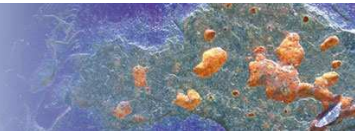


Influence of the sodium chloride concentration and pH of the used artificial saliva on the resistance of dental nickel–base and cobalt–base alloys against corrosion



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Introduction



Fixed partial dentures may be sollicitated...

mechanically (mastication) and chemically (corrosion)



Cosmetic ceramic:
preserved from stresses
thank to the metallic part

Metallic framework:
the emerging part is subjected
to corrosion by some species present in saliva

Dental alloys involved in fixed partial dentures

High Noble (based on Au, Pt...), Noble alloys (e.g. Pd-based),
and also:

Predominantly Base alloys (Ni-based, Co-based): cheaper
alternative alloys

PB alloys: mechanically resistant with a corrosion resistance
generally based on chromium

Compositions of some PB alloys: Ni–based

about 60–65 wt.% Ni with 20–25 wt.%Cr and minor elements

Alloys (wt.%)	Ni	Cr	Mo	Si	Mn	Al	C	Fe	Cu
4all	61.4	25.7	11.0	1.5	<1.0	<1.0	<1.0	-	-
Wiron	66.0	19.0	5.5	3.5	-	-	-	5.0	-
Remanium CSe	61.0	26.0	11.0	1.5	-	-	-	1.2	-
Isotop	67.0	26.0	5.0	1.0	-	-	-	-	-

Compositions of some PB alloys: Co-based

about 60 wt.% Co with 25–30 wt.% Cr and minor elements

Alloys (wt.%)	Co	Cr	others
Colado CC	59.0	25.5	Mo, W, Ga, Si, Nb, Fe, B
dSIGN30	60.2	30.1	Mo, Si, Ga, Nb, B, Fe, Al, Si
Remanium star	60.5	28.0	W, Si
Remanium secura	58.0	30.0	Mo, W, Si, Ta

Cl⁻ concentration and pH in human saliva

about 60 wt.% Co with 25–30 wt.% Cr and minor elements

Food	chlorides	pH
Orange Juice	-	3.6 ^a
Coca Cola	-	2.5 ^b
Honey	-	4.1 ^a
Chewing gum	10% for some of them ^d	5.8 – 7.3 ^c
Saliva	0.1–0.6 g/L, and possibly much more (e.g. 30g/L after mastication of chewing gum) ^d	-

a: Altun et al. *Pediatric Dental Journal*, **25** 50-53, 2015.

b: Mikulewicz et al. *Journal of Trace Elements in Medicine and Biology*, **31** 74-77, 2015.

c: Pytko-Polonczyk et al. *J. Physiol. Pharmacol.* **68** 807-813, 2017

d: Neyraud et al. *Physiology & Behavior*, **79** 731-737, 2003.

Questions which may arise:

Is there a Cr threshold to respect in order to allow PB alloys well resisting corrosion in particularly high aggressiveness of the buccal milieu (e.g. acidic, high chloride concentration)?

If such Cr limit exists, is there a dependence on the base element of the PB alloy?

How obtaining first answers?

Model alloys with very simple chemical compositions to avoid the possible influences of minor elements

Simplified artificial solutions with different high chloride concentrations and more or less acidified

THIS WORK

(carried out during the Master 1 trainee periods of E. Tran and E. Teriokhina, with the technical help of M. Lierre)

**Binary Ni–based and Co–based cast alloys with varying Cr:
10, 15, 20, 25 and 30 wt.% Cr**

**Artificial salivas very simple and containing various high Cl⁻
concentrations and with two acidic pH values:**

[NaCl] = 5, 10 and 20 g/L – pH=5 and pH=2.5 – 37°C

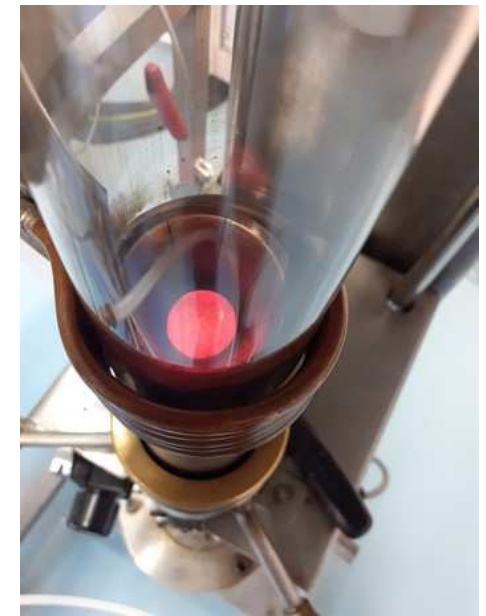
Two types of experiments:

Electrochemical measurements – Long time immersion

Results

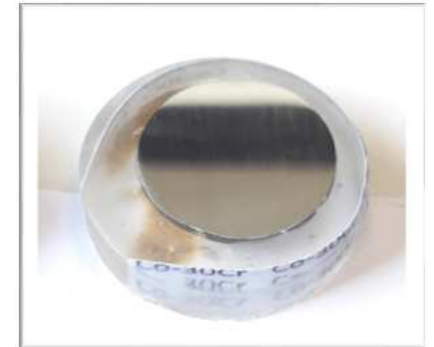
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The obtained alloys



Elaboration

Casting by high frequency induction melting in 500 mbars Ar



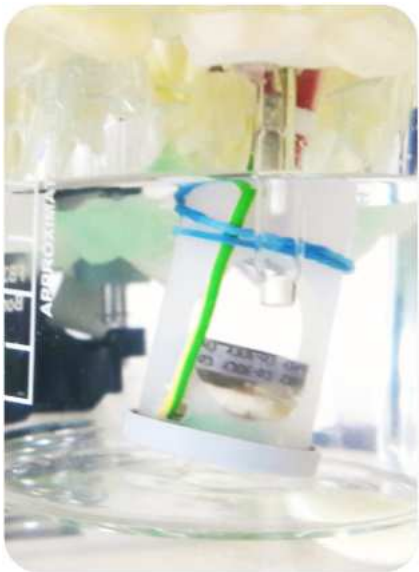
Alliage	Ni-10Cr	Ni-15Cr	Ni-20Cr	Ni-25Cr	Ni-30Cr
%mCr	10	15	20	25	30
%mCo	90	85	80	75	70

Alliage	Co-10Cr	Co-15Cr	Co-20Cr	Co-25Cr	Co-30Cr
%mCr	10	15	20	25	30
%mCo	90	85	80	75	70

Results

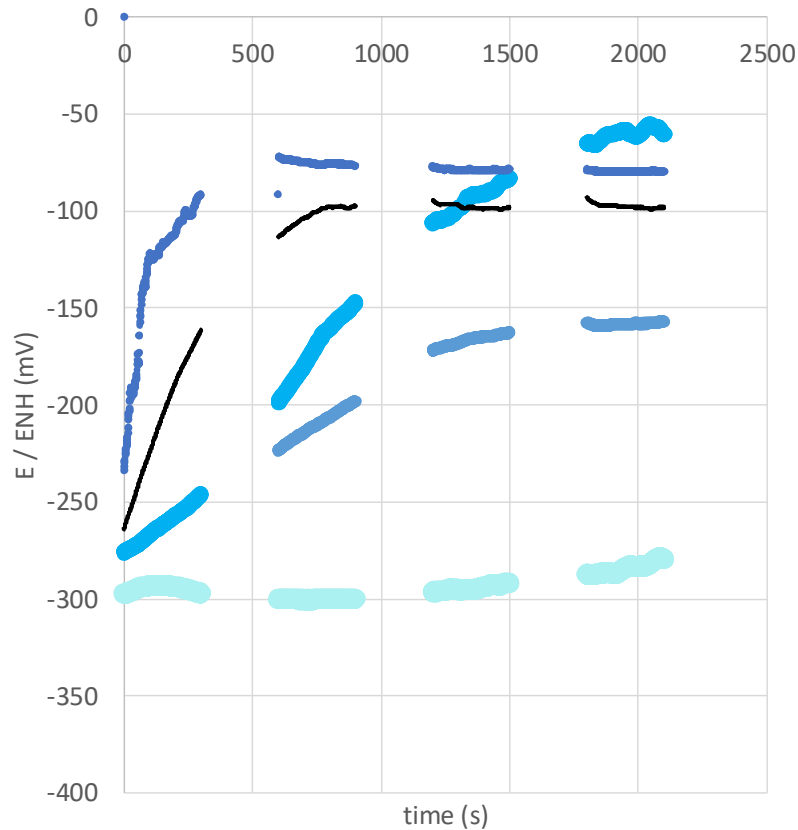


Electrochemical experiments

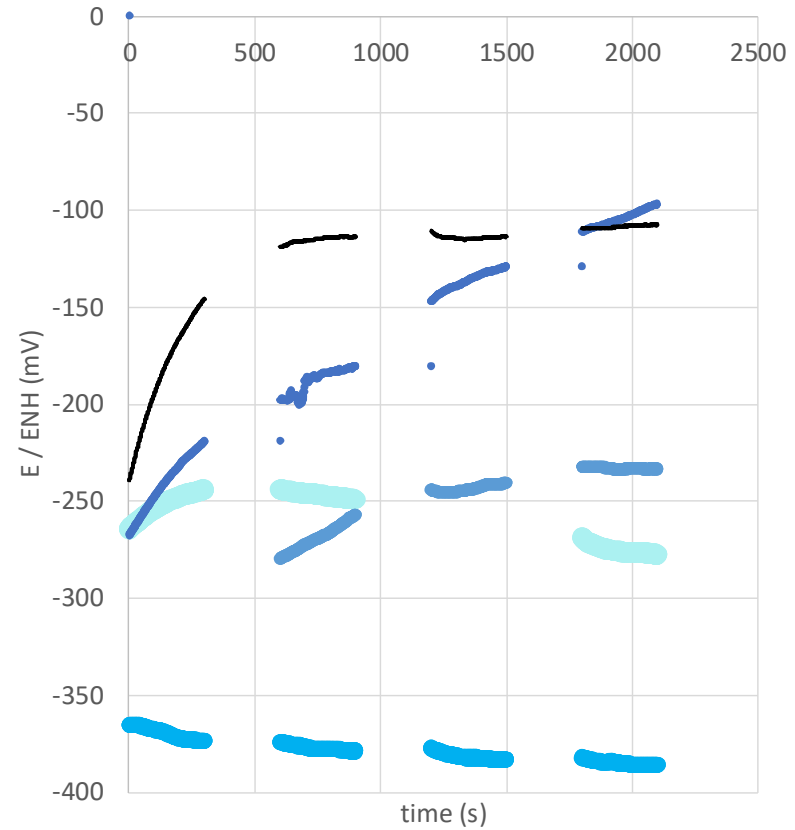


Electrochemical runs: free potentials

Co-xCr alloys: * (global) tendency to increase with Cr
* no clear dependence on [NaCl]



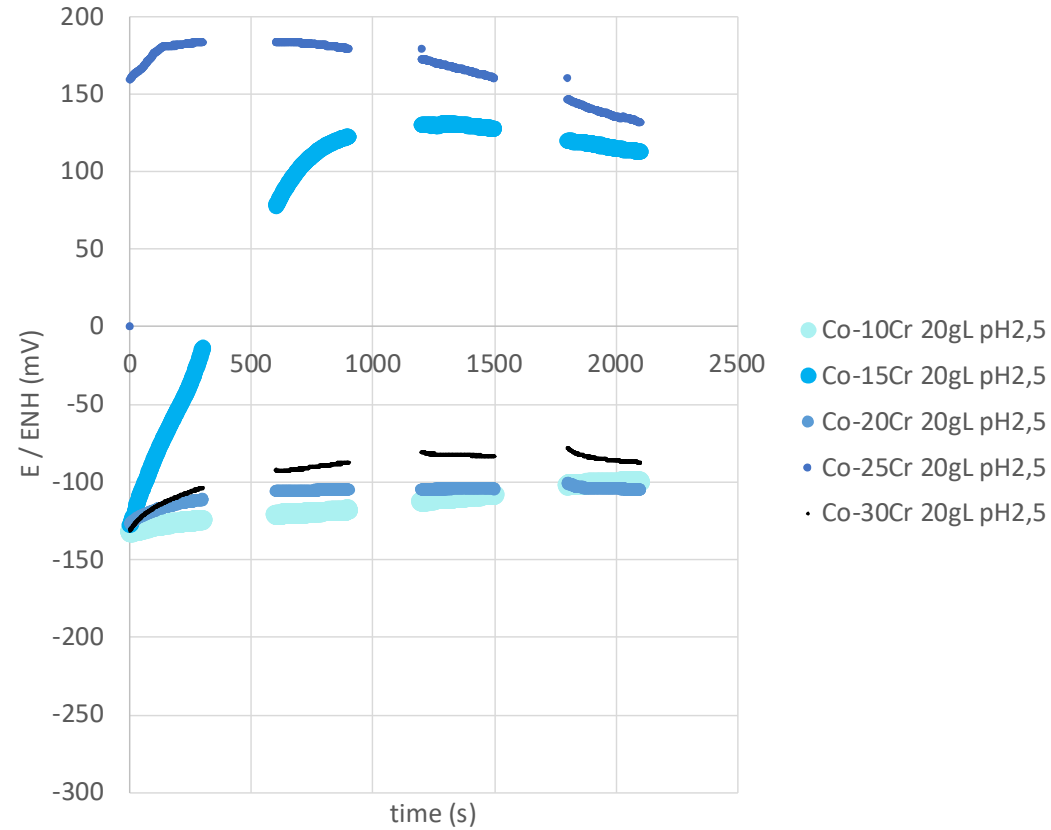
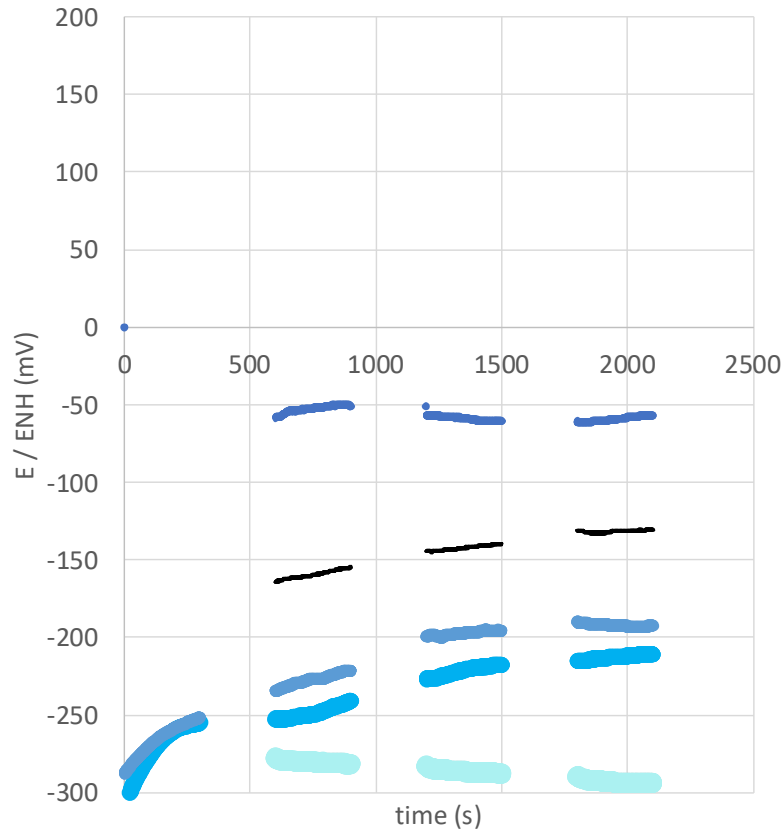
- Co-10Cr 5g/L pH5
- Co-15Cr 5g/L pH5
- Co-20Cr 5g/L pH5
- Co-25Cr 5g/L pH5
- Co-30Cr 5g/L pH5



- Co-10Cr 10g/L pH5
- Co-15Cr 10g/L pH5
- Co-20Cr 10g/L pH5
- Co-25Cr 10g/L pH5
- Co-30Cr 10g/L pH5

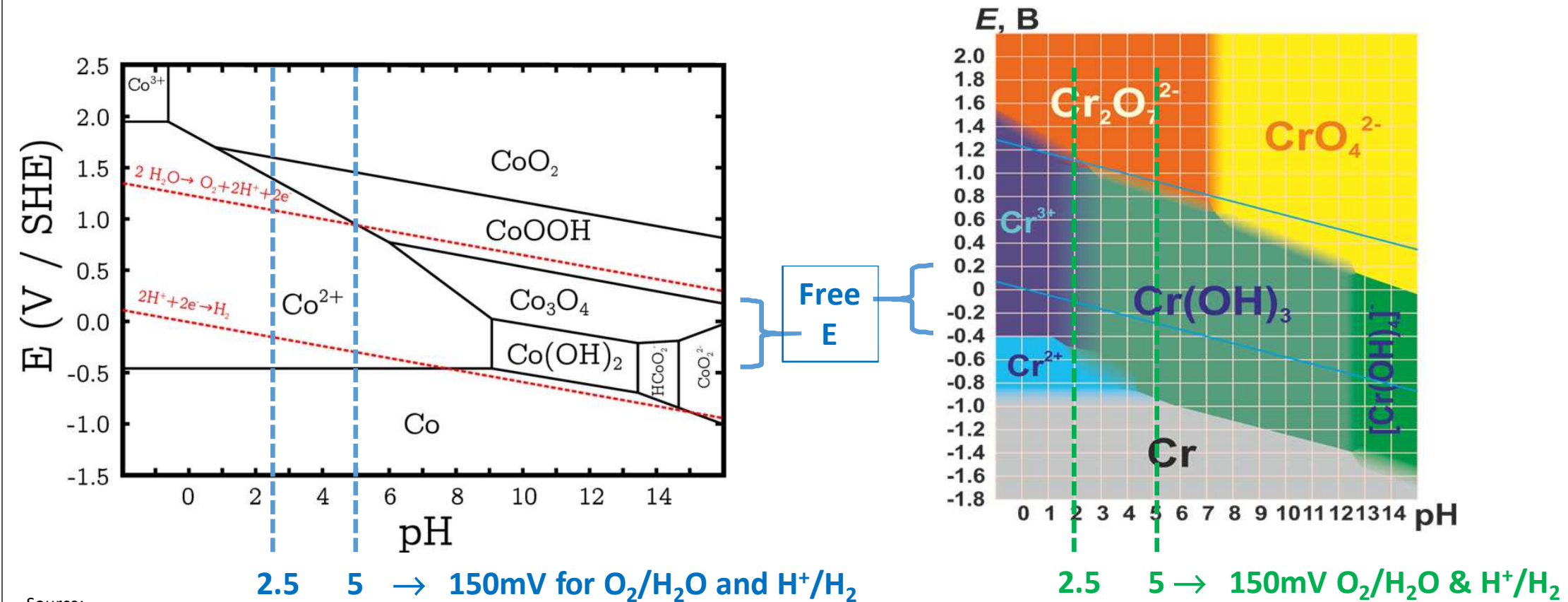
Electrochemical runs: free potentials

Co-xCr alloys: for 20g/L [NaCl] obviously higher for lower pH



Electrochemical runs: free potentials

Co-xCr alloys: corrosion domain of Co and passivation for Cr



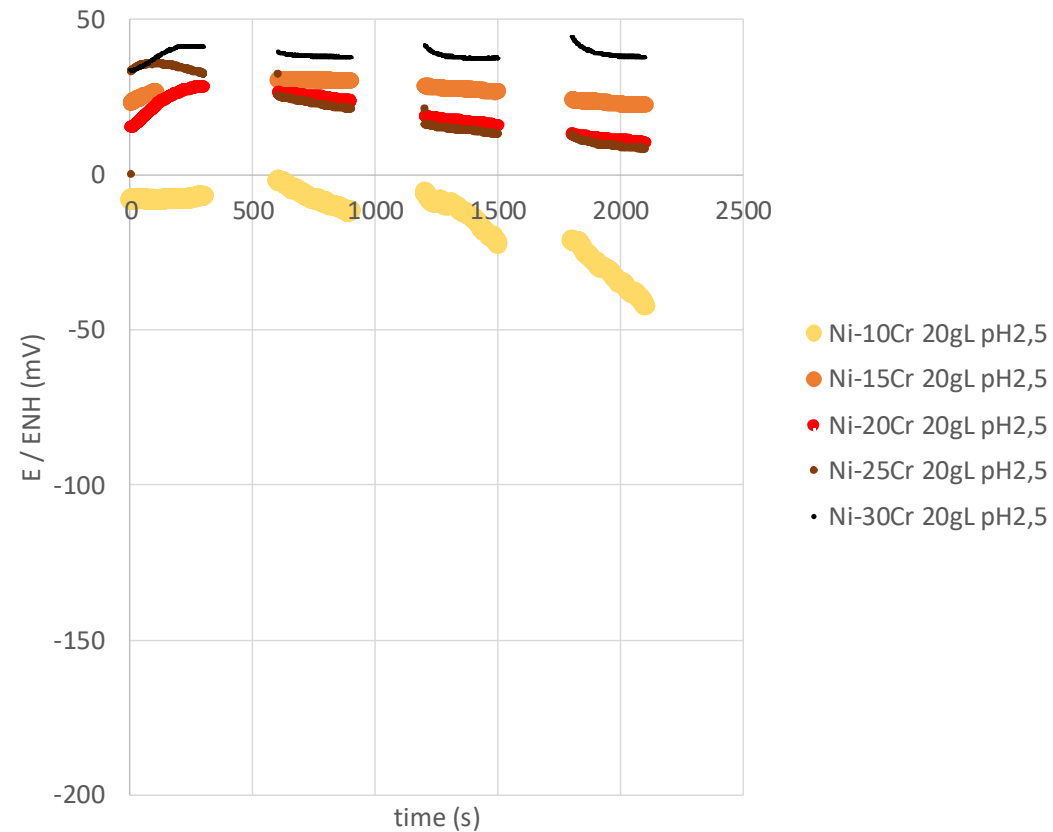
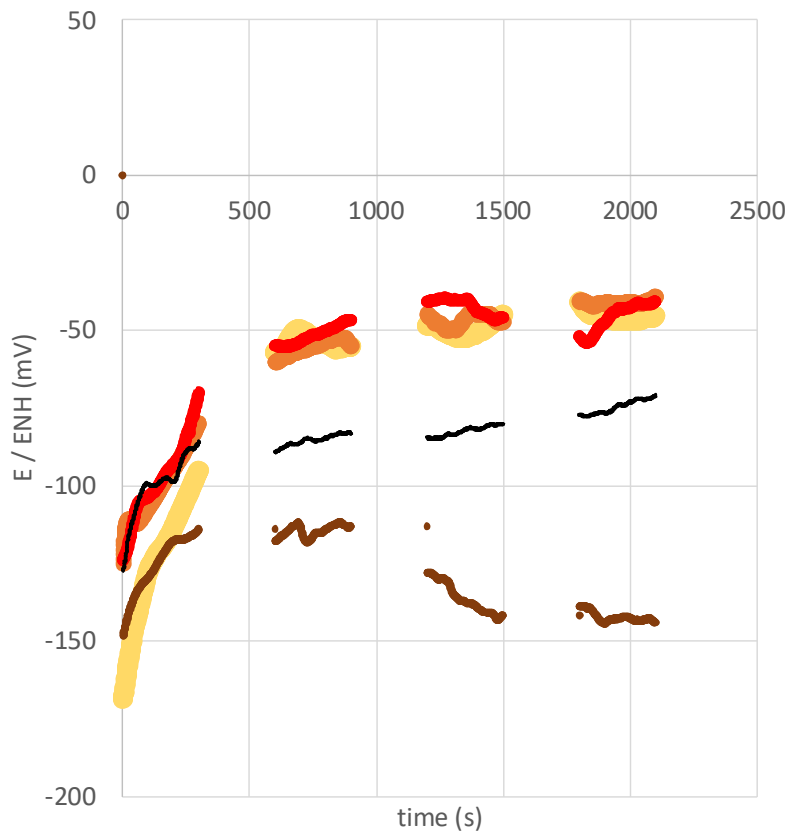
Source:

https://www.researchgate.net/publication/336371307_Etude_par_DFT_de_photocatalyseurs_pour_des_applications_en_photodissociation_de_l'eau/figures?lo=1

Source: <https://commons.wikimedia.org/wiki/File:Pourbaix-cr.png>

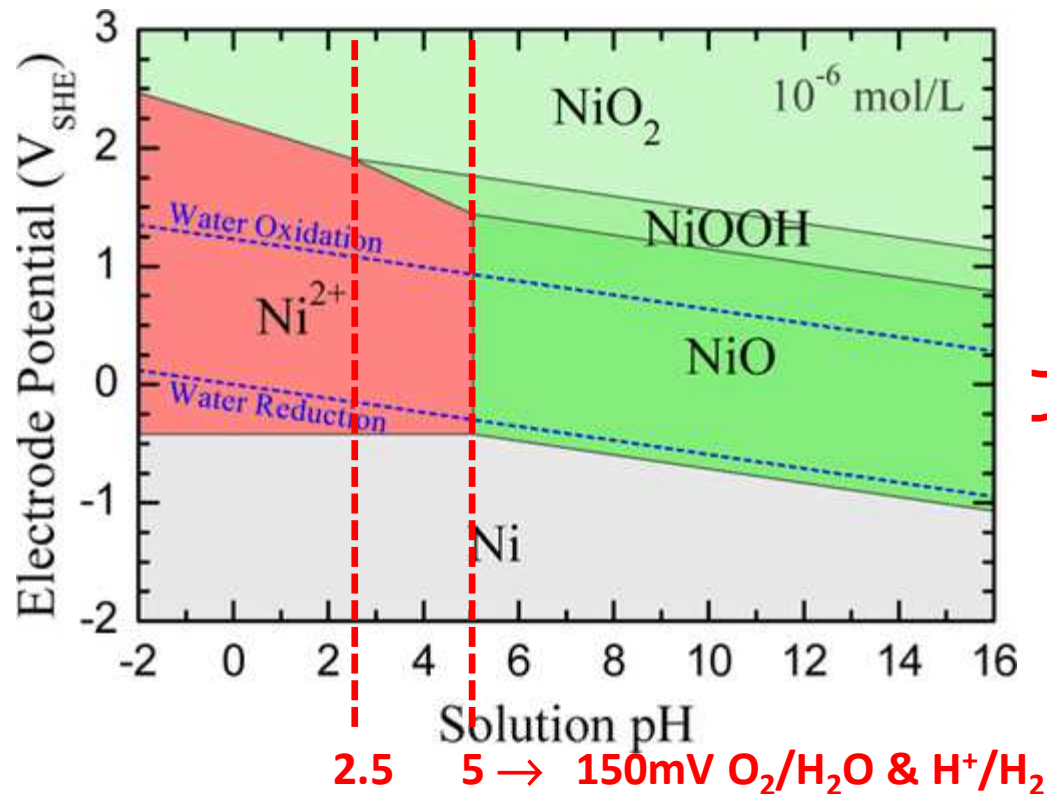
Electrochemical runs: free potentials

Ni-xCr alloys: for 20g/L [NaCl] obviously higher for lower pH

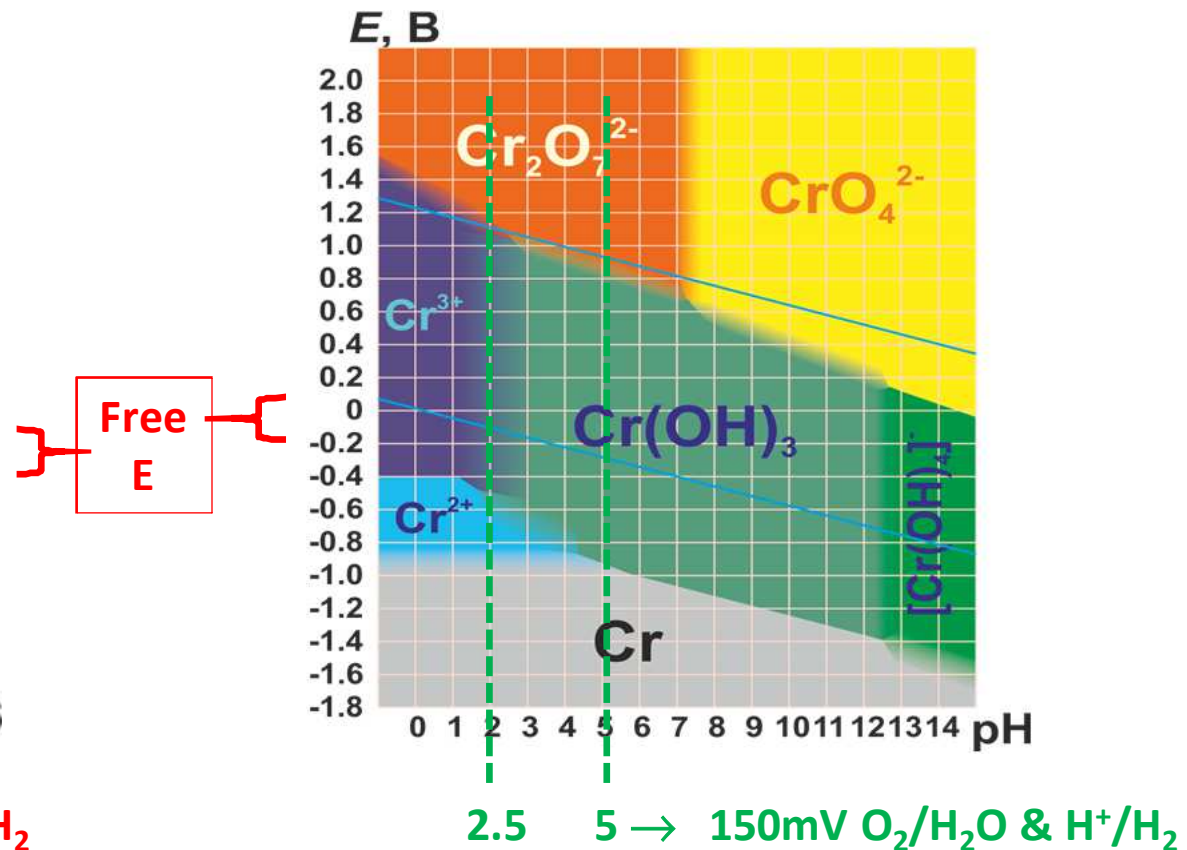


Electrochemical runs: free potentials

Ni-xCr alloys: corrosion domain of Ni and passivation domain for Cr (and for Ni too for pH=5?)



Source: <https://pubs.acs.org/doi/pdf/10.1021/acs.jpcc.7b02771>



Source: <https://commons.wikimedia.org/wiki/File:Pourbaix-cr.png>

Electrochemical runs: polarisation resistances

Co or Ni-xCr alloys:

corrosion resistance better for high Cr, low [NaCl] and Ni vs. Co

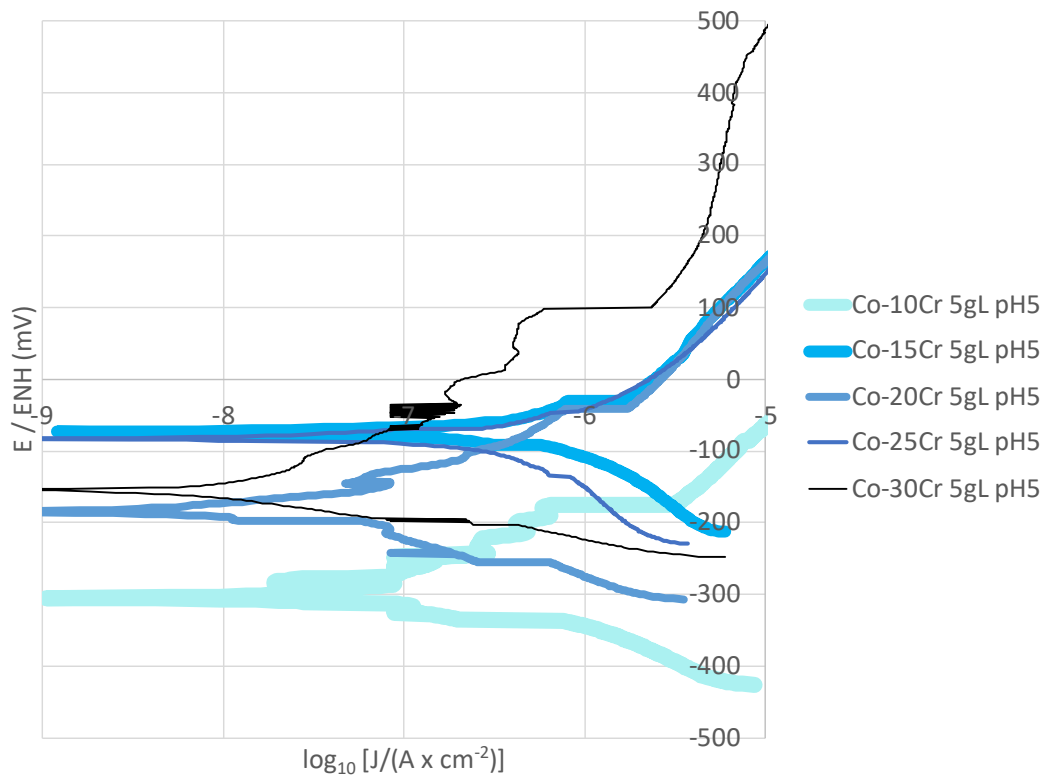
Co-xCr	pH5	pH5	pH5	pH2,5
Rp3 (kOhms cm ²)	5g/L NaCl	10g/L NaCl	20g/L NaCl	20g/L NaCl
x = 10	200	130	36	6
x = 20	610	140	800	470
x = 30	890	940	1110	370

Ni-xCr	pH5	pH2.5
Rp3 (kOhms cm ²)	20g/L NaCl	20g/L NaCl
x = 10	530	1
x = 20	320	210
x = 30	900	1010

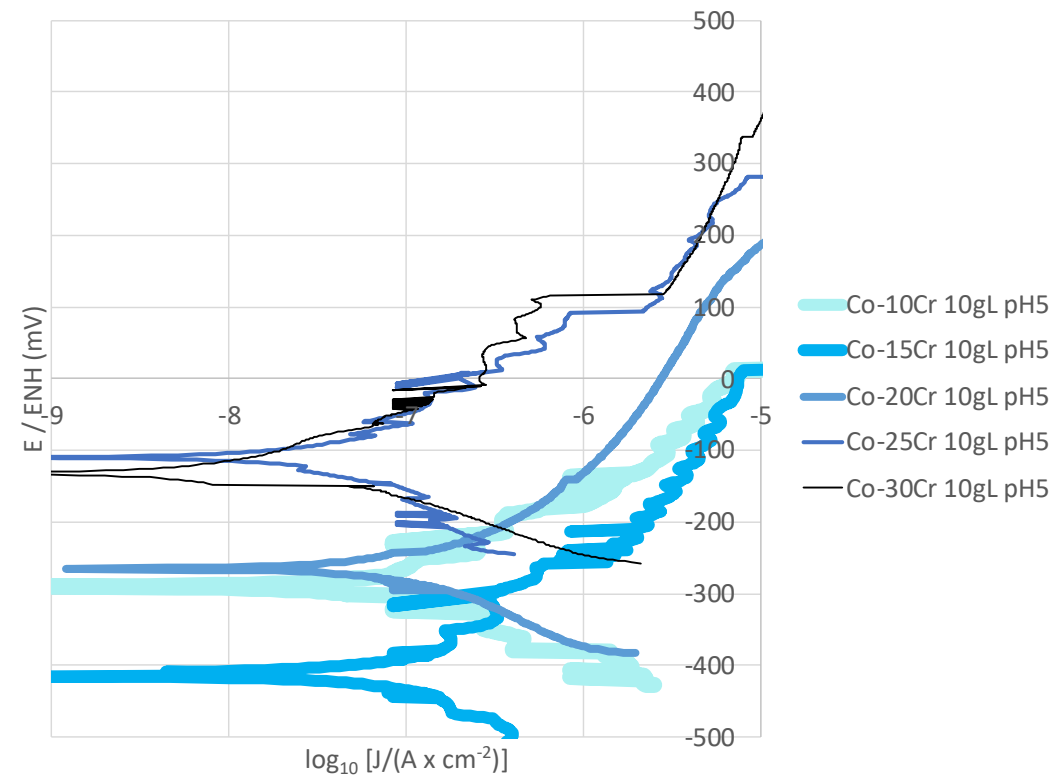
Electrochemical runs: Tafel curves

Co-xCr alloys: $J_{\text{corr}} \downarrow$ when Cr content \uparrow ; no real effect of [NaCl]

Co-xCr 5gL pH5 37°C



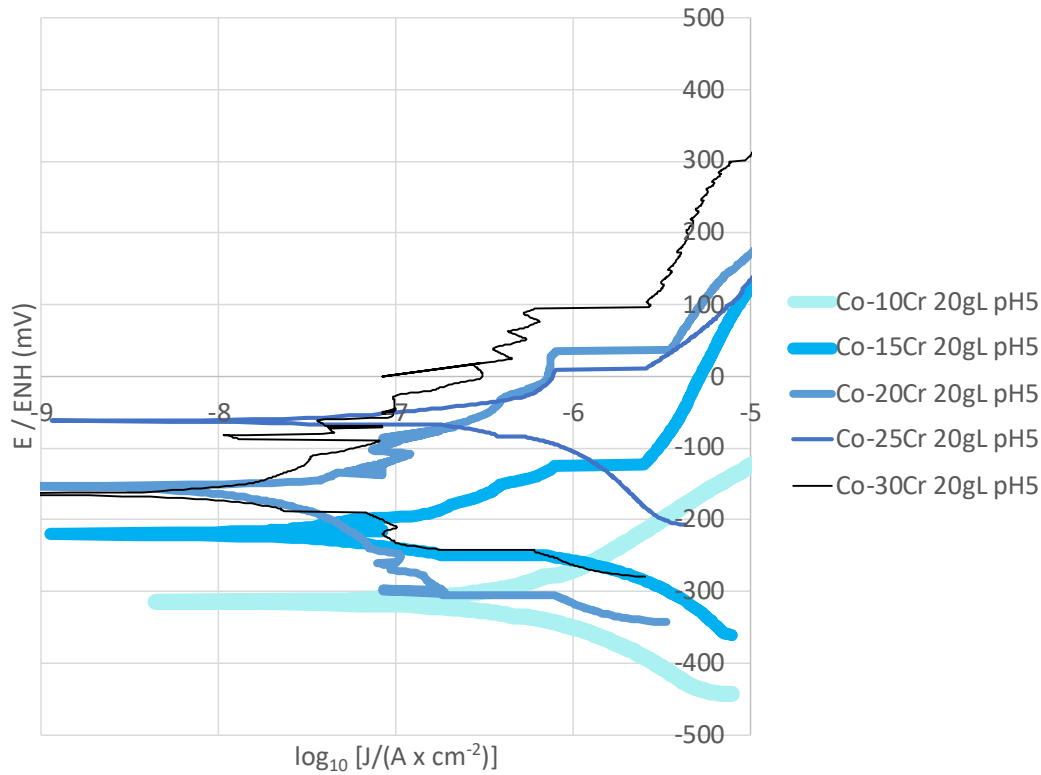
Co-xCr 10gL pH5 37°C



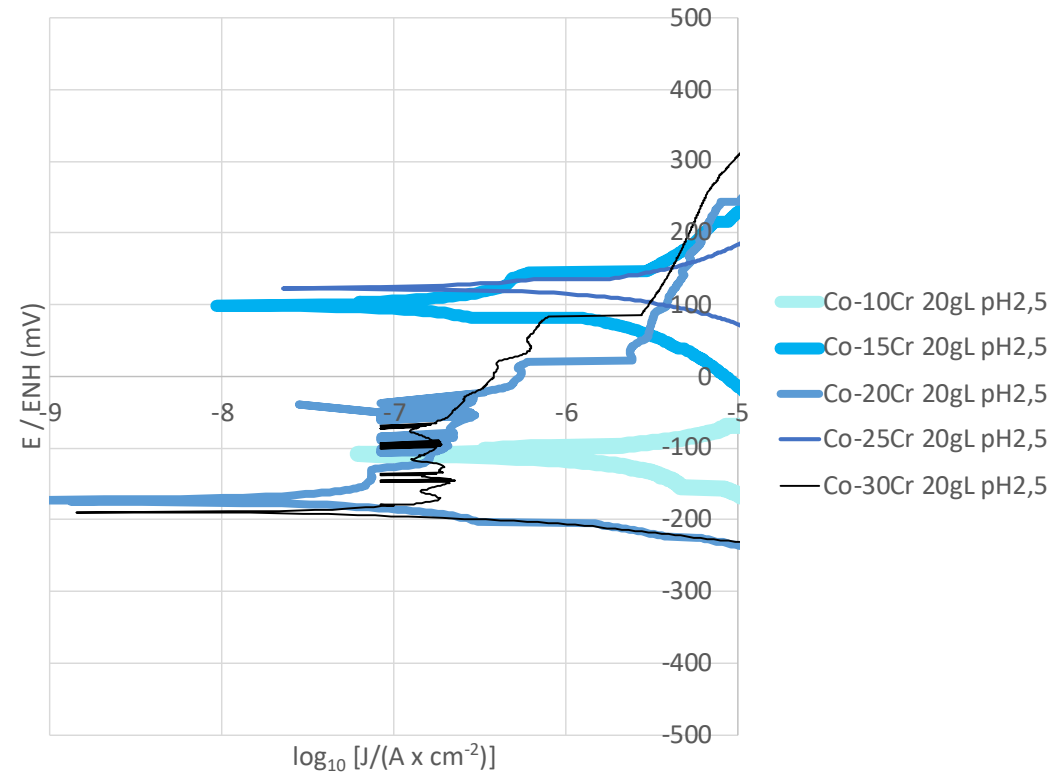
Electrochemical runs: Tafel curves

Co-xCr alloys: at constant [NaCl] $J_{\text{corr}} \uparrow$ when pH \downarrow

Co-xCr 20g/L pH5 37°C



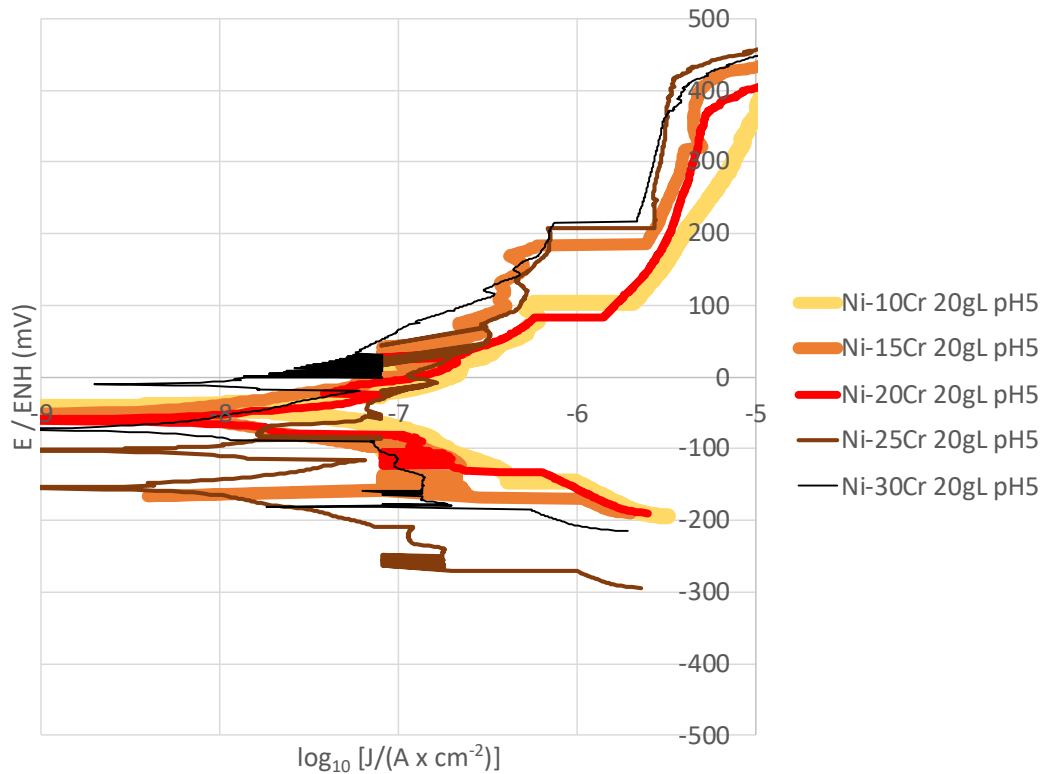
Co-xCr 20g/L pH2,5 37°C



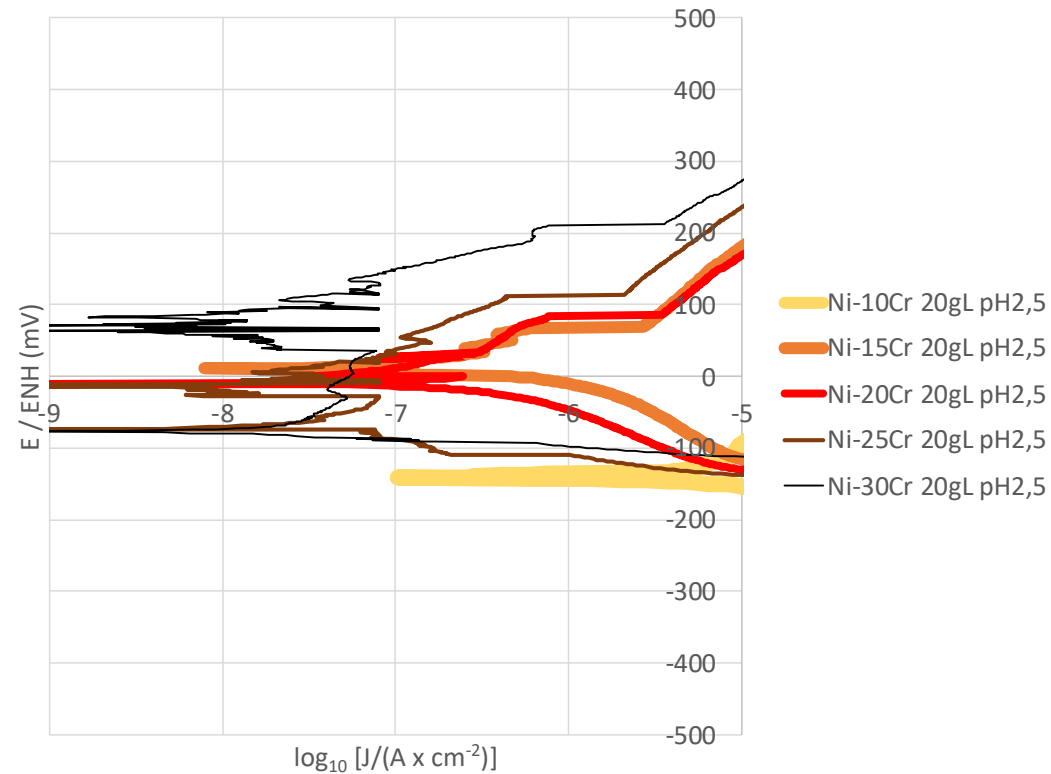
Electrochemical runs: Tafel curves

Ni-xCr alloys: at constant [NaCl] $J_{corr} \uparrow$ when Cr \downarrow and when pH \downarrow

Ni-xCr 20g/L pH5 37°C



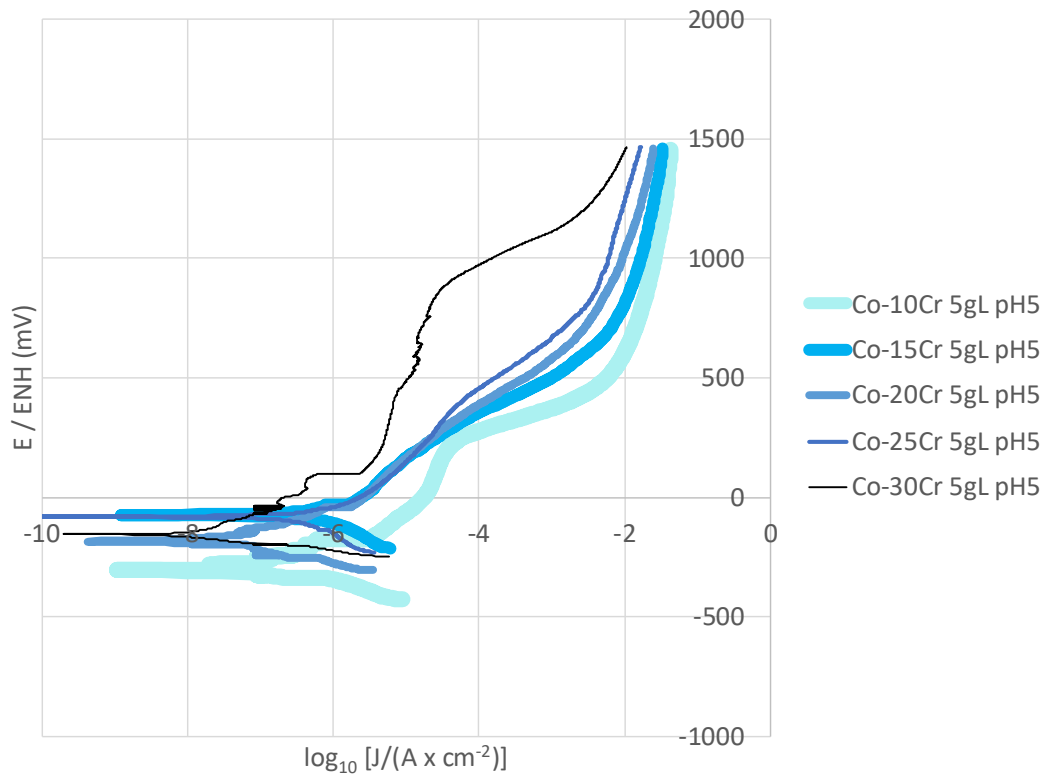
Ni-xCr 20g/L pH2,5 37°C



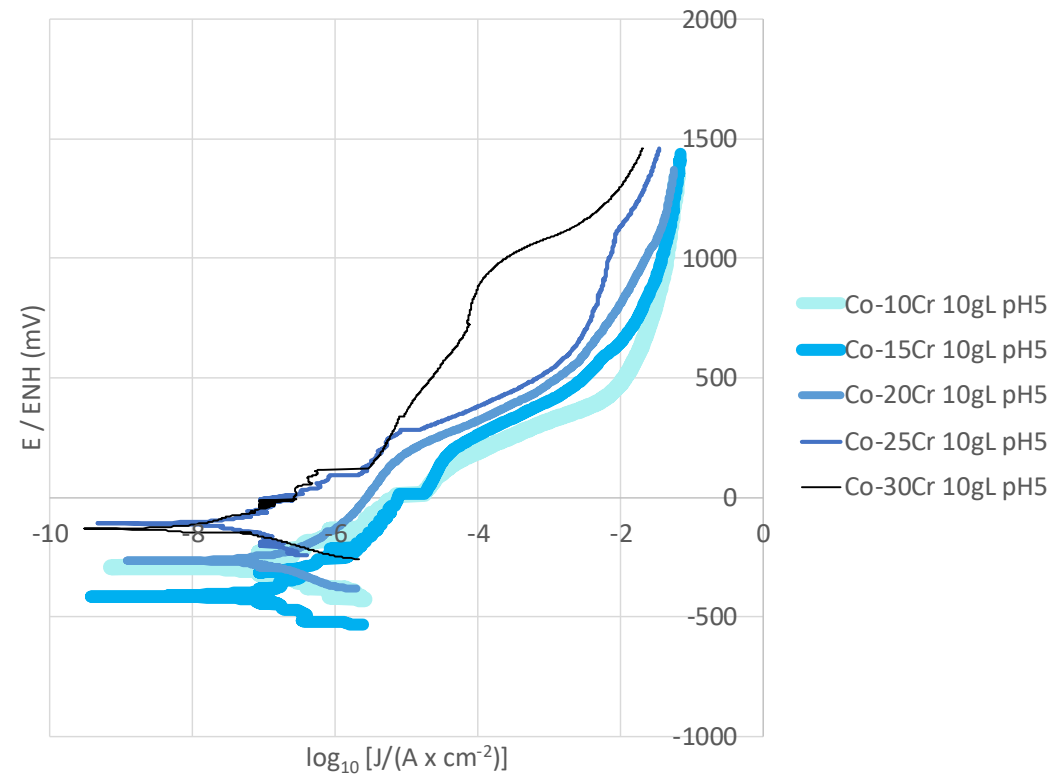
Electrochemical runs: potentiodynamic curves

Co-xCr alloys: anodic current ↓ when Cr content ↑

Co-xCr 5g/L pH5 37°C



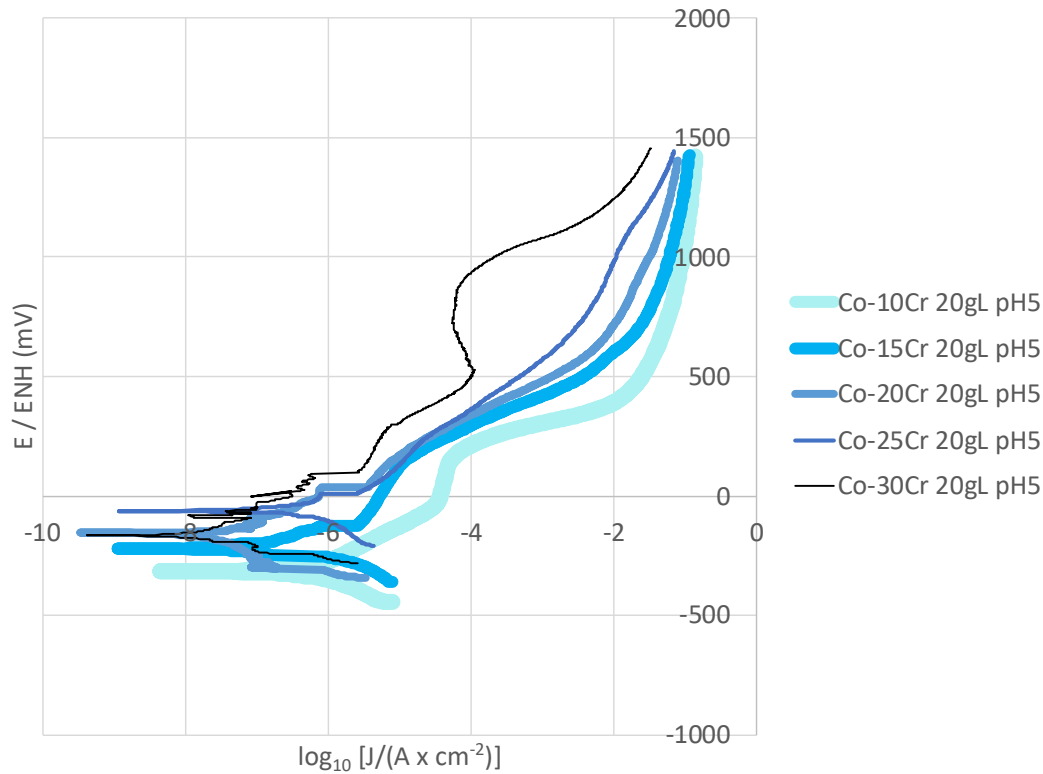
Co-xCr 10g/L pH5 37°C



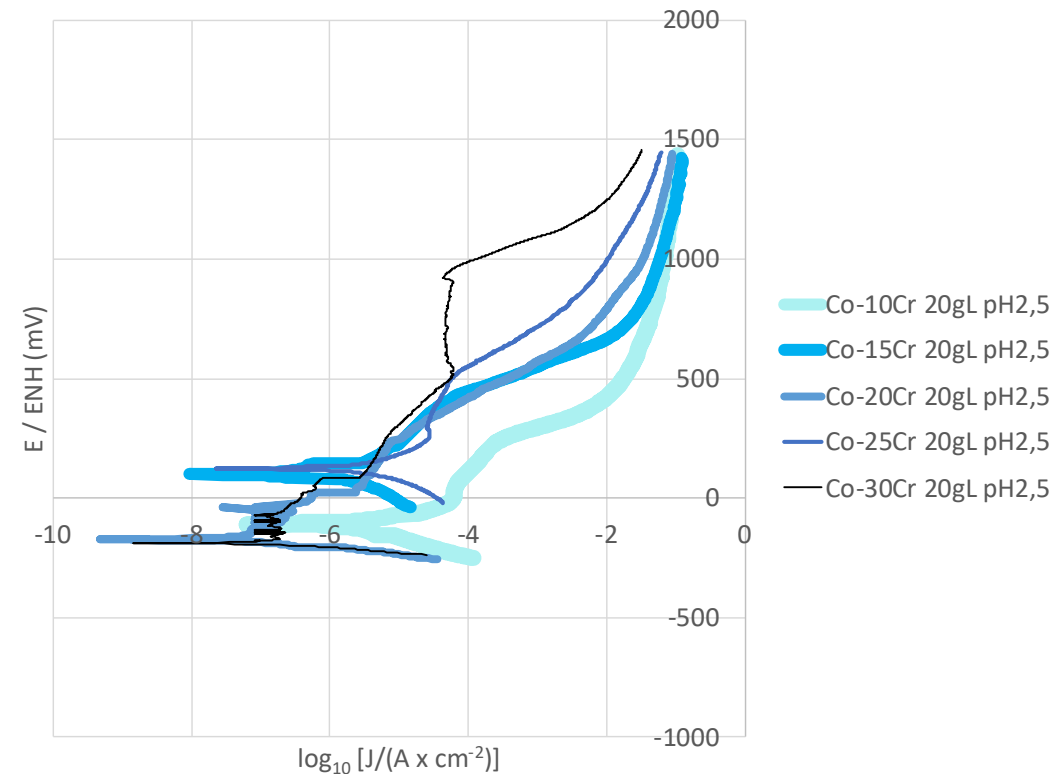
Electrochemical runs: potentiodynamic curves

Co-xCr alloys: no real effect of pH, [NaCl] on the anodic currents

Co-xCr 20g/L pH5 37°C



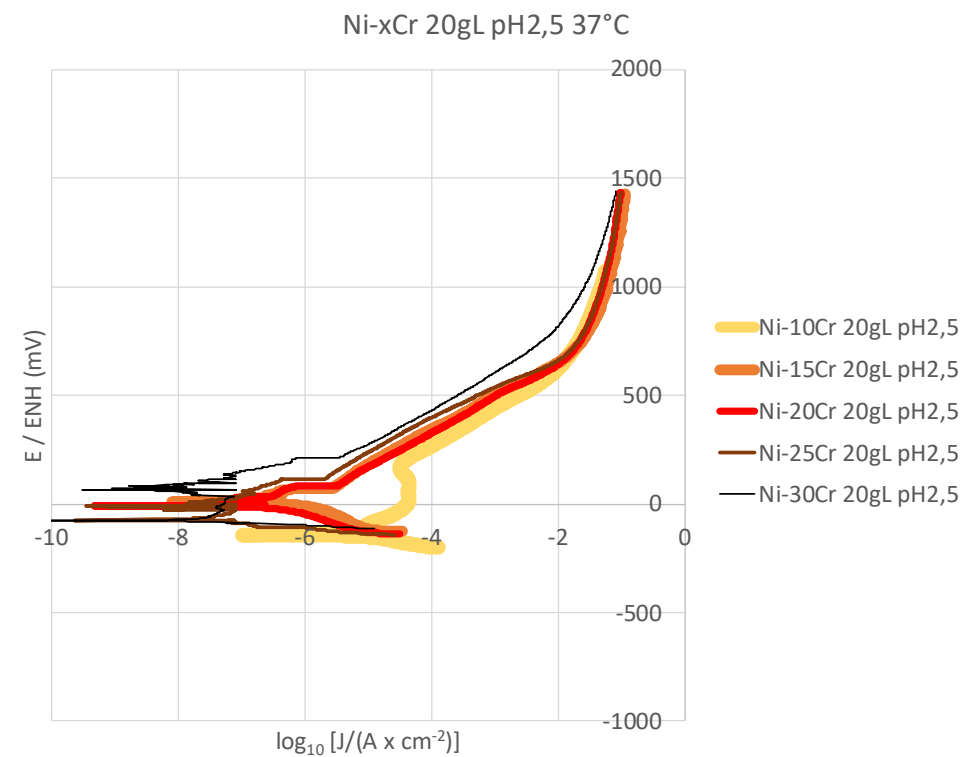
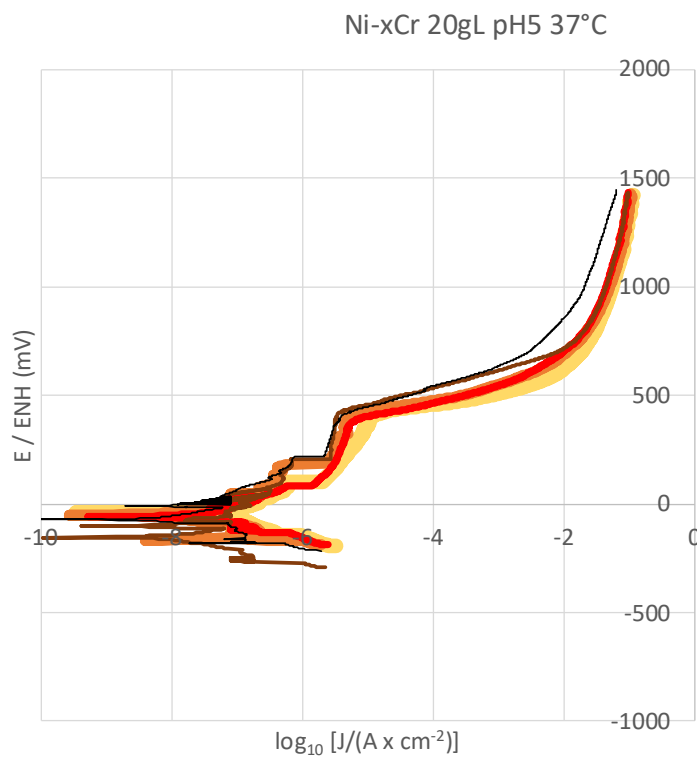
Co-xCr 20g/L pH2,5 37°C



Electrochemical runs: potentiodynamic curves

Ni-xCr alloys: anodic current density ↓ when Cr content ↑; no real effect of pH and [NaCl] on the anodic currents

(except, for pH, on passivation at low Cr)



Results

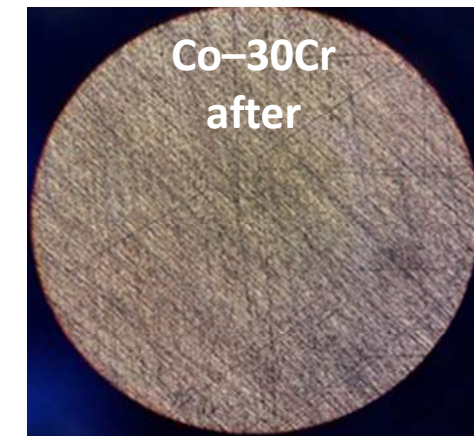
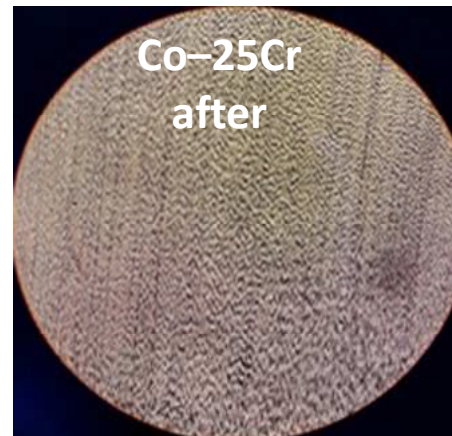
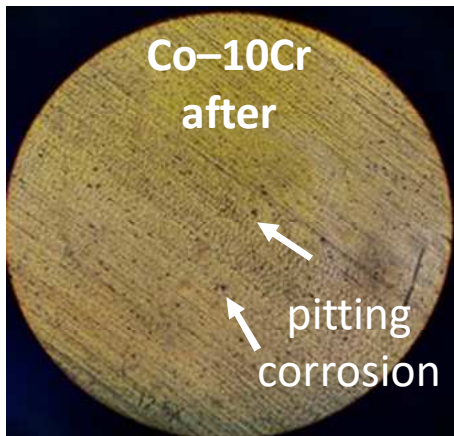
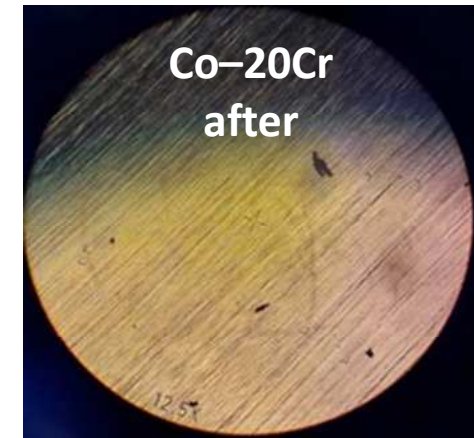
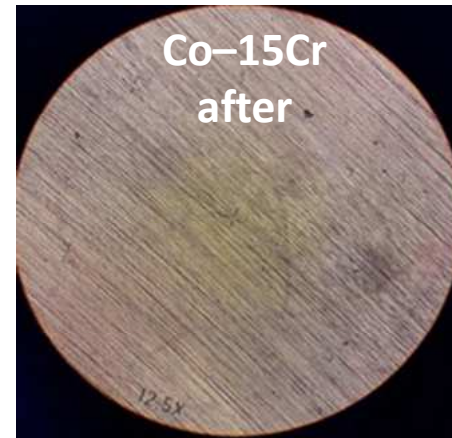
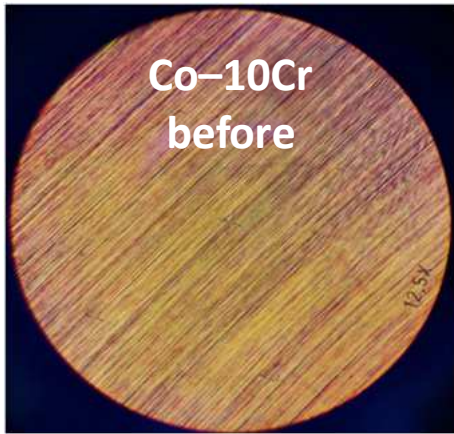
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Immersion tests



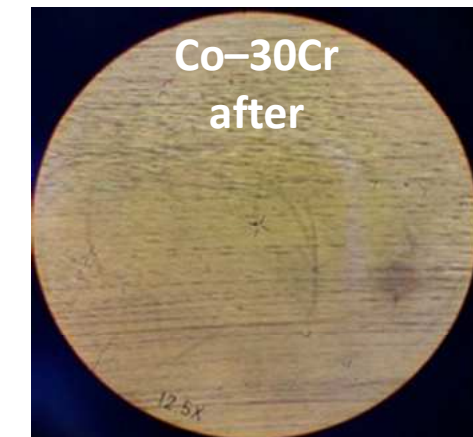
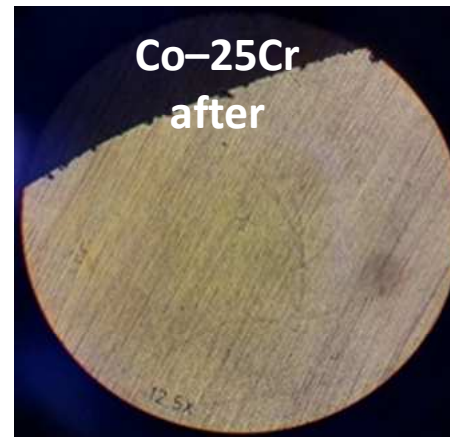
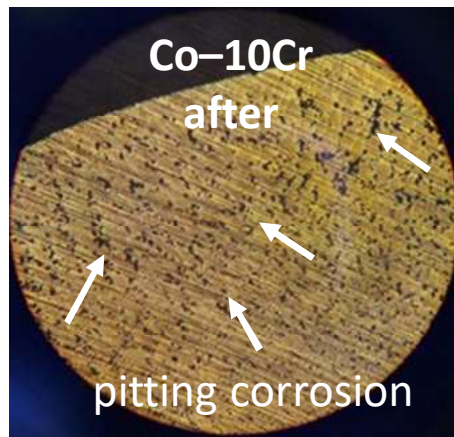
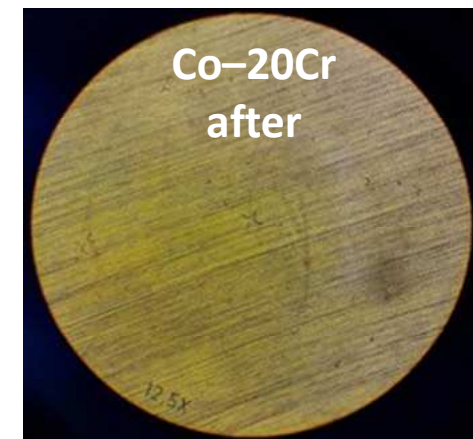
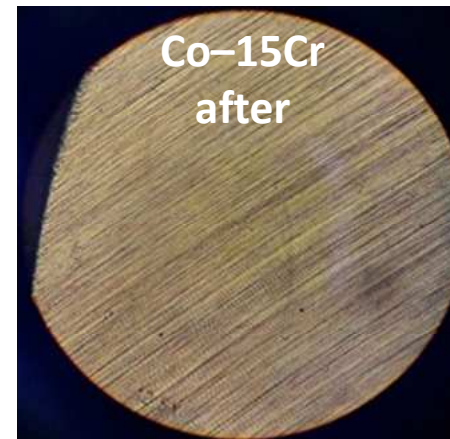
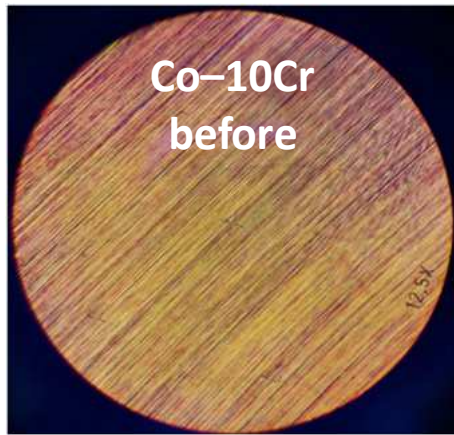
Immersion tests: example of the Co-xCr alloys

20g/L – pH2,5 – 24 hours: slight corrosion of Co-10Cr only



Immersion tests: example of the Co-xCr alloys

20g/L – pH2,5 – 96 hours: extended corrosion for Co-10Cr (only)



Summary



Ni-based and Co-based model alloys

Similar observations concerning the roles of Cr, pH and [Cl⁻]:

for the ranges of pH and [NaCl] considered values...

{E, pH} points ∈ corrosion areas of Co, and of Ni (borderline with passivation at pH5)

{E, pH} points ∈ passivation of Ni (at pH5), and Cr (borderline with corrosion at pH2.5)

The higher the chromium content,

The higher the free potential (except NiCr at pH2.5),

The higher the polarisation resistances (and thus the J_{corr}),

The lower the anodic* currents (*: applied potentials higher than E_{corr})

pH: more influent parameter than [NaCl]

Corrosion potential higher at pH=2.5 than at pH=5

(E_{O₂/H₂O} and E_{H⁺/H₂} both increase in when pH decreases)

Conclusions



Chromium content: the key parameter

The most important one for the resistance of PB alloys against corrosion by saliva

Cr close to 30 wt.%: high resistance whatever pH and [NaCl]

J_{corr} staying $< 10 \text{ nA/cm}^2$ for 30 or 25 wt.%Cr at pH5

(and $< 100 \mu\text{A/cm}^2$ at pH=2.5)

pH (passive and active states) and [NaCl] (pitting corrosion, saliva conductivity...) are also important parameters

Immersion tests not long enough to confirm

Corrosion start only visible for the Cr–lowest alloy (Co-10Cr), even after 4 days

Outlooks



Salivas with enhanced aggressiveness

The present work: only dissolved O_2 , H^+ and Cl^-

Human saliva: presence of bacteria, known to play important role; how the Cr threshold may evolves in presence of bacteria?

Taking into account the other metallic alloys

Frameworks: made of parts PB alloys (*parent alloys*) joined to one another by soldering (*pre-solder and post-solder alloys*)

What about the influence of these soldering alloys on the PB alloys vs. their Cr content? (galvanic coupling effects)

Much longer immersion tests

Individual PB alloys, PB alloys joined with soldering alloys

Thank you



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for your attention!