2nd International Electronic Conference on Materials Science
2-16 May 2016
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Aluminium electrodeposition fron ionic liquid: effect of deposition temperature and sonication

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Ionic Liquids (ILs)

ILs are defined molten salts liquid at nearly room temperature (below 100°C). Their main features for electrochemical purposes are:

Advantages:

- Wide electrochemical window (4 – 6 V respect to 1,23 V of warter based electrolytes).
- High conducibility (Composed only by ionic species).
- Negligible vapour pressure.
- High thermal stability.
- Non flammable.

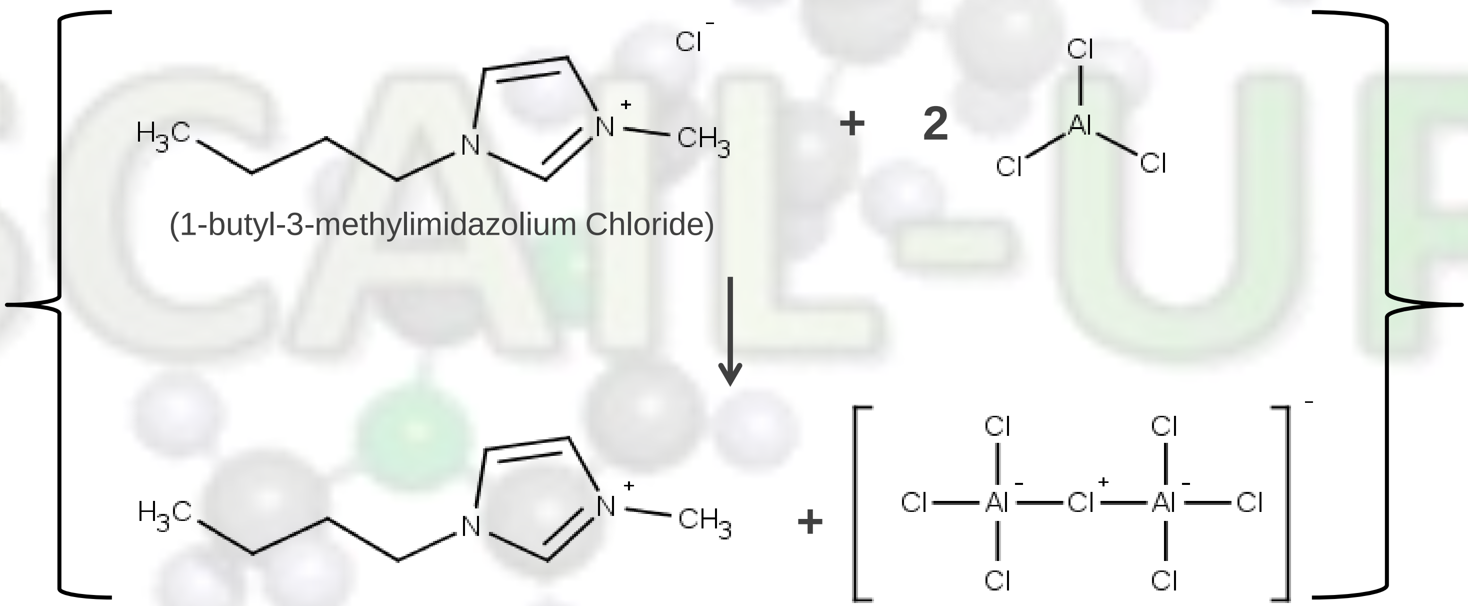
Drawbacks:

- Little knowledge of the processes and reactions witch regulate electrodeposition.
- Some ionic liquids are water sensitive (can develop gaseous HCl in contact with atmospheric moisture);
- High viscosity (slowing of the electrodeposition processes);

Chloroaluminate IL

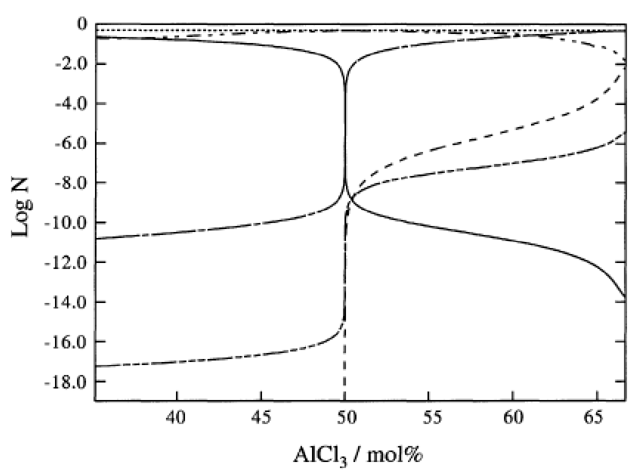
Chloroaluminate ionic liquids are, nowadays, the only way to safely obtain technical (thick) Al coatings via electrodeposition. The most widely used IL is the $AlCl_3$/1-butyl-3-methylimidazolium chloride ([Bmim]Cl) with a molar ratio between 1.5:1 to 2.5:1.

Formation of the electroactive species



The estimated composition of the main chemical species in the IL is:

- $Al_2Cl_7^-$ = 1.708 mol dm^{-3}
- $AlCl_4^-$ = 1.708 mol dm^{-3}
- $AlCl_3$ = 2.161 10^{-7}mol dm^{-3}



Distribution of chloroalluminated species to percentage of molar fraction: $AlCl_3$ a 60°C[3]

- __ : Cl^-
- _ . _ : $Al_2Cl_7^-$
- _ . . _ $AlCl_4^-$
- _ _ _ : Al_2Cl_6
- _ . . . _ : $AlCl_3$.

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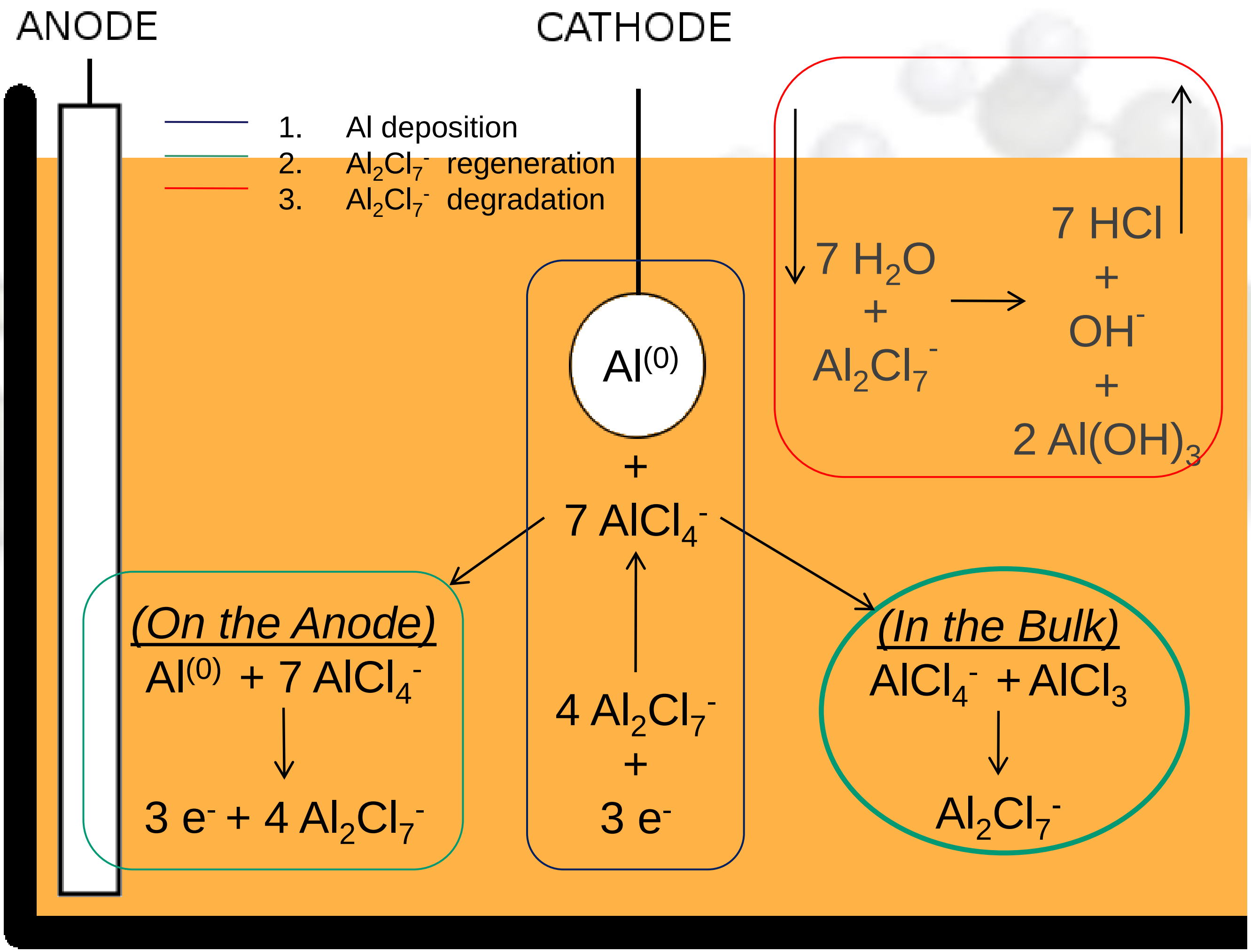
Reaction scheme



Work Plan 1

The aim of this research is to assess the influence of deposition parameters such as temperature and mixing, on the electrochemical process and the Al layers obtained.

Two series of sample produced

Deposition temperature
- 50° C
- 70° C
- 90° C

In a quiet bath

Electroplating solution mixing
- Quiet deposit
- Sonication 1 to 10 sec
- Sonication 1 to 1 sec

At room temperature

Qsonica Sonicator Q500 500W 20kHz

Experimental Set-Up

Cathode: Brass disk (40% Zn) ϕ 12 mm x h 3 mm

Glove Box
to prevent moisture contamination of the IL

Temperature test set-up:

- 25 ml beaker vessel;
- Cylindrical Al anode (ϕ 30 mm x h 50 mm)

Sonication test set-up:

- 500 ml liner vessel;
- Cylindrical Al anode (ϕ 85 mm x h 100 mm)

Electrodeposition Process

Galvanostatic depositions

- 10 mA/cm^2, 2 hours deposition;
- Four samples for each case

m_f^d = sample mass after deposition [g]

m_i^d = sample mass before deposition [g]

m_f^w = sample mass after wash-up [g]

a.m. = Atomic mass [g/mol]

Q_{tot} = Total deposition charge [C]

n = Al ox. number

F = Faraday constant (96485 C/mol)

$$\text{Yeld \%} = \frac{\text{Measured Mass} \cdot 100}{\text{Calc. Mass (Faraday eq.)}} = \frac{(m_f^w - m_i^d)}{\text{a.m.} \cdot Q_{tot} / \text{n} \cdot \text{F}}$$

$$\text{Measured Mass} = (m_f^w - m_i^d) = [m_f^d - m_i^d - (m_f^d - m_f^w)]$$

Cathodic efficiency ~100%, (for galvanostatic depositions made at less negative pot. than -1,1V). The **decrease in yeld** is mainly due to the dendritic deposit (dendritic crystals tend to fall off the sample during the after-deposition washing process) that detaches from the sample in the washup.

Temperature Samples	Yeld
50°C	~ 79 %
70°C	~ 86 %
90°C	~ 88 %

<u>*Temperature depositions:*</u>

▪ Similar yeld between samples due to absence of mechanical effect (low yeld caused by dendritic growth);

▪Small yeld increase with temp.increase due to the lowering of the IL viscosity.

Sonication Samples	Yeld
Quiet	~ 60 %
1 to 10	~ 100 %
1 to 1	~ 100 %

<u>*Sonication depositions:*</u>

▪ Quiet samples lose mass during wash-up process (due to dendritic growth);

▪ Mechanical effect breaks dendritic growth, granting yelds ~ 100%.

Temperature Samples

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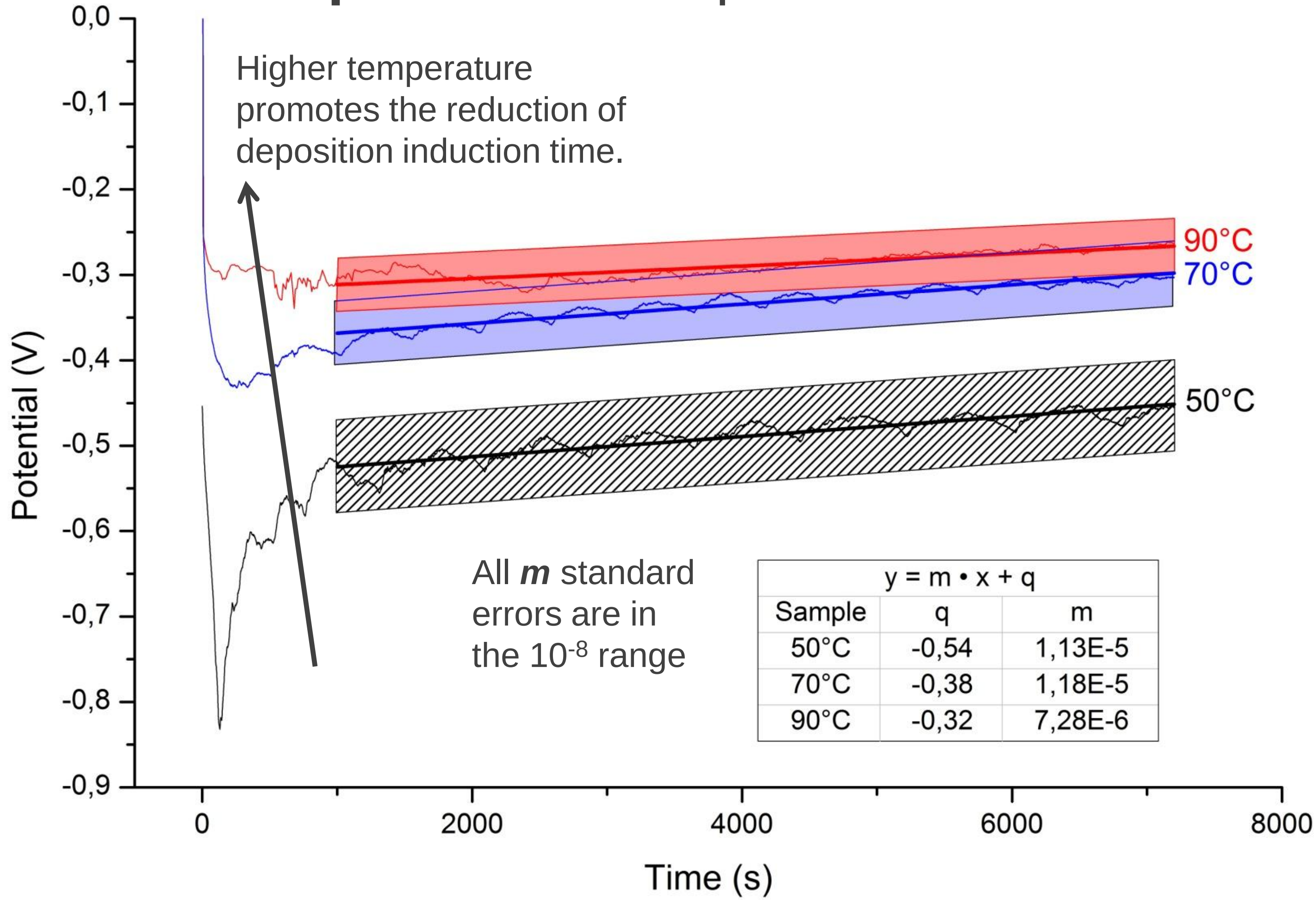
2007 - 2013

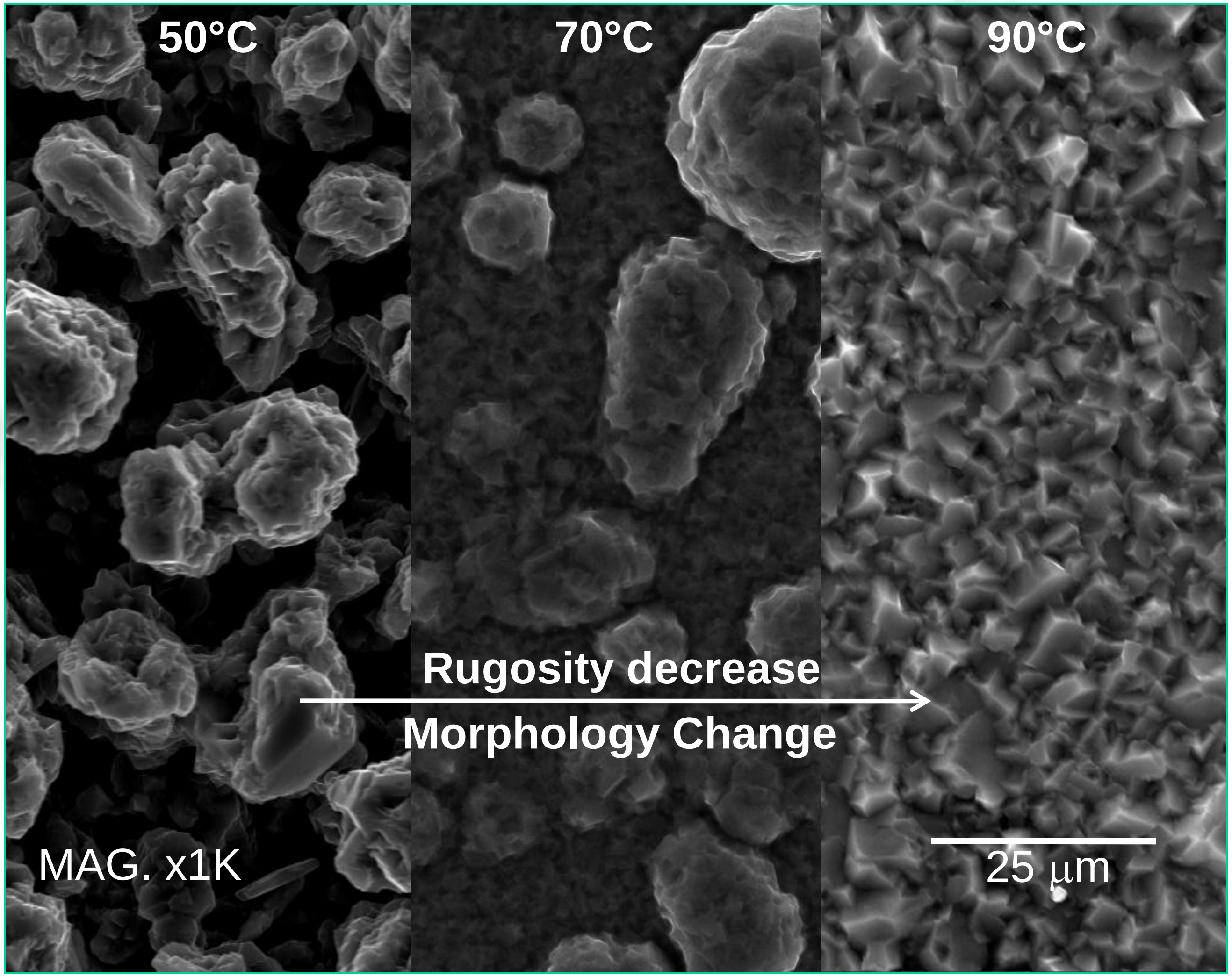
SCAIL-UP

Temperature Samples: Electrodeposition Process

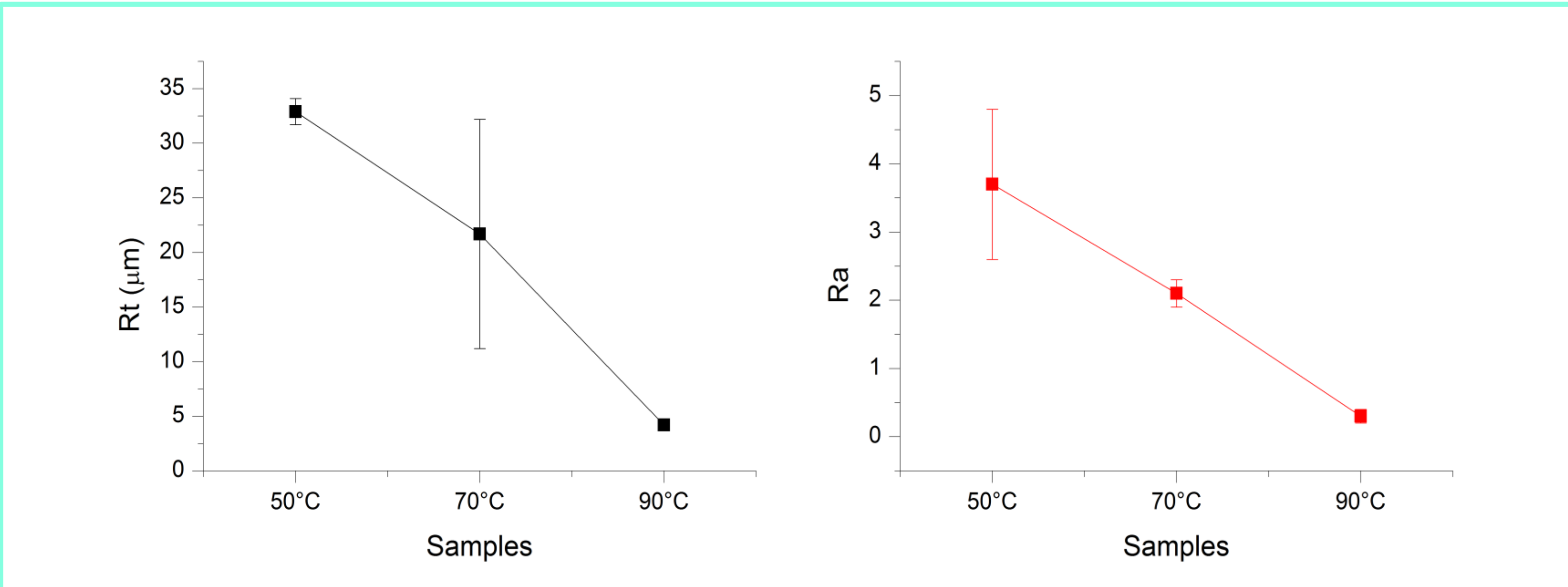


y = m • x + q		
Sample	q	m
50°C	-0,54	1,13E-5
70°C	-0,38	1,18E-5
90°C	-0,32	7,28E-6

Temperature Samples : SEM Morphology Investigation



Temperature Samples : Roughness Measurements



SEM and rugosimetry investigations indicate the reduction of the surface roughness as function of temperature. In accordance with previous investigation [1], larger number of nuclei are formed at higher temperature inhibiting the growth of larger cristals.

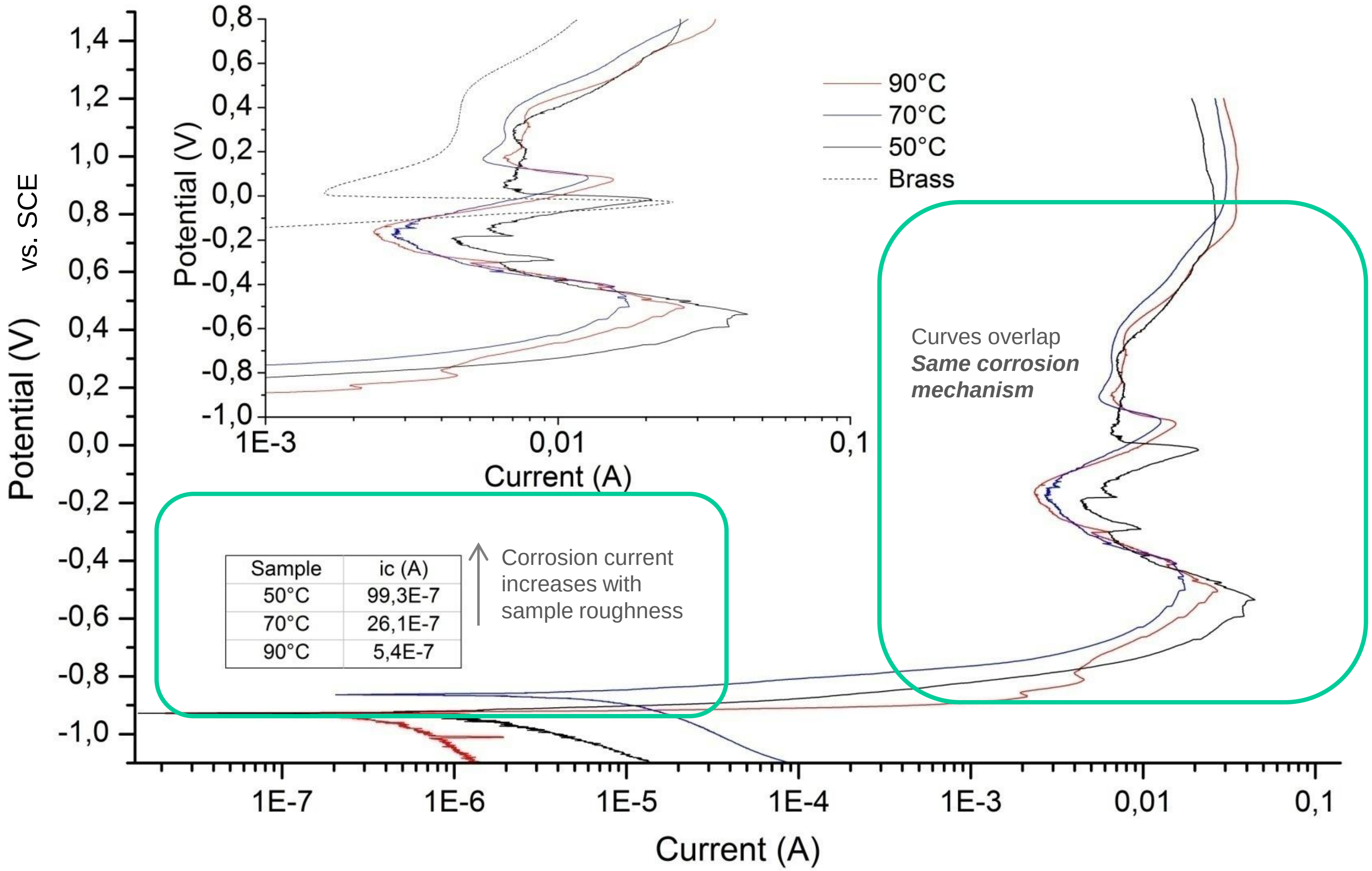
[1] G. Yue, X. Lu et alii. Chem. Engin. J. 147 (2009) 79-86

Temperature Samples : Corrosion behavior

(areated aqueous NaCl 3.5%)

OCP: from -0,80V to -0,95V (after 16 h)

POLARIZATION CURVE: From -0,25V OCP to 1,2V, 0,4mV/sec



Sample	ic (A)
50°C	99,3E-7
70°C	26,1E-7
90°C	5,4E-7

Sonication Samples

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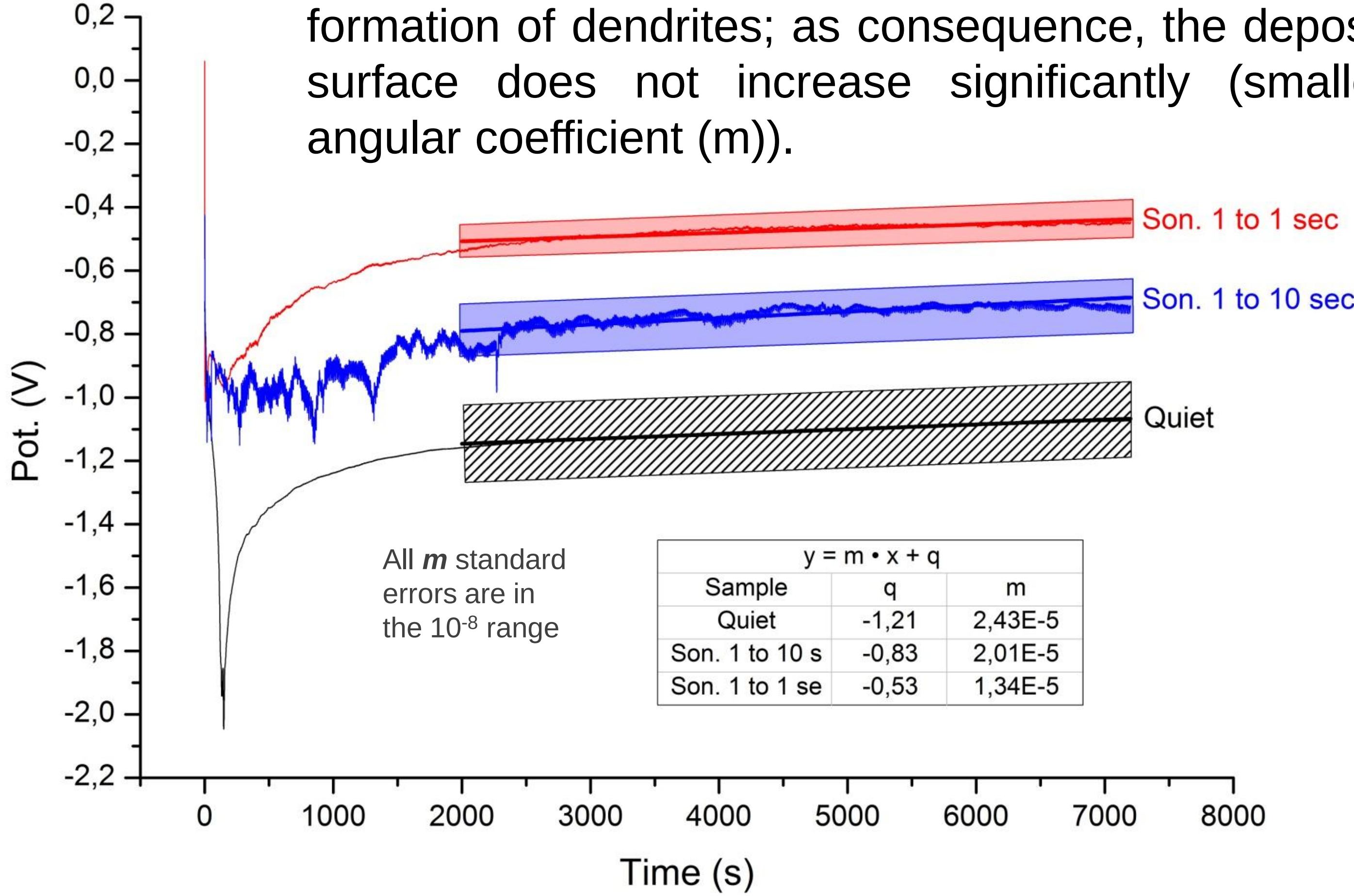
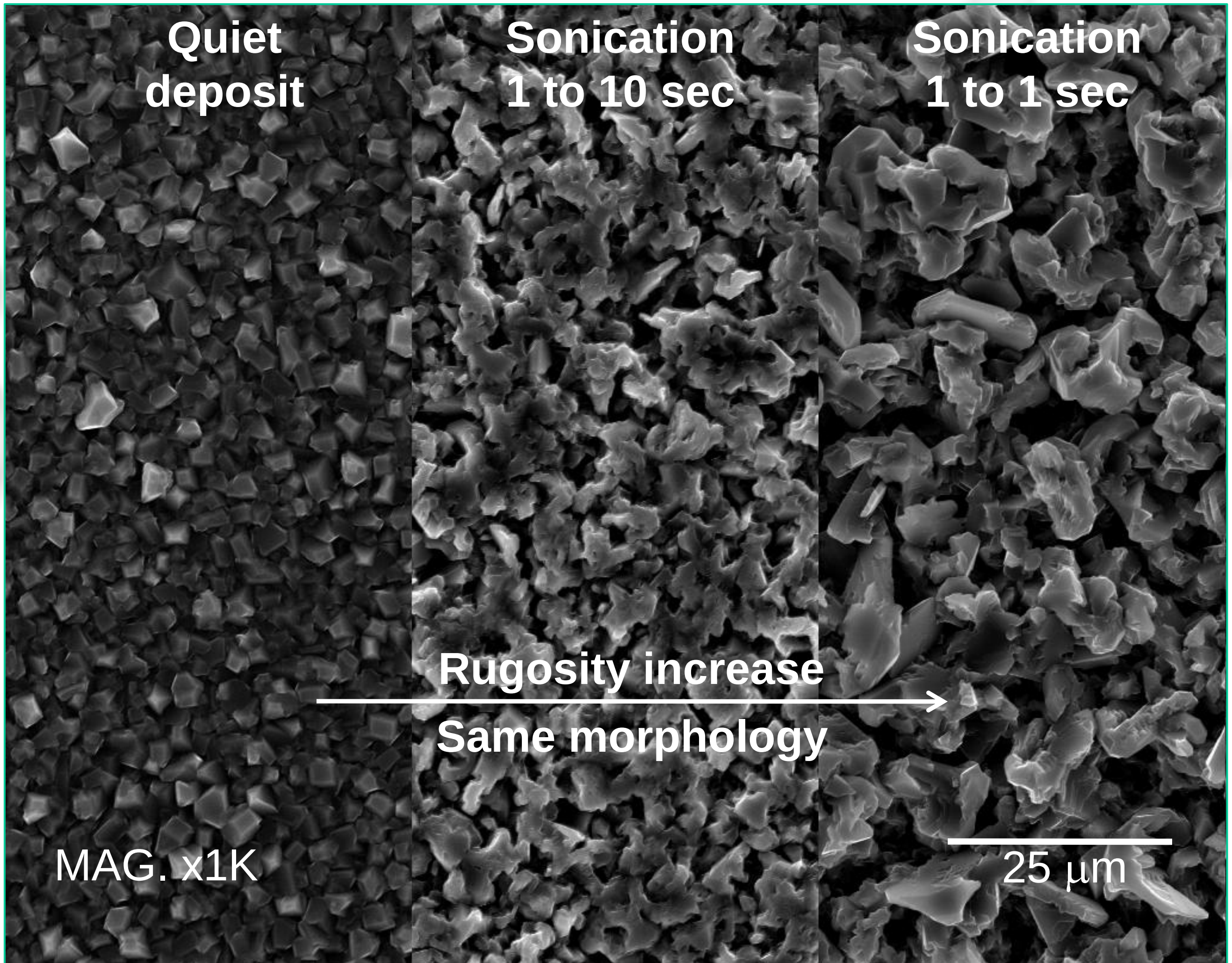
Sonication Samples: Electrodeposition Process

Respect to quiet solution, sonication reduces the formation of dendrites; as consequence, the deposit surface does not increase significantly (smaller angular coefficient (m)).

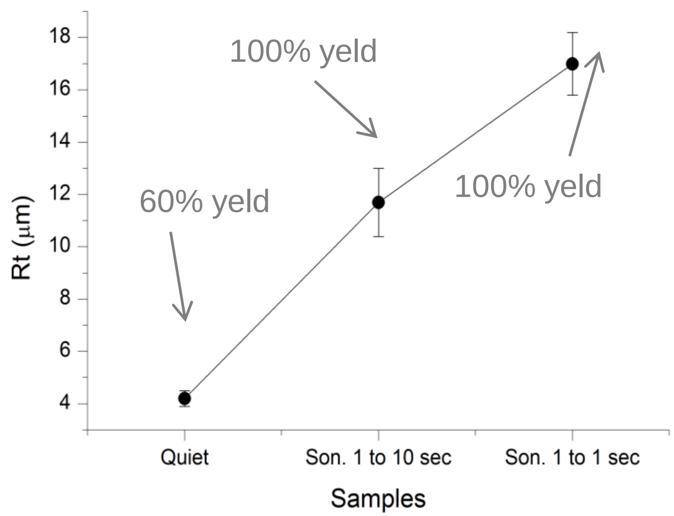


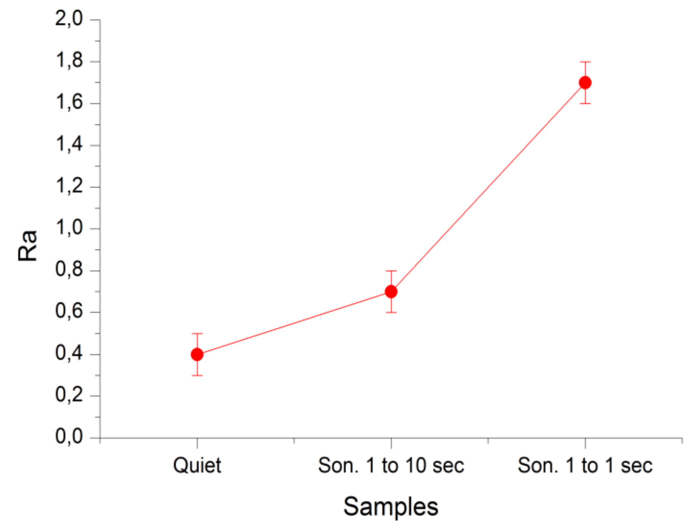
y = m • x + q		
Sample	q	m
Quiet	-1,21	2,43E-5
Son. 1 to 10 s	-0,83	2,01E-5
Son. 1 to 1 se	-0,53	1,34E-5

Sonication Samples : SEM Morphology Investigation



Sonication Samples : Roughness Measurements



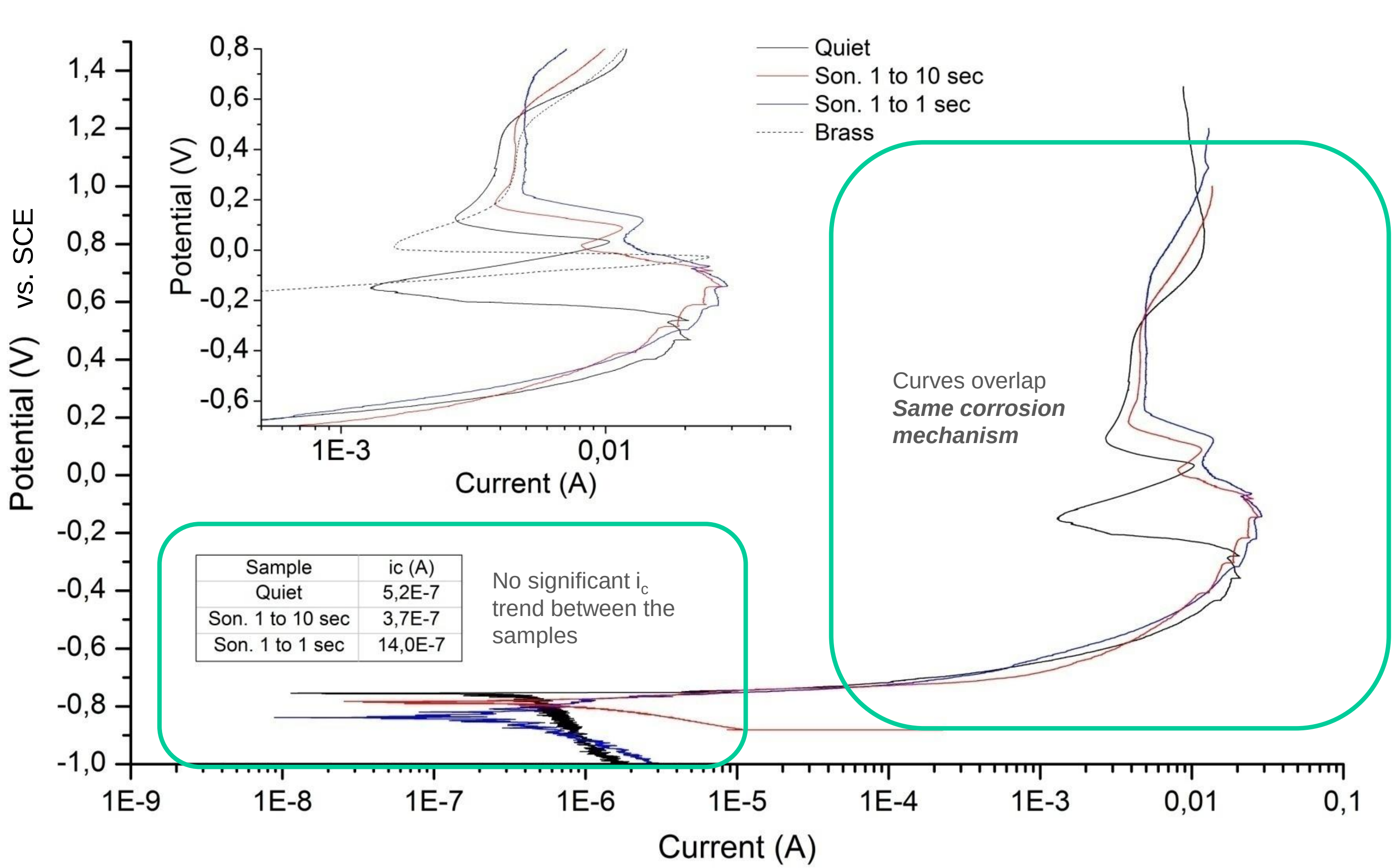


Roughness measurements confirm SEM observation demonstrating the increase of surface roughness as function of sonication. Respect to quiet solution the process yeld increases (no weight loss due to the formation of dendritic deposits).

Sonication Samples : Corrosion behavior

(areated aqueous NaCl 3.5%)

OCP: from -0,75V to -0,85V (after 16 h) ***POLARIZATION CURVE***: From -0,25V OCP to 1,2V, 0,4mV/sec



Sample	ic (A)
Quiet	5,2E-7
Son. 1 to 10 sec	3,7E-7
Son. 1 to 1 sec	14,0E-7

No relevant differences in the corrosion properties among the sonicated samples.

Synergic effect: Work Plan 2

In order to investigate the combined effect of temperature and mixing, a new set of depositions was performed combining the two.

A new experimental set-up was used:

- Bigger cathodes (ϕ = 25 mm x h 3 mm);
- Same vessel and anode used for the *sonication tests* in Work Plan 1 (a bigger tank was necessary to introduce the sonication horn in the bath);

- The used ionic liquid volume was 400 ml.

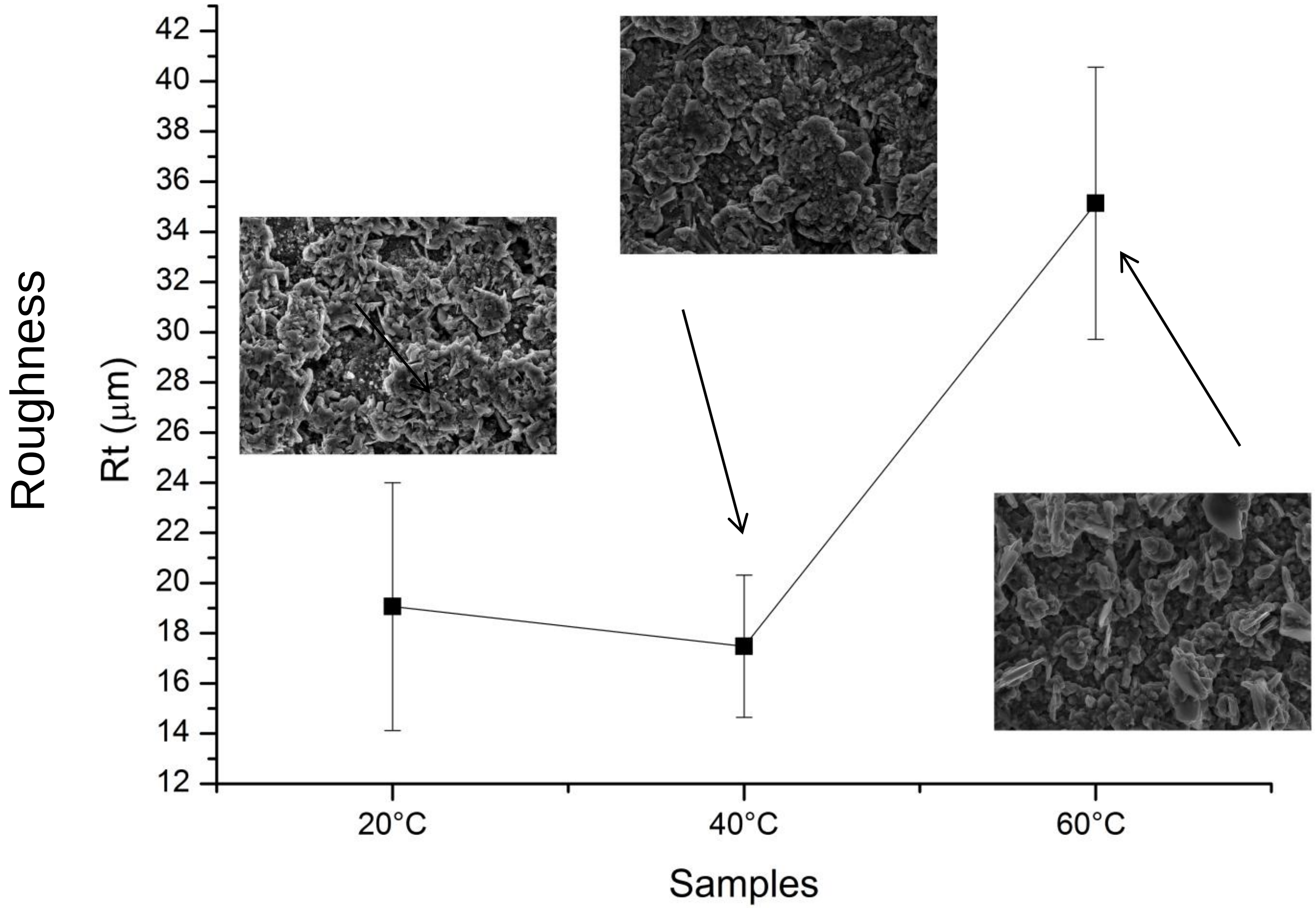
Depositions (galvanostatic conditions):

- 10 mA/cm^2 current density;
- Deposition time of 2 hours.

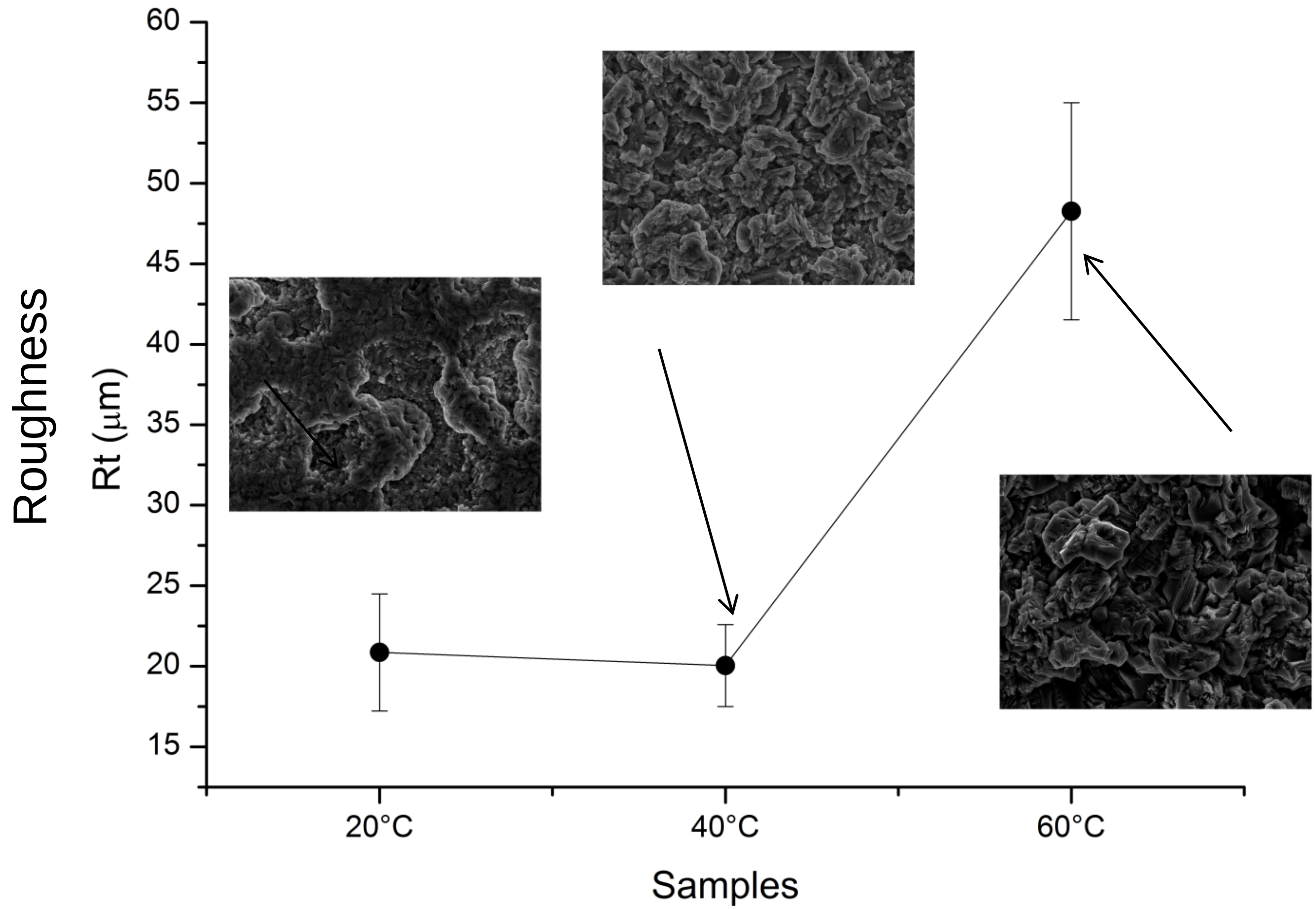
Preliminary depositions performed at T > 70°C returned bad quality deposits; may be due to the thermal degradation of the bath.

Also the use of high power sonication cycles (1 sec every 1 sec quiet) increases the rate of degradation of the IL.

Synergic effect : temperature + stirring



Synergic effect: temperature+Sonication 1:10 duty cycle



Synergic effect: Work Plan 2

Mixing \ Temperature	20°C	40°C	60°C
Quiet deposition	X	✓	✓
Mechanical mixing (320 RPM)	✓✓	✓✓	✓
Sonication 30% 1 sec every 10 sec quiet	✓✓	✓✓	✓

✓ = good
✓ ✓= very good

Similar results were obtained using mechanical stirring or sonication (duty cicle 1:10)
For temperature higher than 40 °C in both cases a steep increase of the crystal size is observed

CONCLUSIONS

Temperature Samples

DEPOSITS:

• Less negative deposition potential with increase in temperature (due to the increase of mobility of the species);
• The deposit roughness **decreases** as function of deposition temperature increase (SEM images, rugosity tests and deposition curves slope);
• Change in deposition morphology upon different temperatures.

Sonication Samples

DEPOSITS:

• Less negative deposition potential with increase in sonication frequency (due to the increase of mobility of the species);
• the deposit roughness **increases** as function of the increase of temperature (SEM images, rugosity tests and deposition curves slope);
• Higher Yelds (limited dendritic growth).

CORROSION TESTS:

• Corrosion current i_c increases with the increase of rugosity for temperature samples;
• Corrosion current i_c does not show relevant differences between sonication samples;
• Polarization tests show the same corrosion mechanism (pitting corrosion).

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