In situ EIS measurements on Colombian bronze statues

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***Abstract* – An *in situ* assessment of the conservation state of some bronze statues exposed outdoor has been carried out in Colombia, in the historical site surrounding the *Puente de Boyacá*. Electrochemical Impedance Spectroscopy (EIS) measurements have been performed by using a portable electrochemical interface and by using measuring probes, specifically designed to be capable of working also on slanted surfaces, to be non invasive, and to be removable without damaging the statues with the final aim of developing a long-lasting maintenance methodology for this important complex of Colombian bronze statues.**

I. INTRODUCTION

The *Campo de Boyacá* (the park of Boyacá), also known as *Puente de Boyacá* (the bridge of Boyacá) is an historical site located at 110 km east of Bogotá, crossing Teatinos river in Colombia.

This site gained a large popularity in Colombia as numerous monuments have been erected in the surroundings of a small bridge (the *Puente de Boyacá*) to commemorate the historic battle of 7th August 1819, known as the *Battle of Boyacá*, which granted independence to *New Granada*. The bridge was built in the early 18th century, and was dedicated as National Monument and memorial of independence in 1920. The other National Monuments present in the park are a triumphal arch, an obelisk and a flags square. Moreover, the metallic statue of Francisco de Paula Santander, the monument of Pedro Pascasio Martínez and, on the hill, the Von Miller Monument are also part of this important historical site.

The Von Miller Monument (Fig.1) is a bronze monument composed by five allegoric female figures, symbolic of Colombia, Venezuela, Peru, Ecuador and Bolivia, holding Simón Bolívar (1783-1830), the liberator from the Spanish government and the first president of *Gran Colombia*.

Fig. 1. Von Miller Monument at Puente de Boyacá.

The bronze statues of the Von Miller monument are apparently in a quite good conservation state even if tourists are allowed to climb the monument, risking of removing the surface patina grown on the metal by the interaction with the atmosphere. However, this anthropic damage is less important respect to the atmospheric conditions the statues are exposed to.

Actually, the monument is located at an altitude of about 2800 m and is exposed to a subtropical climate. In this geographical region, temperature remains all over the year in the range of 7°C to 17°C, with an alternation of more or less dry and rainy seasons, but with a high possibility of rain every day. In fact, the relative humidity can reach 90-100% every day all over the year, leaving the monument exposed to atmospheric corrosion in very aggressive conditions.

For these reasons, an *in situ* assessment of the conservation state of the Boyacá bronze statues exposed outdoor is mandatory to develop effective maintenance protocols and to ensure the long-time preservation of the monument. Electrochemical Impedance Spectroscopy (EIS) measurements were performed on several areas of the Von Miller Monument to assess the corrosion behaviour of the bronze statues and the protective effectiveness of the corrosion patina.

The *in situ* EIS monitoring campaign, still in progress, is performed in the frame of a Joint Project for the Internationalization of Research between Italy and Colombia, financially supported by Politecnico di Torino and Compagnia di San Paolo (Torino, Italy), in cooperation with the Antonio Nariño University (Bogotà, Colombia).

II. IN SITU EIS MEASUREMENTS

Electrochemical impedance spectroscopy (EIS) is a powerful technique, successfully employed for corrosion inspection and monitoring. EIS is commonly used to investigate the protecting properties of organic coatings, to study the corrosion mechanisms occurring on metallic surfaces and to estimate the corrosion rates without the risk of increasing it.

EIS consists in the measurement of amplitude and phase of surface impedance at different frequencies. The frequency is usually varied in the range of 0.01 Hz to 100 kHz, while the impedance values, expected in the range of few Ω to few GΩ, are correlated to the insulating and protective properties of the surface layer. Main advantage of EIS procedures is to stimulate the sample with very small alternating voltages, in the range of 5 to 50 mV, and currents that usually are below some microamperes [1,2,3,4]. Therefore, EIS can be considered a non-invasive measuring technique to obtain reliable information about the conservation state of metallic works of art and can help restorers and conservators in developing tailored conservation strategies. Moreover, having the possibility of using EIS *in situ* would open extremely interesting possibilities letting to evaluate the conservation state of outdoor non-movable artefacts, assessing their long time stability as a function of the exposure time to the atmosphere.

Performing EIS measurements *in situ* on historical artefacts requires the use of a portable electrochemical interface and specifically designed electrochemical cells in order to perform the measurement without damaging the metallic surface. Fig. 2 shows an example of measuring probe, described in details in [5] and specifically designed for *in situ* EIS measurements, both on horizontal and vertical surfaces. The probe made in acrylonitrile butadiene styrene by means of a 3D printer is designed to work as a two-electrodes electrochemical cell. The probe has an external diameter of 30 mm and a circular measuring area of 8 mm in diameter.

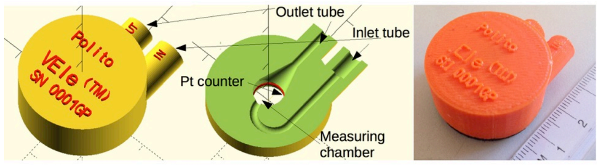

Fig. 2. Measuring probe for EIS in situ measurements designed at Politecnico di Torino.

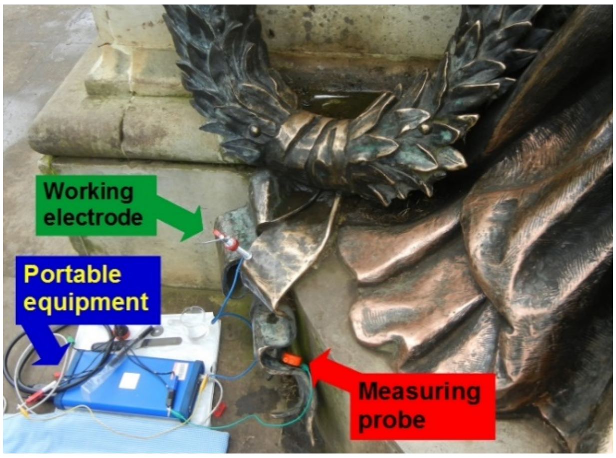

Fig. 3. EIS measuring set up on the Von Miller bronze monument at Puente de Boyacá.

The cell is equipped with a platinum (Pt) wire, which acts as reference/counter electrode, while the artefact is the working electrode. The probe can be attached to the metallic surface by means of tape, which allows easily removing it after the measurement. A soft foam disk insures the probe can attach also to not perfectly flat and rough surfaces. The cell can be filled up with mineral water or other low aggressive electrolytes to perform the measurements without accelerating the degradation of the metallic surface. The probe design with an inner curved pipe allows for measurements on slanted and even vertical surfaces thus letting to assess the surface conditions of most exposed artefacts.

III. EXPERIMENTAL DETAILS

EIS measurements were performed on different areas of the Von Miller Monument presenting different colorations, and so, probably different on-going corrosion processes and conservation state. All the investigated areas are located in the front of the monument, where also the anthropic damage is more probable and in different positions, both vertical and horizontal, to take into consideration different exposure to the rain.

Fig. 3 shows the portable EIS system (*Ivium CompactStat instrument*) and an example of the measuring set-up with a measuring probe in place. EIS measurements were performed on different areas; horizontal and vertical dark areas covered with a black patina, areas coated by green patinas and areas where the bronze fold appear shining. Fig. 4 shows as an example three measured areas with nearly horizontal and vertical orientation.

All measurements were performed in 0.1 M Na_2SO_4 solution to minimize the risk of any measurement-induced corrosion. Impedance measurements were eventually compared to assess the corrosion behaviour of the different areas and to correlate it to the environmental effects.

IV. RESULTS AND DISCUSSION

Fig. 5 shows the impedance data recorded on the four different surface areas. All traces are scaled to an equivalent area of 1 cm^2. The traces immediately show how the blue line, referring to the "black patina (v)" in vertical position exhibits rather high low frequency impedance (up to 10^7 Ωcm^2 at 0.1 Hz), associated to a phase value close to zero, i.e. to a nearly resistive value. Different behaviours are instead observed for the other areas exposed to the atmosphere ("black patina (h)" in horizontal position, "green patina (a)" and "green patina (f)" in a bronze fold). All traces have similar low frequency impedance values, lower than in the previous case (up to 10^4 Ωcm^2 at 0.1 Hz) and associated to a higher phase values (50 degrees) suggesting the presence of corrosion products layers characterised by micro-porous phases.

The electrochemical behaviour of the " black patina (v)", which resembles a capacitor-*like* behaviour, can be correlated to the presence of a protective coating on the bronze substrate. In facts, according to the restorers, the monument was in the past treated several times with protective film based on acrylic resins. Since this measuring area is in a vertical position, it is less affected by the anthropic damage, so that the coating is still compact and capable of protecting the metallic substrate.

On the contrary, the other "black patina (h)" horizontally positioned and characterised by a lower impedance has probably the coating damaged possibly because it is more exposed to the abrasive action of the tourists that climb the monument to take pictures. The recorded phase, which suggests the presence of porosities in the surface layer corroborates this hypothesis raining a warning on the possible long time protective effectiveness of the polymeric coating.

Similar impedance is also characterising the other areas coated by a green patina: also in these cases the lower impedance and the phase suggest the possibility of a not really-effective protecting coatings characterised by porosities or small defects. These areas are directly exposed to the atmosphere and present a greenish colouring even though one of them is partially hidden in a bronze fold: the impedance measurements allow one to predict a lower protective effectiveness of the patina towards aggressive agents.

All these experimental findings indicate that, where the protective coating originally used to protect the bronze is

(a)

(b)

(c)

Fig. 4. Pictures of three areas analyzed by EIS with the two-electrode probe: (a) green area directly exposed to the atmosphere; (b) green area in a bronze fold; (c) black area in a vertical position.

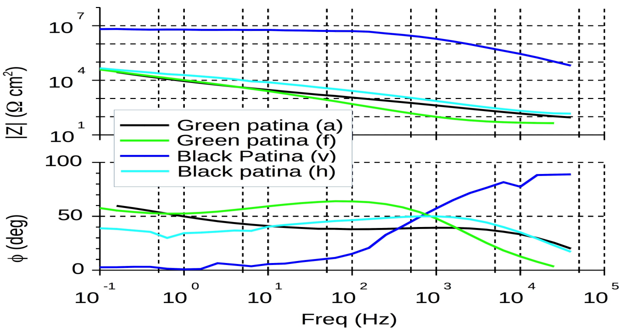

Fig. 5. EIS spectra collected on the Von Miller monument, by using a 0.1 M Na_2SO_4 solution on the four different measuring areas.

still present, no on-going corrosion process may be detected and the metal is protected. This is mainly true in areas where no anthropic related degradation is present and no water stagnation occurs like in either vertical of highly slanted surfaces.

On the contrary, in other areas either more affected by water stagnation and/or the anthropic behaviour, the protecting coating is damaged and its protective capability very poor. Specifically, the probable presence of porous behaviour may trigger the risk that corrosion processes with different corrosion rates are occurring.

The measuring campaign is still in progress both to confirm these preliminary results and to assess the corrosion behaviour of the bronze statues as a function of the exposure time to atmospheric corrosion. In addition, the EIS monitoring performed as a function of the exposure time should be important to highlight either further degradation of the protecting coating and damages of the corrosion patinas.

V. CONCLUSIONS

In this study, a portable Electrochemical Impedance spectroscopy (EIS) and specifically designed measuring probes were used to asses *in situ* the conservation state of the bronze statue of the Von Miller Monument located at the *Puente de Boyacá* in Colombia. This monument is exposed outdoor and is affected by very aggressive climatic conditions and anthropic behaviour.

The corrosion behaviour of different areas located in different positions and coated by different corrosion patinas and protective coatings where compared.

Preliminary results show that, where the protective coatings are still present, no corrosion processes were detected. On the contrary, the areas more exposed to the climatic and anthropic stress, present different on-going corrosion processes, due to the presence of damaged protective coatings as well as to the presence of green patinas formed by corrosion process still on-going and characterised by low protective effectiveness.

In conclusion, the EIS system used in the monitoring campaign in the *Puente de Boyacá* confirms to be a powerful device for *in situ* assessment of the conservation state of large unmovable metallic artefacts, such as the Colombian Von Miller National Monument.

These preliminary results will be utilized for the development of a maintenance program of the monument, in cooperation with the Colombian Ministry of Culture.

VI . ACKNOWLEDGEMENTS

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