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ELECTRO-POLISHING STUDIES



AT CEA SACLAY

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Work carried out using the SUPRA Tech GIS infrastructures with the financial support from Region d'Ile de France.

OUTLINE

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R&D on Single-Cell Cavities

- EVALUATION OF CHLOROFORM RINSING
- LOW VOLTAGE EXPERIMENTS / SULFUR CONTAMINATION

R&D on Samples

- EP CONTROLLED BY DIFFUSION
- BETTER UNDERSTANDING OF THE PROCESS AND OF ITS EVOLUTION WITH AGING
- IMPEDANCE SPECTROSCOPY: A WAY FOR QUALITY CONTROL OF THE ACID?

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R&D on Single-Cell Cavities

F. Eozénu, Y. Gasser, J-P Charrier, S. Berry, D. Reschke

RF RESULTS AT LAST TTC

Results with standard EP + Ethanol Rinsing + HPR

Strong F.E

Recipe	R#1	R#2 [*]		R#3	R#4		R#5	R#6
Test	T#1	T#1	T#2	T#1	T#1	T#2	T#1	T#1
Cavity	1DE1	1DE1	1DE1	1DE1	1DE3	1DE3	1DE3	1C03
EP @	S	S	S	S	S		S	S
Baking @	D	D	D	S	D		S	S
Test @	D	D	S	S	D		S	S
Eacc Max	42,73	36,30	44,13	39,80	43,92	40,41	41,87	20,00
Average Eacc	42,70	40,21		39,80	42,16		41,87	< SPEC
Q0 @ EaccMax	9,70E+09	1,21E+10	7,82E+09	9,11E+09	2,46E+10	1,87E+10	1,40E+10	
Average Q0	9,70E+09	9,96E+09		9,11E+09	2,16E+10		1,40E+10	

- 1C03 Heavily polluted (mistake during pumping)

- Need for a very efficient rinsing recipe

Choice of chloroform: it is a very good solvent to extract sulphur in EP Mixtures.

❖ K. Saito, et al. "R & D of superconducting cavities at KEK". in 4th workshop on RF Superconductivity. 1989

❖ Aspart et al. "Aluminum and sulfur impurities in electropolishing baths". Physica. C. Superconductivity (Phys., C Supercond.) ISSN 0921-4534. 2006, vol. 441, no 1-2 (13 ref.), pp. 249-253

→ Should be efficient to remove field emission

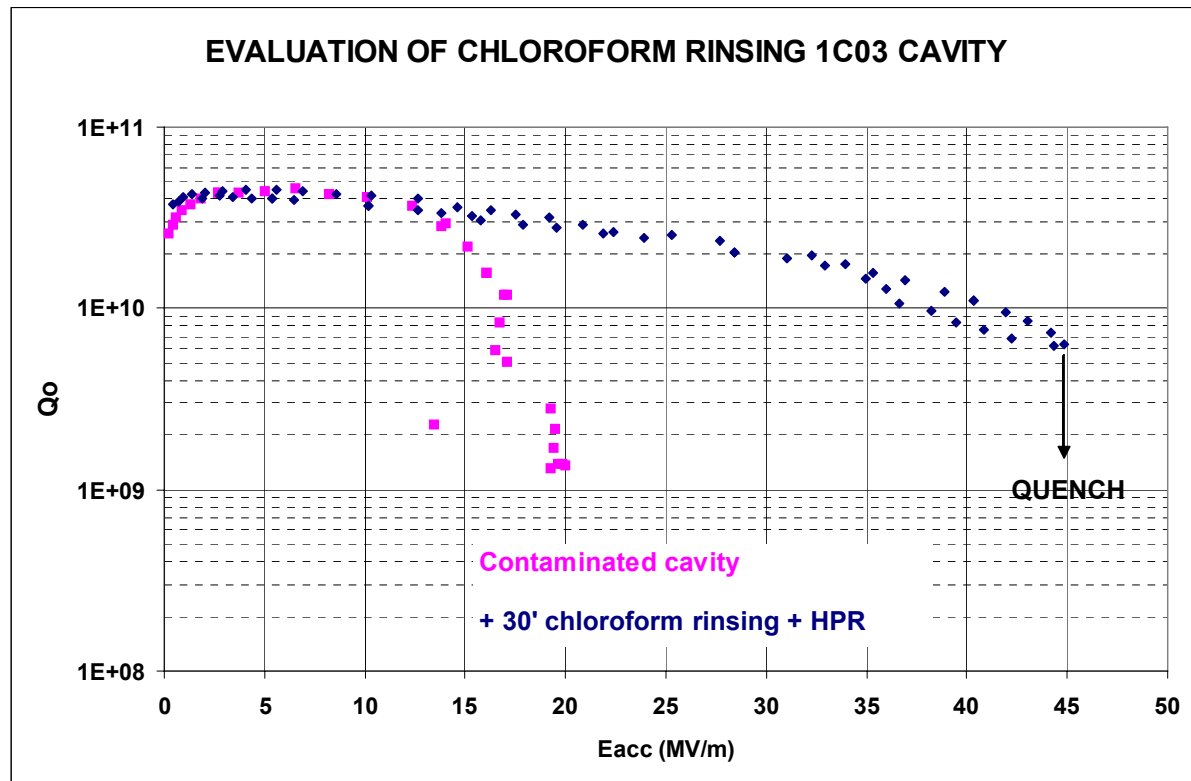
EVALUATION OF CHLOROFORM RINSING

Test on 1C03 (Tesla Shape Cavity)

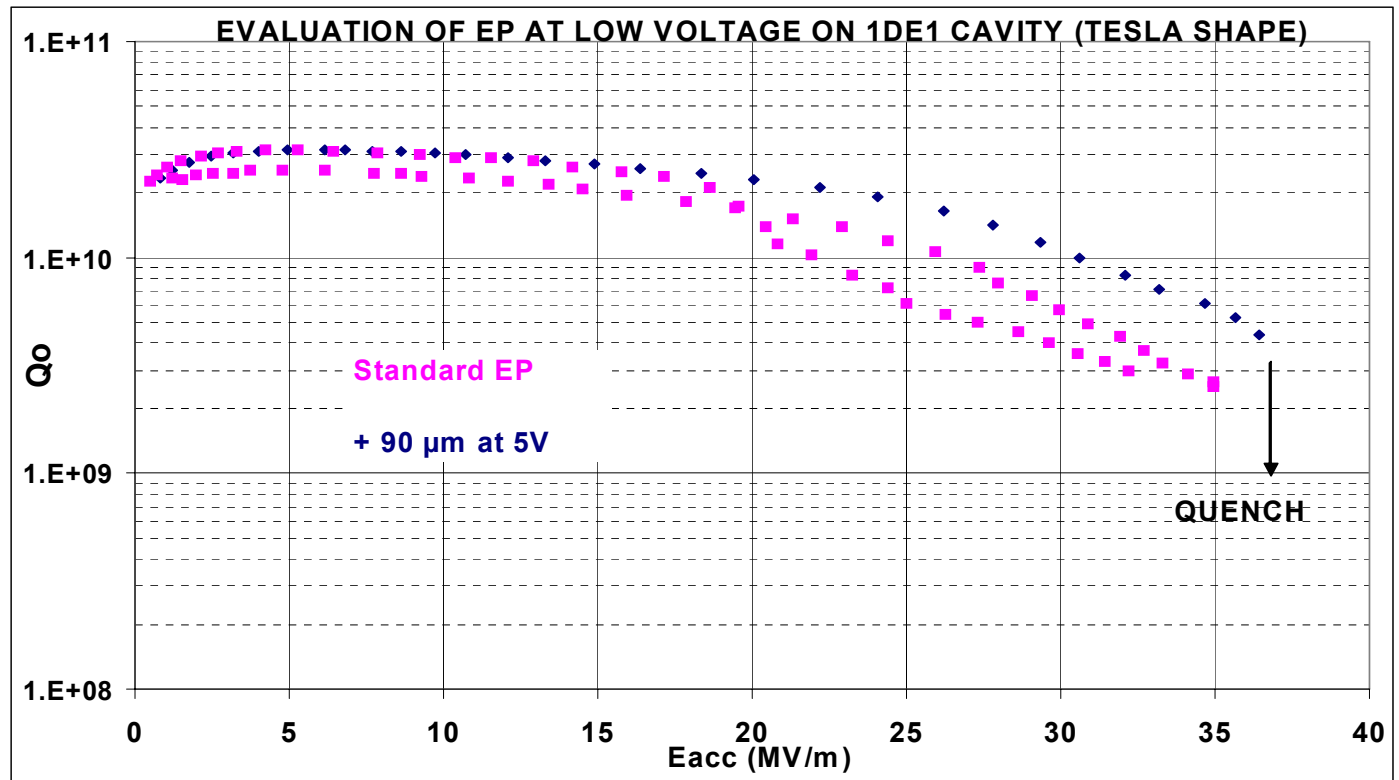
+ 30' Chloroform Rinsing + HPR: Suppression of emitters + Excellent Gradient:

Eacc ~ 45MV/m at 1.5K

Seems efficient for Rinsing of Cavity! (Sulphur highly soluble in chloroform)

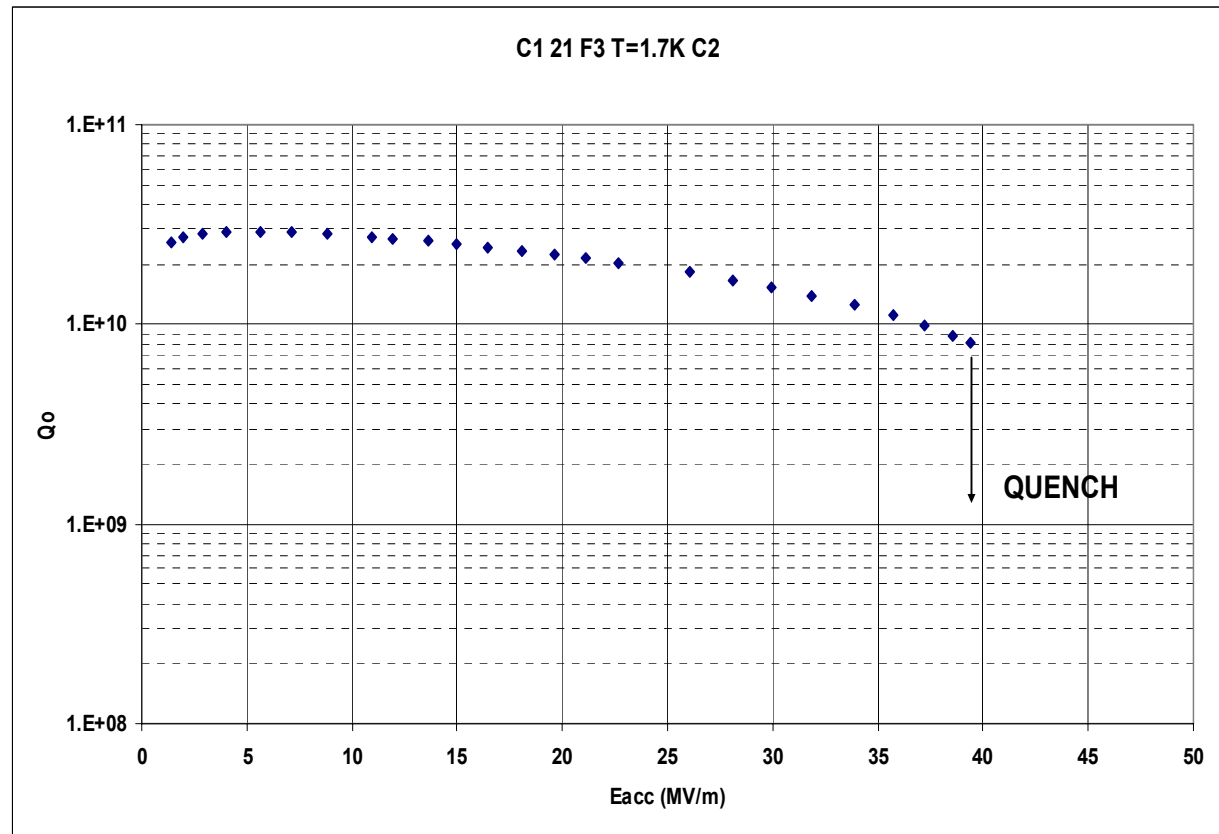


ELECTRO-POLISHING AT LOWER VOLTAGE (5V)



Preliminary Result: Voltage has no/little influence on RF Result?
It questions the theory of the mandatory viscous layer during EP!

RESULT ON 1C21 AFTER 150 μ m OF LOW VOLTAGE EP



Quench located at the equator.

No need of viscous layer during EP to reach high gradients!

Smoothing of the surface not necessary?

MAIN REASON TO TRY LOW VOLTAGE EP

= Theoretical way to reduce Sulfur Contamination (experience on going)

Reduction Reactions at the Cathode

Reduction of H^+ : $2 H^+ + 2 e^- \rightarrow H_2$ (Predominant)

Reduction of SO_4^{2-} : $SO_4^{2-} + 8H^+ + 6e^- \rightarrow S + 4H_2O$

Does the cathodic overpotential provoked by a too high voltage an increased sulphur generation?

→ Two Niobium samples electro-polished at 5V and 20V for a similar heavy removal with 1-9-1 Mixture

Sample A, 20 Volts:

9.18g removed

51 hours EP

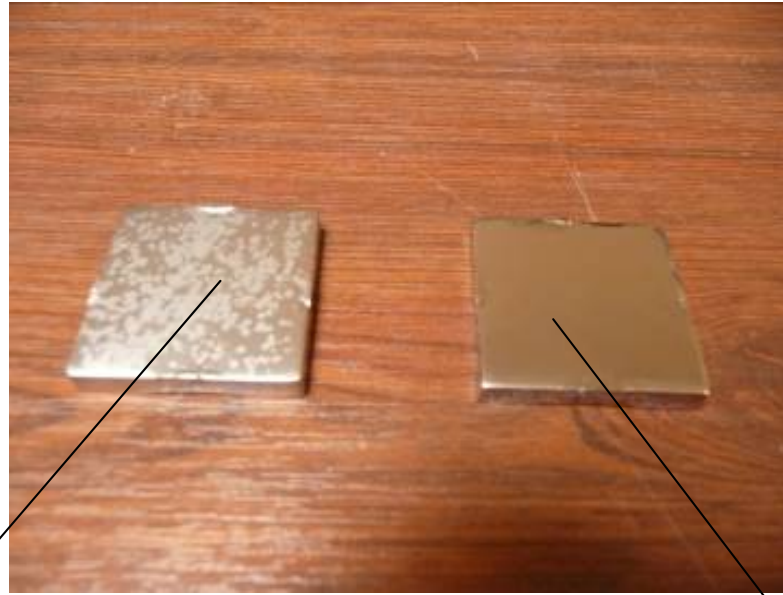


Sample B, 5 Volts:

9.11g removed

115 hours EP

LARGE CONTAMINATION WITH THE SAMPLE EP AT 20V



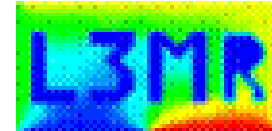
Numerous sticking spots on
the surface.

Some spots on the surface.

Not removed by ethanol nor
chloroform

The experiment is on going: The 2 EP mixtures are “washed” with
chloroform to extract sulfur.

At the present time, sulfur has for the moment been found in A mixture



R&D on Samples

F. Eozénou, S. Berry, M. Bruchon, N. Larabi-Gruet, Y. Charles

ONGOING R&D ON SAMPLES



- Use of a Rotating Disc Electrode
- \varnothing sample: 10 mm
- Ag/AgCl Reference Electrode



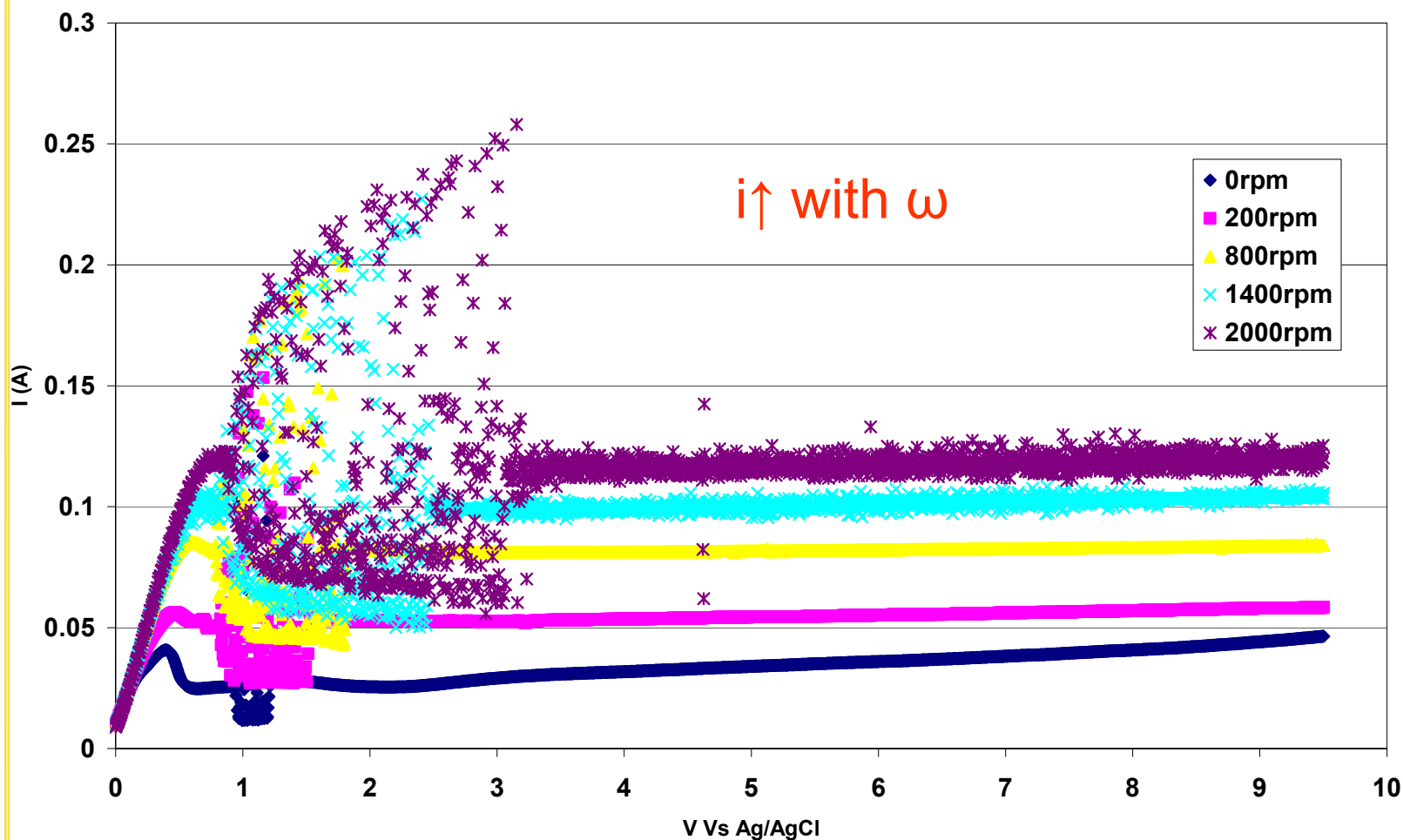
Measurements:

- $I(V, \omega)$ measurements
- $I(t, \omega)$ measurements
- Impedance Spectroscopy for different mixtures, Voltage, ω

I(V) CURVES FOR DIFFERENT ROTATION SPEEDS

Ex: 1volHF(48%)-9volH₂SO₄(95%) Mixture

I=f(V) for Different Rotation Speeds 1volHF(48%)-9volH₂SO₄(95%) Mixture



EP CONTROLLED BY DIFFUSION?

Levish criterion

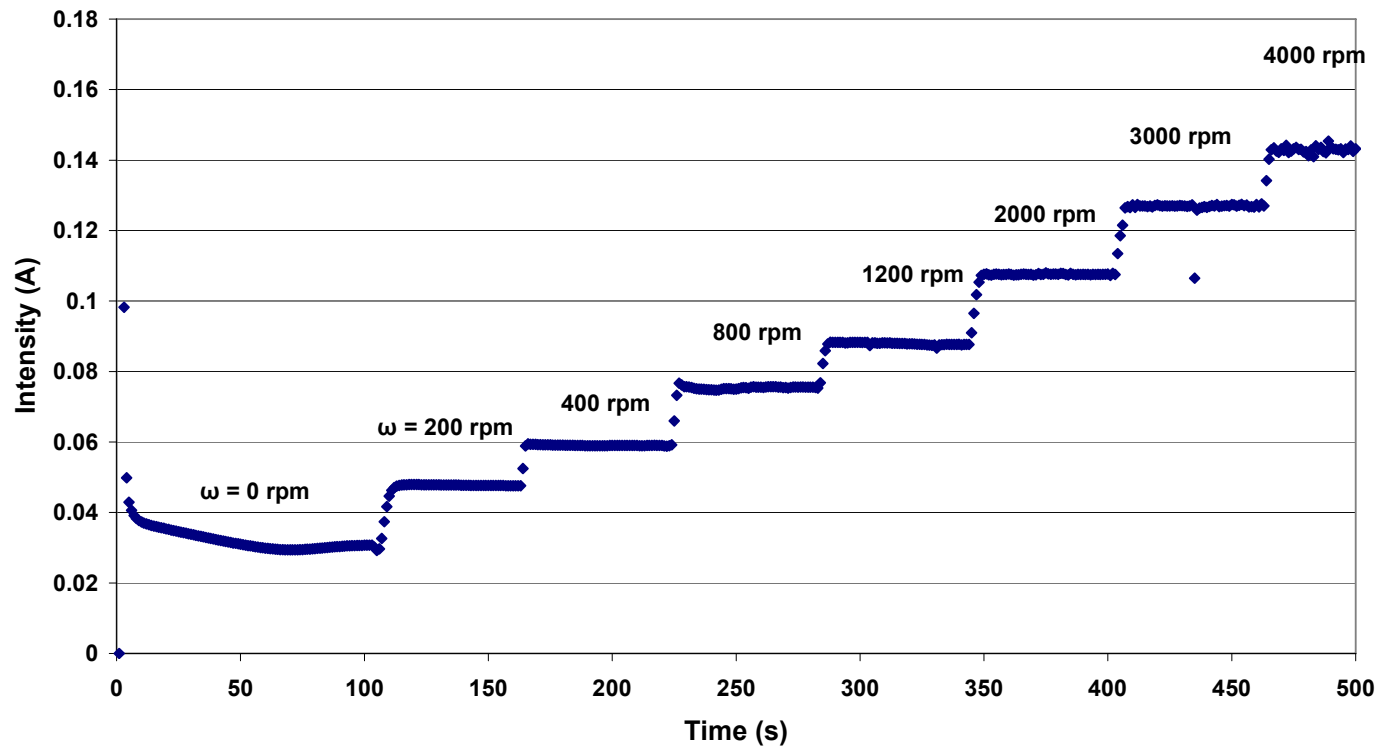
$$i_{ss} = 0.62 E^{-3} n F S D^{2/3} \nu^{-1/6} \omega^{1/2} C$$

- i_{ss} : current at the steady state (A)
- n : number of electrons involved
- S : electrode surface (cm²)
- D : diffusion coefficient (cm².s⁻¹)
- ν : viscosity (St) → H₂SO₄ to simplify calculation
- ω : rotation speed of the electrode: rad.s⁻¹
- Concentration of the active specie (mol.L⁻¹)

GRAPHS $I=f(t)$ FOR DIFFERENT ROTATION SPEEDS

Ex: 1volHF(48%)-9volH₂SO₄(95%) Mixture 5V Vs Ag/AgCl

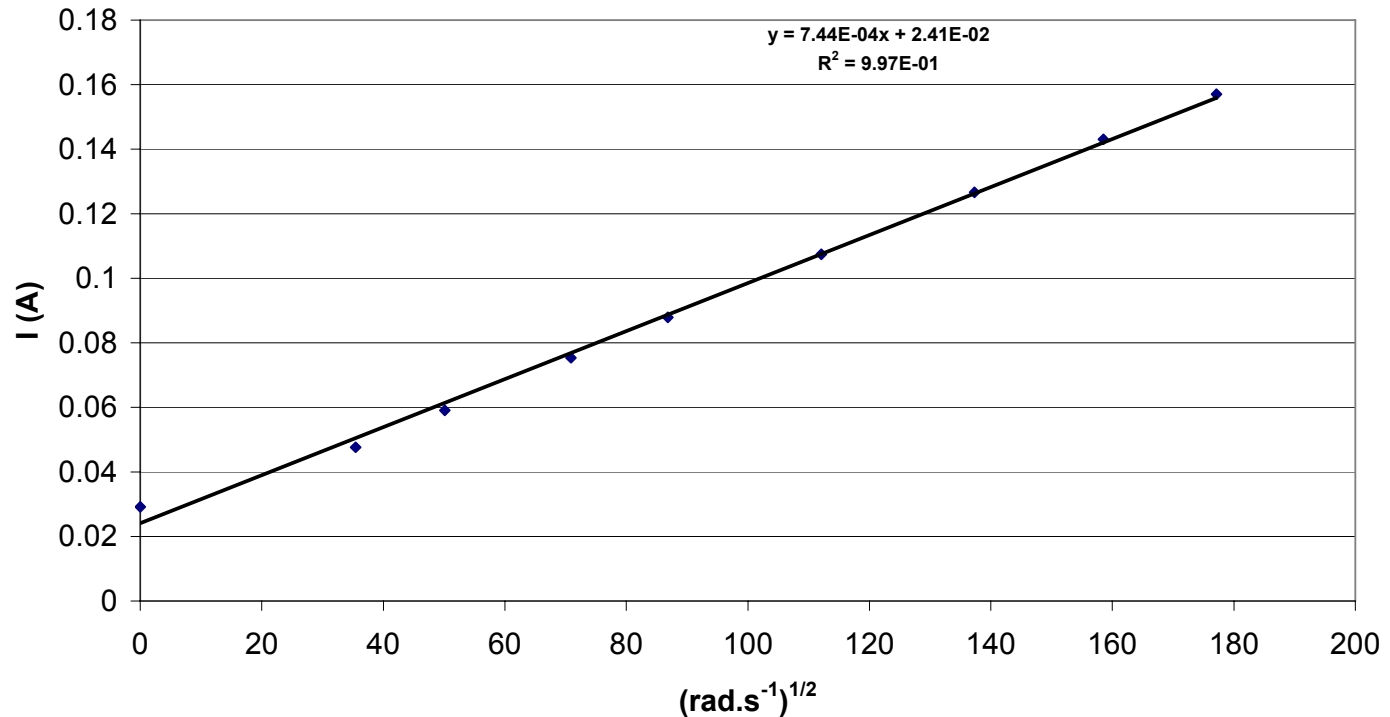
$I=f(t)$ for Different Rotation Speed 1-9 (48%) 5V Vs Ag/AgCl



Intensity increases with ω but it does not depend on potential (~same result at 9.5V). Is it proportional to $\omega^{1/2}$?

I = f($\omega^{1/2}$) 1volHF(48%) – 9 vol H₂SO₄(95%) MIXTURE

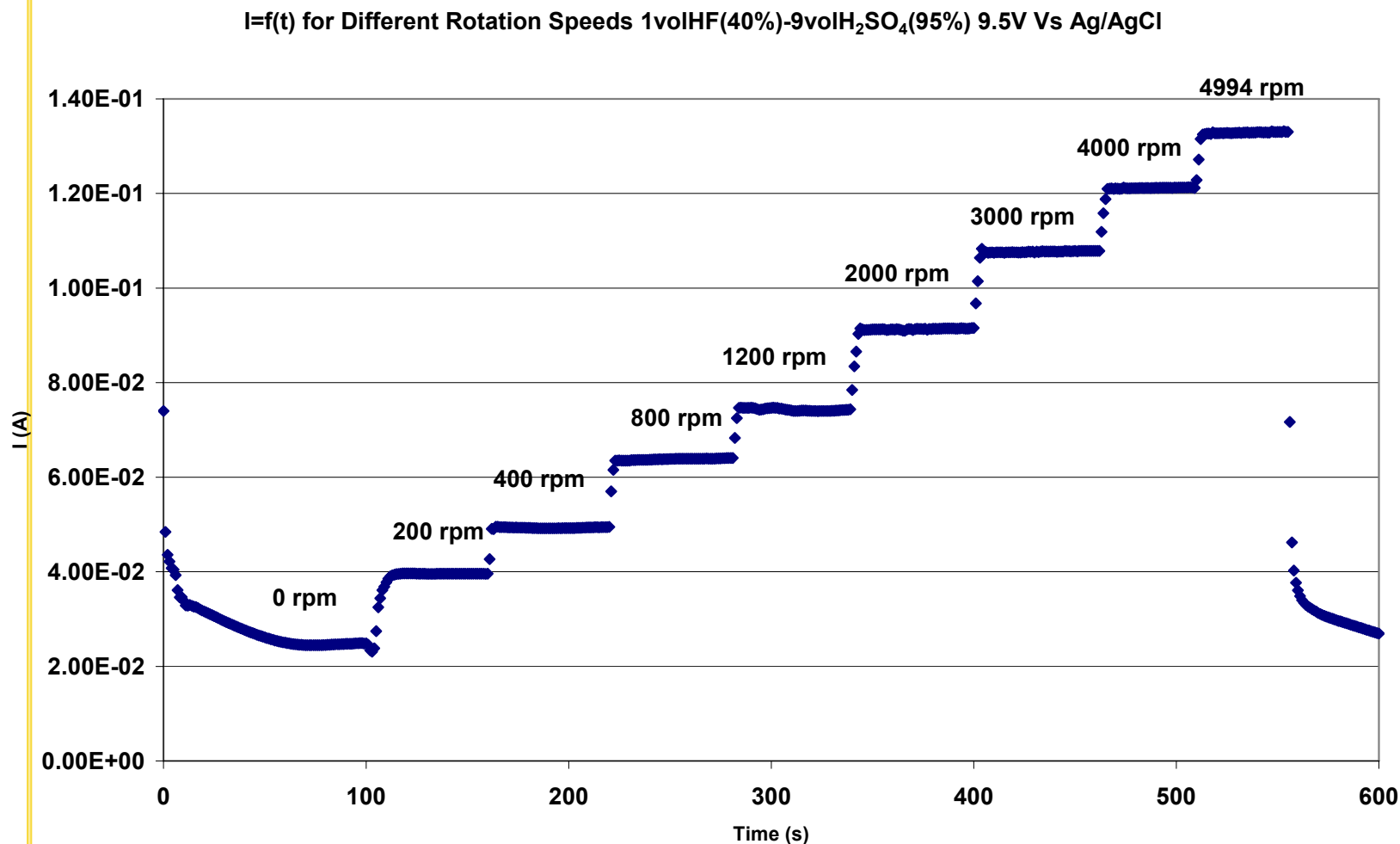
I=f($\omega^{1/2}$) 1volHF(48%)-9volH₂SO₄(95%) Mixture 5V



Proportionality verified:
current controlled by F⁻ diffusion → D calculation

$$D = 7.99E-9 \text{ cm}^2\text{s}^{-1}$$

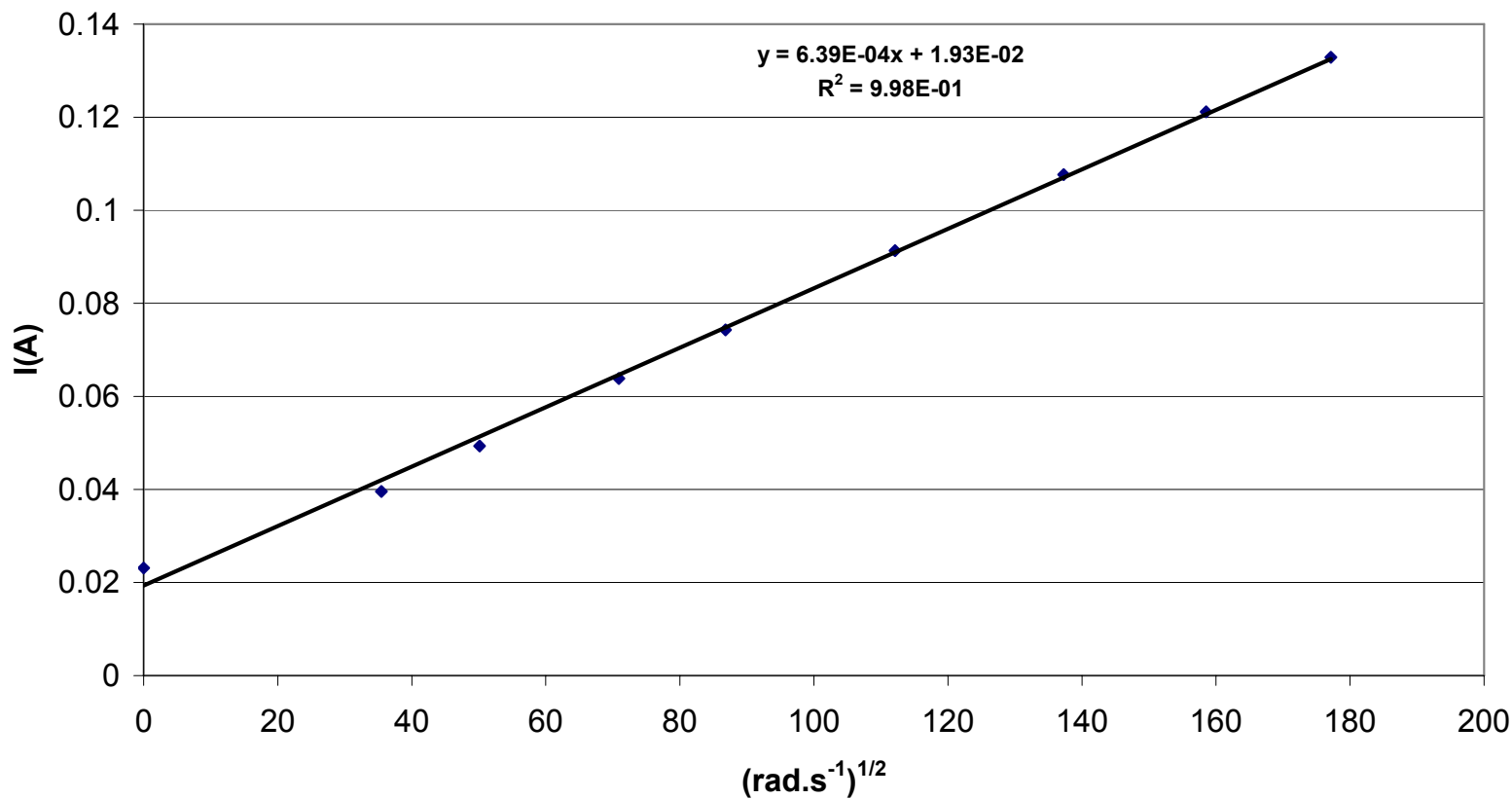
RESULTS FOR 1volHF(40%) – 9 vol H₂SO₄(95%) MIXTURE 9.5V



Intensity also depends on ω for lower HF concentration

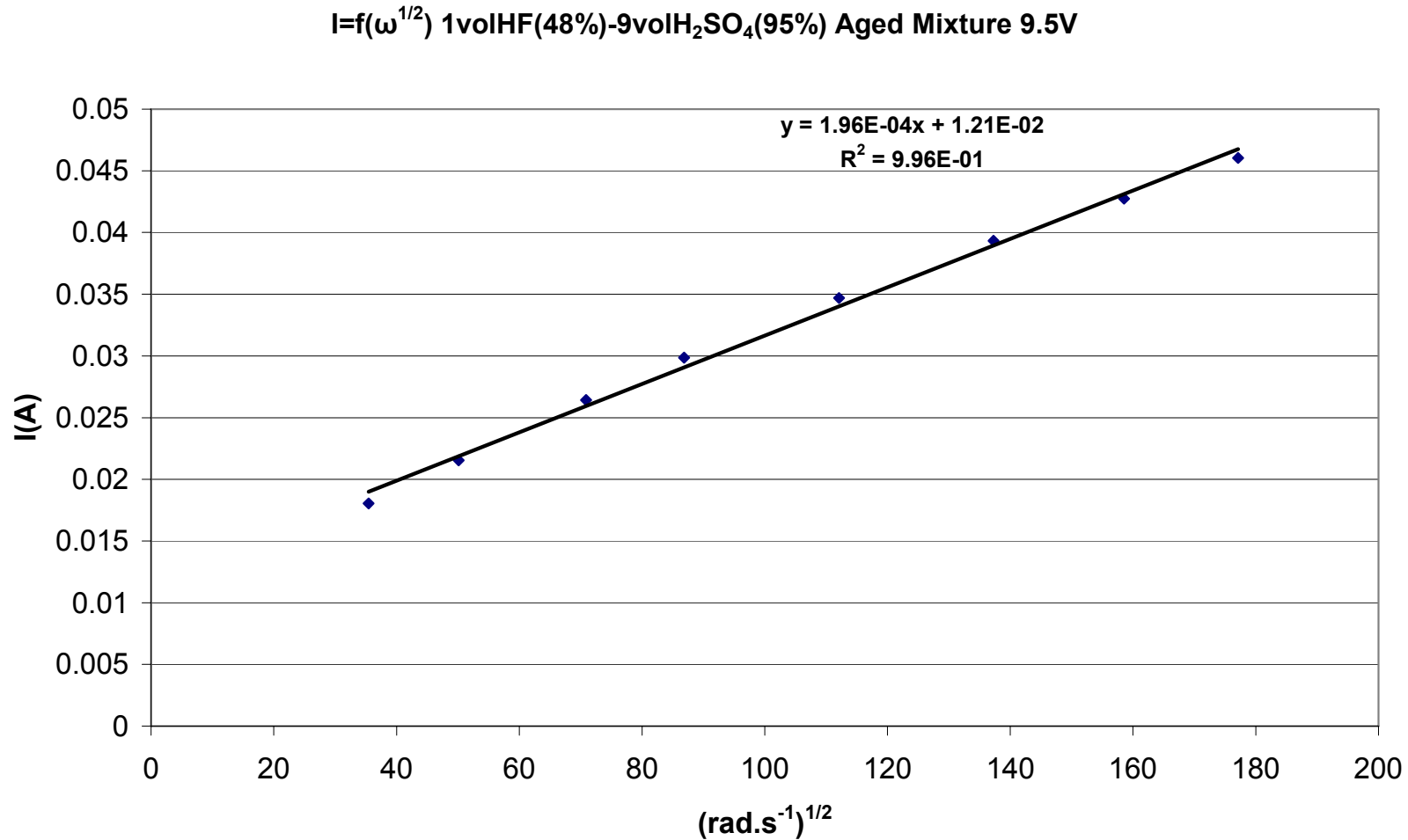
LEVISH CRITERION VERIFIED FOR DIFFERENT CONCENTRATIONS?

$I=f(\omega^{1/2})$ 1volHF(40%)-9volH₂SO₄(95%) Mixture 9.5V



Criterion verified for 1volHF(40%)-9volH₂SO₄(95%)

CRITERION VERIFIED FOR AGED MIXTURES?: TEST WITH 1volHF(48%) – 9 vol H₂SO₄(95%) MIXTURE



Criterion Verified: But Diffusion decreases with the aging of the bath!

CONCLUSIONS CONCERNING DIFFUSION COEFFICIENTS

Mixture	Voltage (V)	Diffusion Coefficient (cm ² .s ⁻¹)
Fresh 1-9 (48%)	5	7.41E-09
Fresh 1-9 (48%)	9.5	7.99E-09
Fresh 1-9 (40%)	5	8.02E-09
Fresh 1-9 (40%)	9.5	8.04E-09
1-9 (48%) with 9g/L Nb	5	4.87E-09
1-9 (48%) with 9g/L Nb	9.5	4.76E-09
Aged 1-9 (48%)	5	2.69E-09
Aged 1-9 (48%)	9.5	2.53E-09

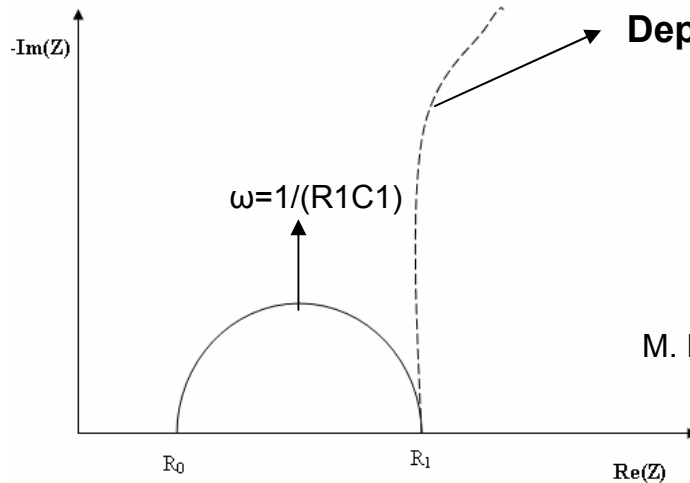
- Diffusion Coefficient decreases dramatically

with aging of the bath

- Dissolved niobium provokes a decrease

For all Mixtures, Brightening of the surface with the rotation!!!

EIS TO CHARACTERIZE THE SURFACE DURING EP. STATE OF THE ART.



R_0 : high frequency limit: resistivity of the electrolyte (+ surface film)

R_1 : Diameter of the high frequency loop

M. Matloz. Modeling of Impedance Mechanisms in Electropolishing. Electrochimica Acta. Vol 40, N°4, pp 393-401, 1995

Results presented at the 13th SRF Workshop in niobium's case:

•H. Tian et al. "Novel Characterization of The Electropolishing of Niobium With Sulfuric And Hydrofluoric Acid Mixtures"

Characteristic feature @ the high frequency (* C = constant)	Salt Film Models						Adsorbates -Acceptor Model		
	Porous Film			Compact Film			R_s	R_p	C_{dl}
	R_s	R_p	C_{dl}	R_s	R_p	C_{dl}			
Different Potential (↑)	↑	C	C	C	↑	↓	C	C	C
Different Rotation (↑)	↓	↓	C	C	↓	↑	C	↓	C

• R_0 (=Rs) does not depend on potential

• R_1 (=Rp) depends on potential

→ **Evidence for a compact film**

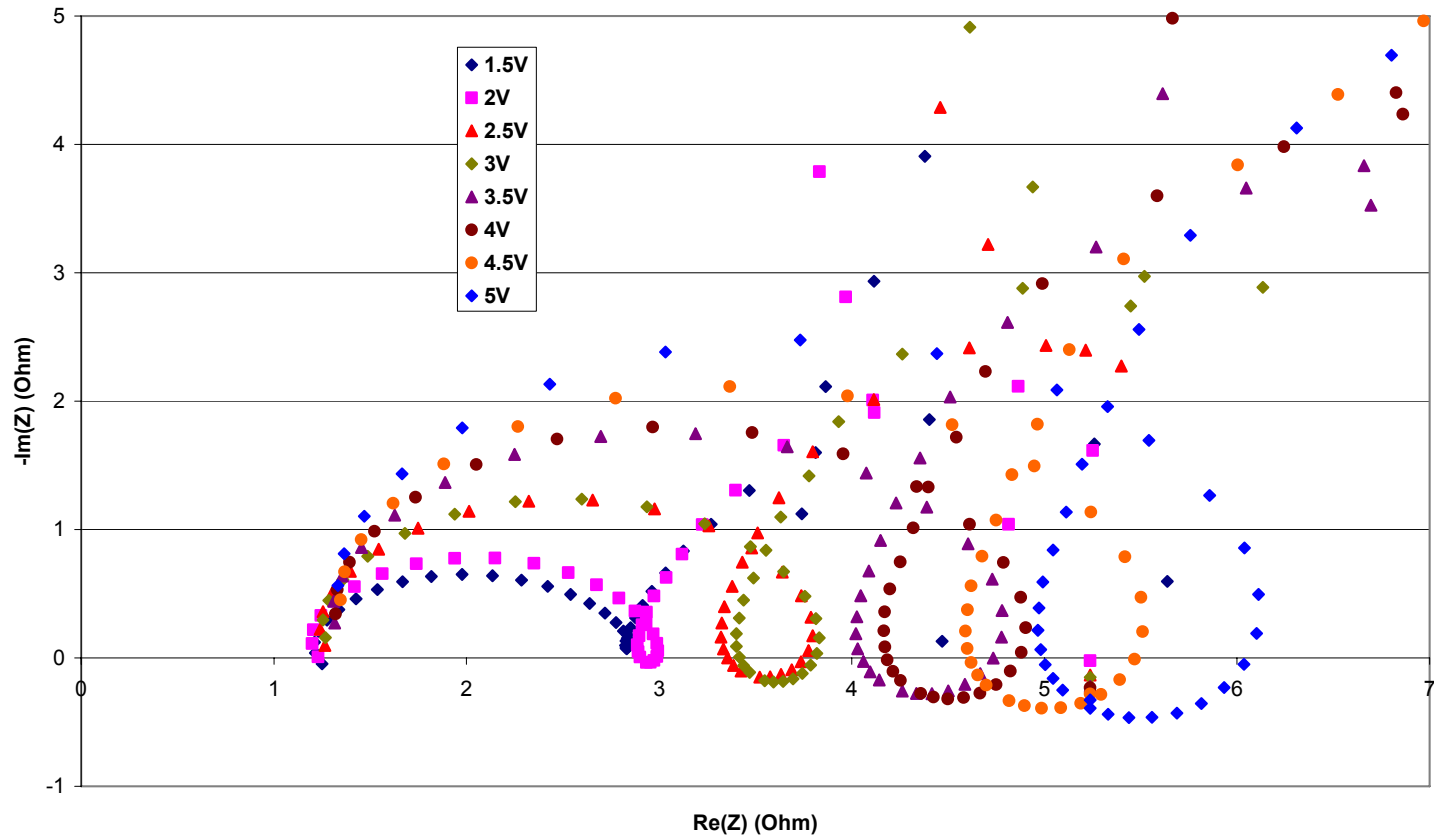
•F.Eozenou et al. "Parameters investigation for niobium electro-polishing".

Features of the diagrams depend on the concentrations → additional investigation

ADDITIONAL RESULTS WITH EIS: TESTS WITH DIFFERENT MIXTURES

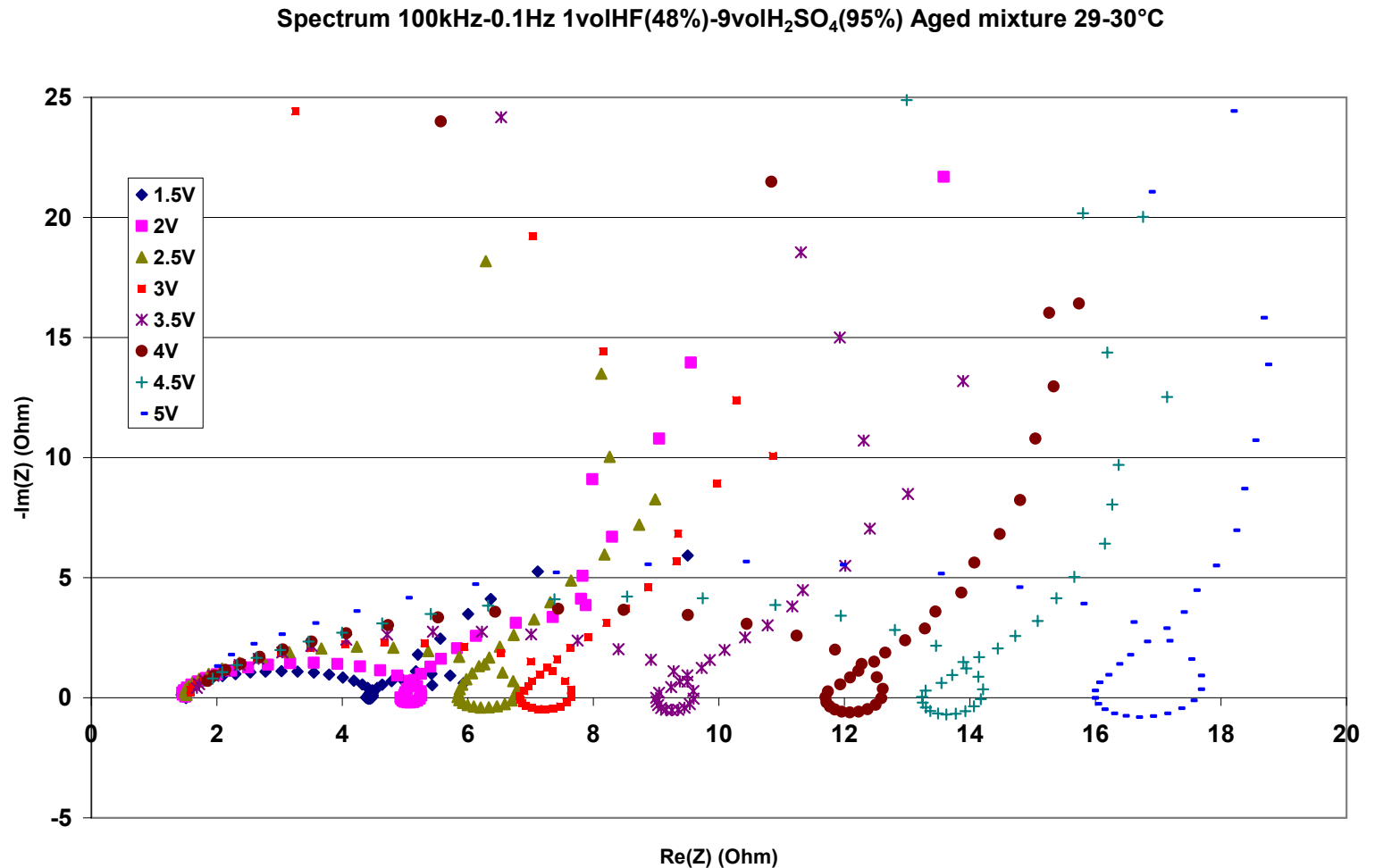
Ex: 1volHF(40%)-9volH₂SO₄(95%) Mixture 5V Vs Ag/AgCl

Spectrum 100kHz-0.1Hz 1volHF(40%)-9volH₂SO₄(95%) 30°C



Limit for high frequencies slightly increases with the potential

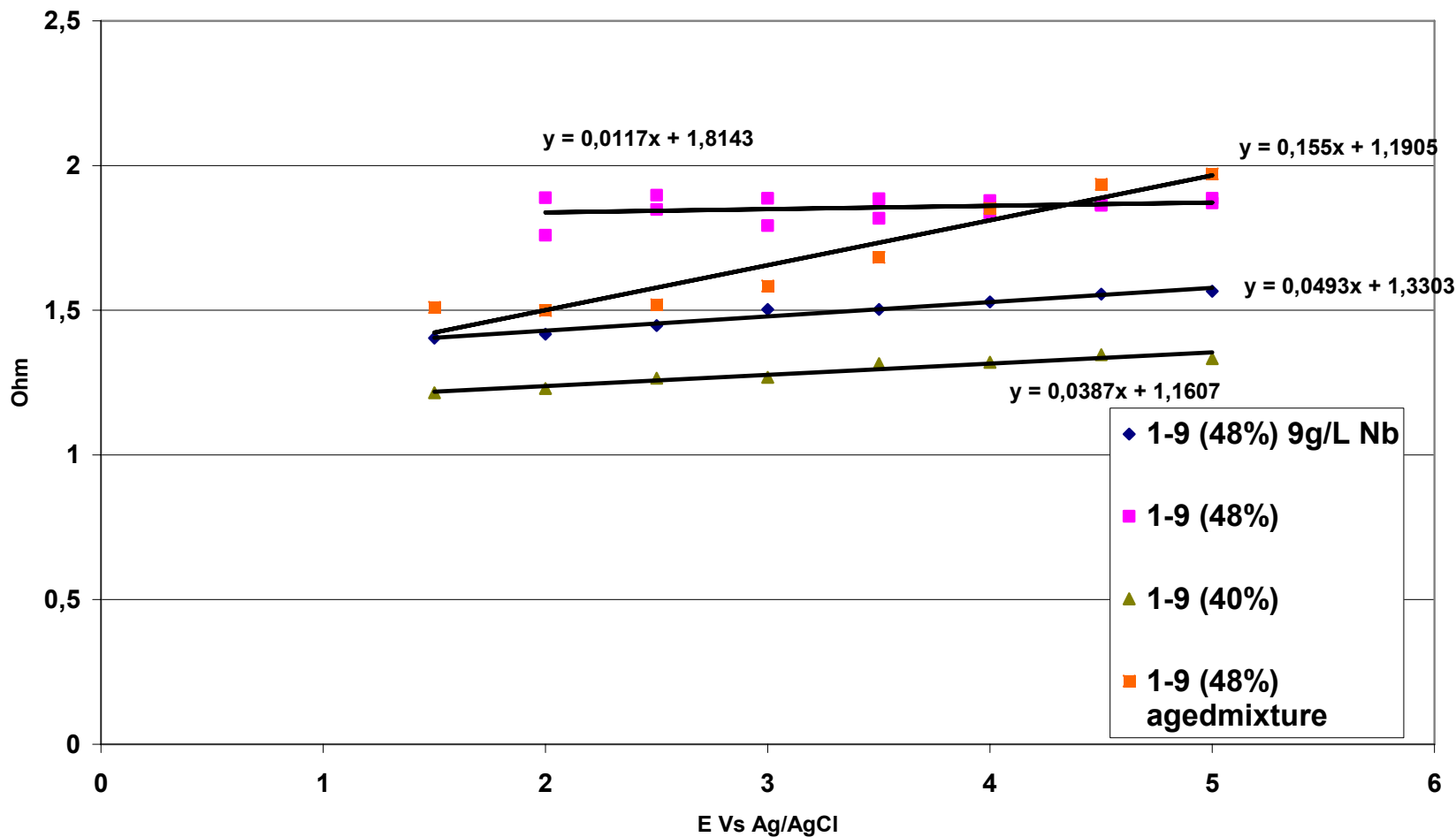
WHAT DOES HAPPEN FOR AGED MIXTURES?



R_0 and R_1 resistances are more dependant on potential

HIGH FREQUENCY LIMIT V_s VOLTAGE DEPEND ON AGING

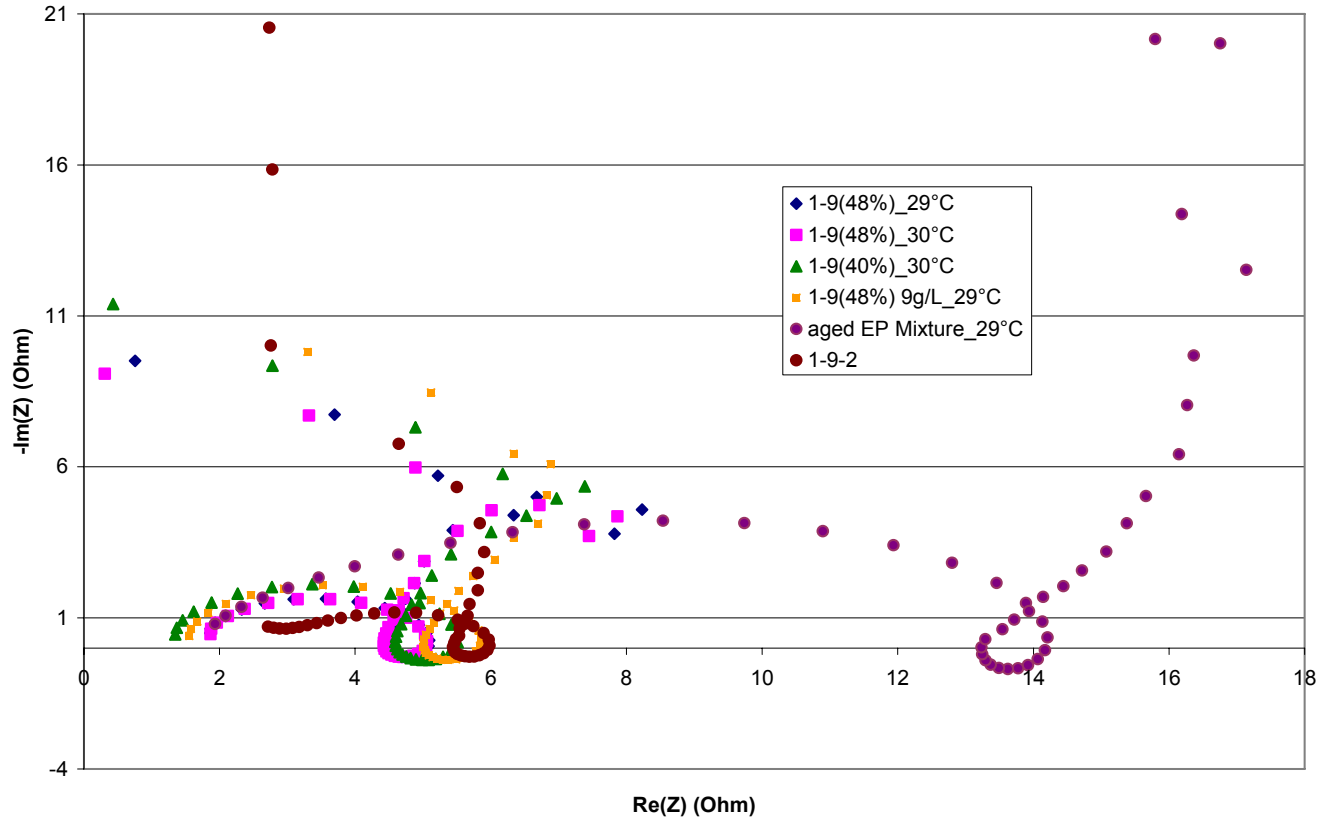
R_0 Resistance as a Function of the Potential for Different Mixtures.



The slope increases with the decreasing of HF/H₂O ratio: Signature of a porous film. Probable “duplex” structure of the surface film.

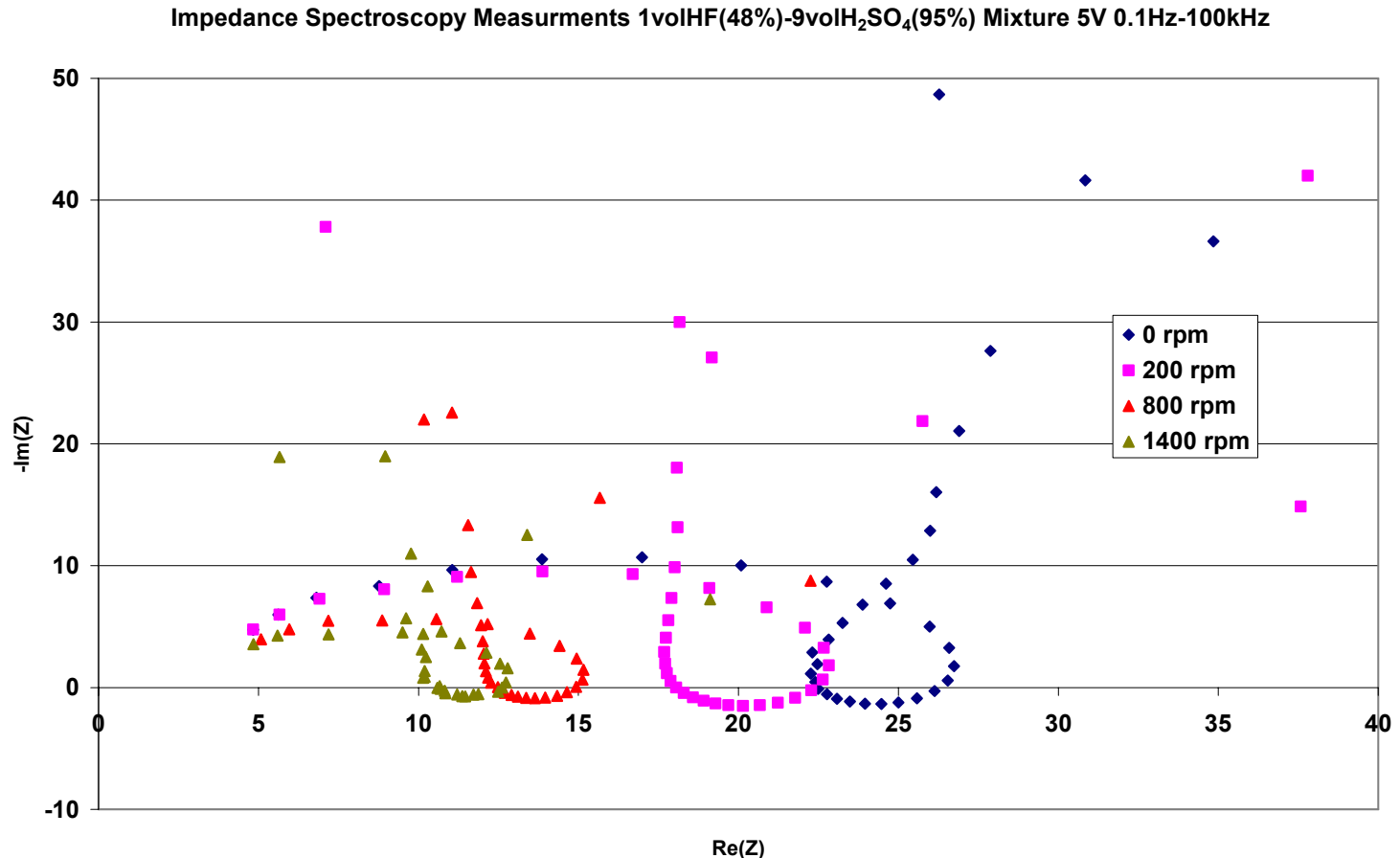
FEATURES DEPEND ON BATH COMPOSITION

EIS Diagrams for different EP Mixtures at 4.5 V Vs Ag/AgCl. Range 100kHz-0.1Hz.



A (cheap and easy) way to control the quality of the acid?

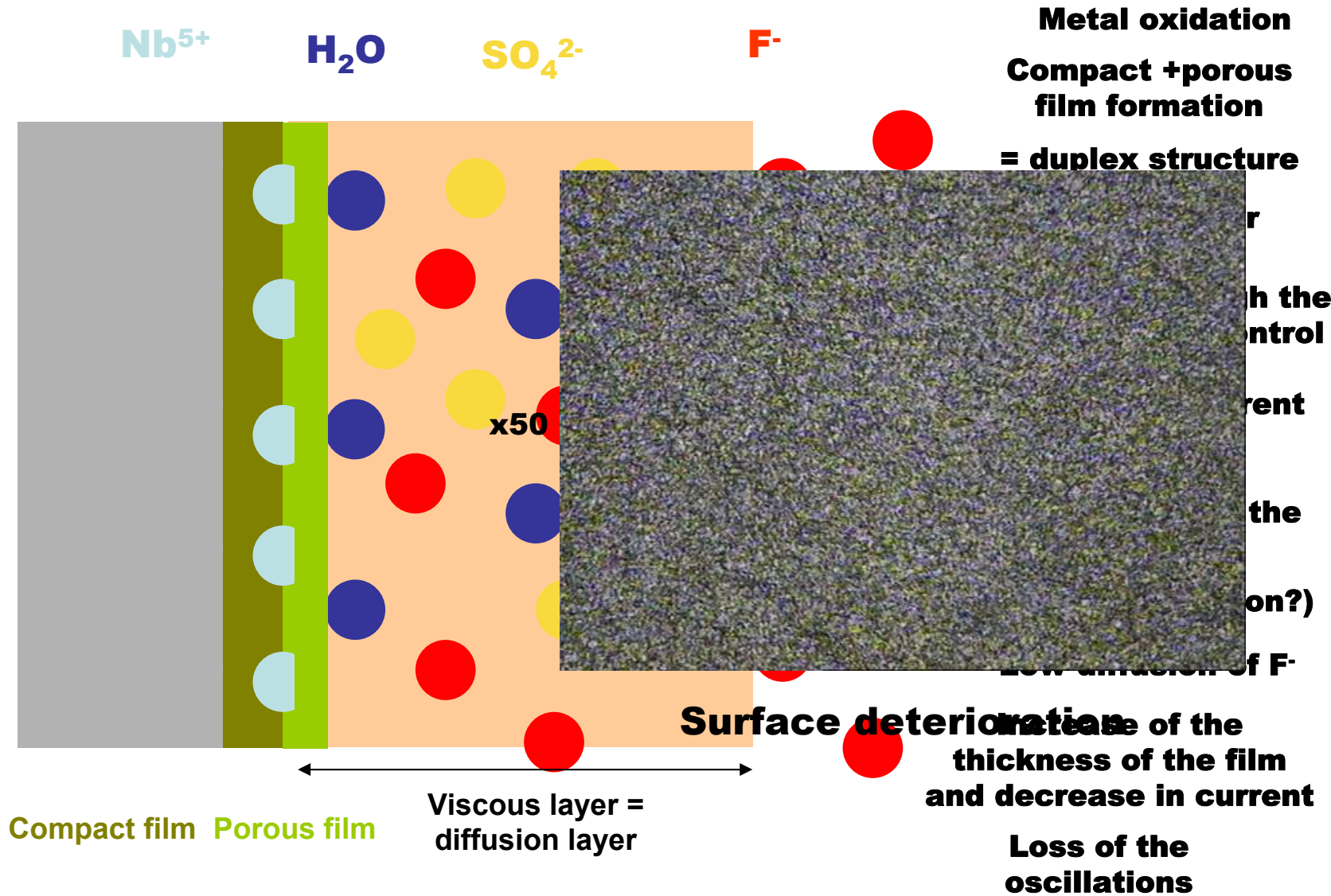
CONFIRMATION OF THE INFLUENCE OF THE DIFFUSION



R_1 depends on the electrode rotation: It is proportional to $\omega^{1/2}$!!!

IN ACCORDANCE WITH THE ADSORBATE ACCEPTOR MODEL

PROBABLE SCENARIO FOR Nb ELECTROPOLISHING



CONCLUSIONS

CHLOROFORM RINSING SEEMS PROMISING

LOW VOLTAGE ELECTRO-POLISHING GIVE GOOD RESULTS

- ✓ INTEREST FOR LOWER CONTAMINATION (On going experiment)
- ✓ NO NEED FOR A VISCOUS LAYER (=SURFACE LEVELLING) DURING EP (MORE DATA REQUIRED)

AMPEROMETRY AND IMPEDANCE SPECTROSCOPY GIVE PRECIOUS RESULTS

- ✓ PROCESS LIKELY TO BE LIMITED BY FLUORINE DIFFUSION IN PRESENCE OF A “DUPLEX” SURFACE FILM
- ✓ AFTER PROPER CALIBRATION, THESE TOOL COULD BE USED TO CONTROL THE QUALITY OF THE ACID.

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