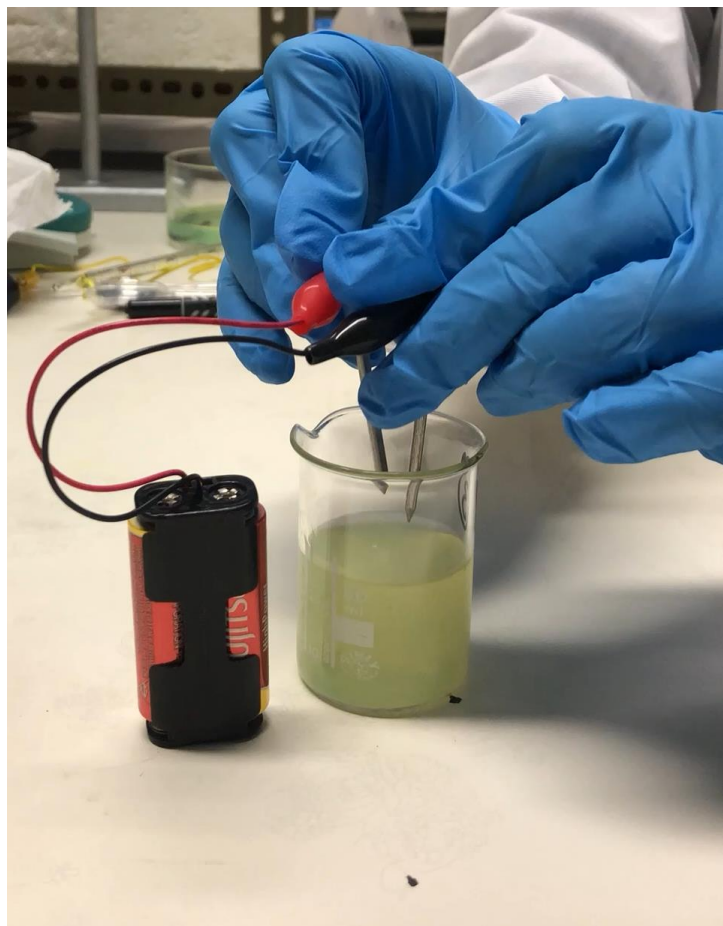
Ânodo
(Ox)



Cátodo
(Red)

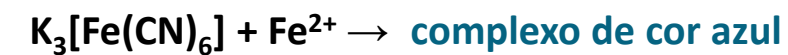
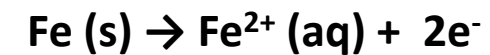


Experiência 4. Proteção por potencial imposto

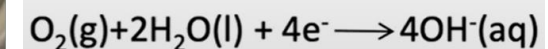
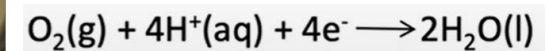


(Corrosão)

Ânodo
(Ox)



Cátodo
(Red)



Bolhas gasosas (H_2)

Discussão dos resultados

- Explicar as funções dos diferentes componentes do gel (água, agar-agar, NaCl, fenolftaleína, $K_3[Fe(CN)_6]$, HCl)
- Explicar porque foi preciso polir os pregos e a barra do zinco
- Explicar a diferença entre os pregos dobrado e não dobrados
- Identificar ânodo e cátodo em cada pilha
- Escrever as reações anódicas e catódicas
- Explicar as cores junto aos pregos
- Explicar a formação do gás na última pilha

