Report Short Term Mobility (STM)

ñIn situ electrochemical techniques for metal artworks conservationò

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The main goal of this STM plan was to better characterise and compare electrochemical measurements on metal surfaces of interest for Cultural Heritage (CH). The general setup considered were:

1. the one developed in Genoa: contact probe CP with a commercial cloth soaked with the electrolyte (Letardi 2004)
2. the one developed in Madrid: gel cell GP with gelled electrolyte (Ramìrez Barat 2015)

In order to not affect CH surfaces, low conductivity electrolytes should be used which can make the cell impedance not negligible (Chechirlian 1990), even though the reduced distances between Working Electrode (WE) and Reference electrode (Ref) and between Counter Electrode (CE) and Ref adopted with both setup 1 and 2 help to reduce the uncompensated electrolyte resistance.
Among others, AISI316 Stainless Steel has been recognised to be a stable and well characterised WE which makes its choice quite effective in order to focus on possible parasitic contributions of the different elements of the experimental setup on the measured impedance. To this end, quite an extensive measurements plan has been executed to address the possible influence of different choices on acquired spectra. The configurations considered were:

- a standard cell setup (STD), with a standard Ag/AgCl Reference Electrode (Ref) or a stainless steel pseudo-reference, and a mesh (m) or spiral (e) Counter Electrode (CE);
- the contact probe setup (CP), with the design developed in Genoa (ST15) and the one tested in Madrid (MD);
- the gel cell setup (GP), with a standard Ag/AgCl Reference Electrode (Ref) or a stainless steel pseudo-reference and Agar (A) or Agarose (AR) as gelling agent;

the measurement plan is summarised in Table 1.
Measurements both with the selected electrolyte (a ten-fold concentrated artificial rain (Letardi 2016)) and the 100x more concentrated one were acquired in order to better enlighten the role of low conductivity electrolyte on systems performance. The three setup compared are shown in figure 1. All measurement have been acquired with a Gamry Ref600 with the same sequence which consist in:
- Open circuit potential (OCP) measurement for 1800s
- Linear polarisation resistance (LPR) measurement from -10mV to +10mV around equilibrium OCP
- Open circuit potential (OCP) measurement for 300s
- Electrochemical Impedance Spectroscopy (EIS), in the range 100KHz-10mHz with ±10mV around equilibrium OCP

Several setup were measured more than once, in order to better characterise the differences among the three measurement cells compared to the repeatability of each one.
At a first glance, the different features which characterise measured spectra in the high frequency region may be attributed to the non negligible impedance of the experimental setup in the measured frequency range, which can then be characterised (Petrescu 2013). The identification of an appropriate model to describe and fit the measured data is under way. This would allow to get the information necessary to separate the electrochemical response of the systems of interest from the contribution of the measuring setup. Moreover setup improvements may be identified and/or the more appropriate setup to be used can be selected according to the system under examination.

Table 1 - measurements on AISI316 Stainless Steel

sample	filename	label	date	probe												electrolyte			Area [cm2]
				STD				GP						CP		Mineral Water [G]	Artificial Rain 10X [AR] n	Artificial Rain 1000X [AX]	
				Ref		CE		gel		Ref		CE							
				Ag/AgCl	Inox	m	e	A	AR	Ag/AgCl	Inox	m	e	ST15	MD				
AISI316 Stainless Steel	A04ND4-1STG	ACPG1	17/11/2016											x		x			2,3
	A04ND4-1STGrip	ACPG2	17/11/2016											x		x			2,3
	EISPOT_A04ND4-1	ACPG3	17/11/2016											x		x			2,3
	A04FJ32-1ASTARrip	ACPAR1	23/11/2016											x			x		2,3
	EISPOT_A04P2FJ32-1ASTAR	ACPAR2	23/11/2016											x			x		2,3
	EISPOT_A04P1FJ32-2STAR	ACPAR3	28/11/2016											x			x		2,0
	EISPOT_A04P3FJ32-2STAR	ACPAR4	28/11/2016											x			x		2,1
	EISPOT_A04CFJ32-2STAR	ACPAR5	28/11/2016											x			x		2,0
	EISPOT_A04P1FJ38-1STARx	ACPARX1	05/12/2016											x				x	*2,1*
	EISPOT_A04P2FJ38-1STARx	ACPARX2	05/12/2016											x				x	*2,1*
	EISPOT_A04P1FJ39-1CPMAR	ACPMAR1	07/12/2016												x		x		*2,8*
	EISPOT_A04B1FJ39-1CPMAR	ACPMAR2	07/12/2016												x		x		*2,5*
	EISPOT_A04P2STD-GPEmAR	AGPRAR1	02/12/2016					x		x		x					x		3,1
	EISPOT_A04B1GP-EmAR	AGPAR1	22/11/2016					x			x	x					x		3,1
	EISPOT_A04P1GP-EmAR	AGPAR2	02/12/2016					x			x	x					x		3,1
	EISPOT_A04B1GP-EmARx	AGPARX1	05/12/2016					x			x	x						x	3,1
	EISPOT_A04P3GP-EmARx	AGPARX2	05/12/2016					x			x	x						x	3,1
	EISPOT_A04CSTD-GPEmARx	AGPSARX1	09/12/2016					x		x		x						x	3,1
	EISPOT_A04P2STD-GPEmARx	AGPSARX2	09/12/2016					x		x		x						x	3,1
	EISPOT_A04GAP-EmAR	AGAAR1	23/11/2016						x		x	x					x		3,1
	EISPOT_A04P3GAPEmAR	AGAAR2	12/12/2016						x		x	x					x		3,1
	EISPOT_A04B1STD-GAPEmAR	AGASAR1	12/12/2016						x	x		x					x		3,1
	EISPOT_A04P3STD-GAPEmAR	AGASAR2	12/12/2016						x	x		x					x		3,1
	EISPOT_A04STDAR	ASReAR1	23/11/2016	x			x										x		2,8
	EISPOT_A04CSTDeAR	ASReAR2	01/12/2016	x			x										x		2,8
	EISPOT_A04STD-P-mAR	ASRIAR1	22/11/2016		x	x											x		2,8
	EISPOT_A04P2LIQAR	ASRIAR2	01/12/2016		x	x											x		2,8
	EISPOT_A04CSTDmAR	ASRAR1	01/12/2016	x		x											x		2,8
	EISPOT_A04CSTDARx	ASRARX1	05/12/2016	x		x												x	2,8
	EISPOT_A04CSTD-P-mARx	ASRIARX1	07/12/2016		x	x												x	2,8

Figure 1 - Measurement setup (from left to right): Standard Cell (STD); Gel Cell (GP); Contact Probe (CP).

To verify the model to be derived from AISI316 measurements on metal surfaces of interest for metal outdoor monuments, other coupon (Figure 2) have been measured; namely:
- Corten, naturally weathered in Madrid for 3 years
- Quaternary bronze, naturally weathered in Genoa for 18 months (Letardi 2016)
- Quaternary bronze with a brown foundry patina, naturally weathered for 16 months in Madrid
- Quaternary bronze with a brown foundry patina and coated with Incralac, naturally weathered for 16 months in Madrid.

The measurements sequence OCP-LPR-OCP-EIS has been used with both the Gel Cell (with Agar and pseudoref) and the Contact Probe (ST15).

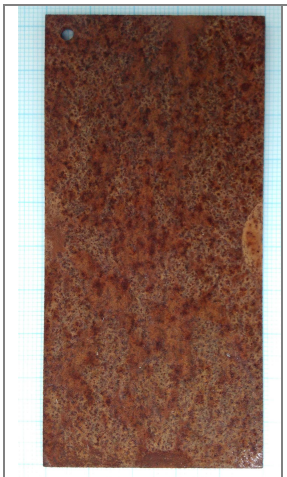	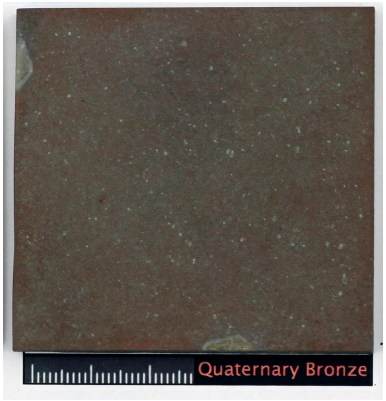		
Corten	Quaternary Bronze (Genoa)	Foundry patina	Foundry patina + coated

Figure 2 - test samples

For in situ measurements at the "Museo de escultura de Leganés"[1], two statues have been selected (figure 3) for a first comparison of results on bronze and steel statues:
- Segador, bronze
  (http://www.leganes.org/MuseoEsculturas/coleccionesf41b.html?id=10)
- Mediterranea III, stainless steel
  (http://www.leganes.org/MuseoEsculturas/colecciones7429.html?id=15)


Figure 3 - field measurements: El Segador, bronze (left); Mediterranea III, stainless steel (right)

On the bronze statue the WE contact was made on sound metal with alligator clip, while on the stainless steel one the WE contact was obtained through a pressure pin (figure 4).

[1] http://www.leganes.org/MuseoEsculturas/index-2.html


Figure 4 - WE contact methods: alligator clip on scratched hidden area on bronze (left); pressure pin on stainless steel (right)

Due to weather conditions and available time, only a couple of measurements were possible on each monument. Nonetheless, they were worth to both share the different skills developed for field measurements and a first comparison of results with GP and CP setup. Moreover, measurements on Mediterranea III looks quite similar to the ones obtained on AISI316 coupon, which give an even more value to the detailed analysis on the measurements listed in Tab.1.

During the stay at CENIM priority was given to the acquisition of joint measurements on several systems of interest for metal cultural heritage and to identify possible shared goals for future work. The next step will be:

- modelling of AISI316 measurements results and characterisation of parasitic impedance of the field measurements setup;
- further cooperation on cell design to allow both laboratories to work with both field measurements setup
- parallel exposure in Genoa and Madrid of four bronze coupons with foundry patina
- further cooperation on field measurements on monuments (acquisition and data analysis), with a special interest on bronze statues

Reference List

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