IMEKO International Conference on
Metrology for Archaeology and Cultural Heritage
Lecce, Italy, October 23-25, 2017

Electrochemical measurements and microscopy on hybrid coatings for metallic artefacts

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Abstract **– Electrochemical Impedance Spectroscopy and Scanning ElectroChemical Microscopy are employed to characterize innovative hybrid coatings, which can be proposed for the corrosion protection of cultural metallic artefacts. In this paper hybrid TEOS and Graphene Oxide epoxy coatings have been tested in view of their possible employment as protective coatings for archaeological iron artefacts. The coatings have been deposited on low carbon steel and exposed to aggressive solutions. The performance of EIS and ElectroChemical Microscopy have been compared with the final aim of investigating if the proposed measuring approaches can easily give useful results to help the restorers in the choice of the conservation methodology. Comparing results from the two techniques can give a deeper knowledge of the coating performance and of their degradation mechanism.**

I. INTRODUCTION

Protecting metallic artefacts from corrosion is an issue of paramount importance in cultural heritage preservation. The most common way to achieve a protection with respect to an aggressive environment is to apply on the artefact surface a coating able to act as a barrier against the aggressive agents.

Polymeric coatings are the most common solution with many favourable characteristics and nowadays highly performing products are either already available on the market or under investigation in order to fit the main requirements of archaeologists and restorers, such as coating transparency, high corrosion protection, high chemical stability and reversibility.

Thus one important need for researchers working in this field is to have instruments and measurement procedures that can easily be used to allow assessing the coating protective effectiveness and collecting information on the coating failure mechanisms.

A traditional tool is Electrochemical Impedance Spectroscopy (EIS), used so as to quantify the protection effectiveness of organic coatings for industrial applications [1]. The specimen (the metal of interest coated with the paint under investigation) is placed in an electrochemical cell and EIS measurements are performed at regular intervals as a function of the exposure time to an aggressive solution. In this way it is possible to simulate an accelerated degradation of the materials under study. The EIS technique has several advantages, such as the possibility to perform the measurements by applying a very low signal without accelerating the corrosion of the metallic substrate. However, its main limit is that EIS measurements are usually performed on a large surface area, so the measurement response is affected also by the presence of small defects. A small leak in the polymer film can drastically reduce the measured impedance, even though the overall behaviour of the coating is still good [2].

Another relatively new technique for the characterization of polymeric coatings is the Scanning ElectroChemical Microscopy (SECM) [3-4]. With this technique, a probe scans the surface detecting oxidation reactions occurring on the sample surface. A variation in the current profile measured by the instrument is a clue of a degradation of the protective coating. In this way, single small defects can be detected and the coating electrochemical behaviour could be monitored as a function of the immersion time in the electrolytic solution, having information also on the degradation mechanism.

Aim of this research work is to compare the measurements carried out with these two techniques in order to fully characterize two different coating typologies. The investigated coatings are hybrid epoxy networks filled respectively with TEOS (tetraethoxysilane) and with Graphene Oxide.

Several studies have been performed on hybrid coatings and they have demonstrated an improvement in thermal properties (increase of glass transition temperature), mechanical properties (superficial hardness and scratch resistance) and barrier properties (e.g. water vapour transmission rate) [5-7] of the polymer due thanks to the filler addition. The idea is therefore to observe how the

addition can increase the corrosion resistance to assess if these coatings could be used also in the corrosion protection field.

Previous literature works highlighted that the coating properties changes are related to the presence of the nanometric filler inside the polymeric matrix. Therefore it is expected that the diffusion paths that external agents have to follow to reach the metal surface is increased, and the diffusivity is decreased. This is particularly true for the graphene oxide coatings, as this filler has a lamellar structure that favours this behaviour [7]. Moreover, it should be underlined that the weight percentage of filler is so low to guarantee the coating optical transparency.

This study has been developed in the framework 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. EXPERIMENTAL DETAILS

The material used as the substrate was low carbon steel (Q-Panel Standard Test Substrate purchased from Q-Lab). Three different coatings have been tested: two of them containing TEOS (purchased from Alfa Aesar) in different weight percentages (15wt% and 30wt%) and one containing Graphene Oxide (0.05 wt%).

The epoxy resin (3,4-epoxycyclohexylmethyl - 3', 4' - epoxycyclohexyl carboxylate - CE purchased from Sigma-Aldrich) was mixed with the photoinitiator (Irgacure 250 by Basf) and the respective fillers in order to prepare the coating.

The coating was then spread on the substrate with a wire-wound rod in order control the film thickness and UV-irradiated for 2 min to cure the thermosetting resin. Samples coated with the TEOS formulation underwent a heat treatment to complete the sol-gel reactions [8].

Coated samples were characterized by means of EIS, SECM and SEM (Scanning Electron Microscopy) in order to investigate their corrosion protective effectiveness.

EIS measurements were performed in a conventional electrochemical cell filled with 0.1 M NaCl (sodium chloride) aerated solution. An Ag/AgCl electrode was used as the reference electrode. The measurements were performed in the range of 0.01 Hz to 100 kHz and with an applied voltage of 100 mVpp to stress the coating similarly to the SECM analysis described below. The exposed area was of about 0.8 cm^2; all the results were scaled to the equivalent area of 1cm^2.

SECM analysis, were carried out in 0.1 M KCl (potassium chloride) and 5 mM $K_4Fe(CN)_6 \cdot 3H_2O$ (potassium ferrocyanide**)** solution. The measuring cell was composed of the tip (set as working electrode), the reference electrode (Ag/AgCl electrode) and the counter electrode (Pt wire). The tip was positioned at a distance of 10 µm (equal to the tip diameter) from the sample surface.

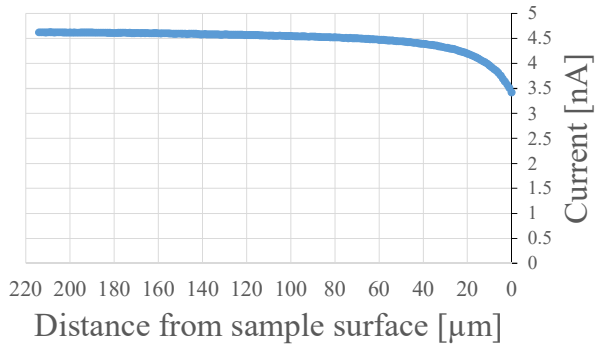

Fig. 1 – Line-scan with SECM approaching the sample surface.

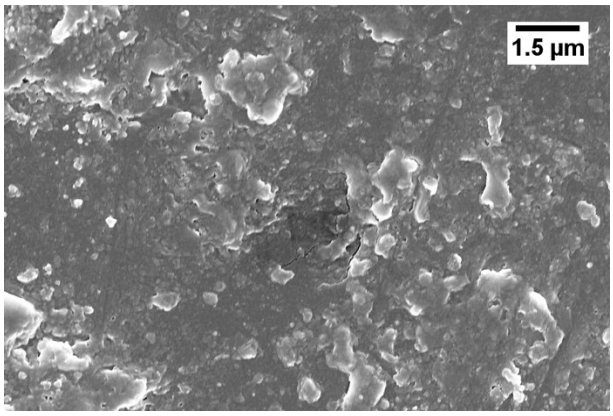

Fig. 2 - SEM micrograph of the 15 wt% TEOS hybrid coating after 96h of exposure to the 0.1M NaCl solution.

This was detected with a vertical line-scan in feedback mode as the height at which a 25% reduction of the current was measured by the probe respect to the value in bulk solution (see Fig. 1).

The tip was set at a potential of 0.5 V respect to the Ag/AgCl reference electrode. The current that is measured between working and counter electrode is due to the oxidation reactions inside the solution:

$$Fe(CN)_6^{4-} \leftrightarrow Fe(CN)_6^{3-} + e^-$$

Actually, being the sample non-conductive, approaching the surface, oxidation reactions are limited by the limited diffusion of new species near the tip, so the current measured decreases [9].

SECM measurements were performed on areas of 500x500 µm.

III. RESULTS AND DISCUSSION

Firstly, the coated samples were characterised by electrochemical impedance spectroscopy and scanning electron microscopy. Each specimen was placed in the electrochemical cell and the measures were performed every 24h for 5 days in order to assess the coating stability. The coating morphology was observed before and after the

electrochemical test.

Fig. 2 shows as an example the morphology of the 15 wt% TEOS coating after 96 hours of immersion in the chloride containing solution, while the EIS spectra collected on the different coating formulations as a function of the immersion time are shown in Figs. 3-5.

From the EIS plots, it can be observed that all coating formulations show a typical R-C (resistive-capacitive) behaviour. In all cases the impedance modulus, |Z|, reaches values up to 10^7, indicating the good protective effectiveness of the hybrid coatings towards the aggressive environment. Moreover, the electrochemical behaviour remains almost stable during the 5 days of immersion in the aggressive solution.

An increase in the impedance values can be observed after 24h of exposure, but this effect can be mainly attributed to the stabilization of the sample electrochemical potential in the electrolyte. The SEM micrographs, at the end of the EIS measurements, put in evidence only a slight degradation of the polymeric matrix in correspondence of some clusters of the filler, which aggregate during the film deposition, as it is possible to observe in Fig.2.

SECM was employed to investigate the coating evolution during the immersion time in the aggressive environment. The dimension of the scanned surface was chosen in order to have an analysed area representative of the coating morphology and to take also into account the effect of the coating roughness. As a matter of facts, since the scans were performed at a constant distance between the tip and the sample surface, it should be avoided that the tip comes in contact with the sample damaging the coating. A scanned area of 500x500 µm and a distance of 10 µm between the tip and the specimen surface are a good compromise.

Interesting differences in the behaviour of the different coatings were observed. In particular, a different behaviour was observed between the 15wt% TEOS hybrid coating and the epoxy film filled with graphene oxide. Actually it was noticed that in the first case, the presence of a defect led to an increase of its dimension during time (see Fig. 6). On the other case, the coating showed to be more stable.

As can be observed in Fig. 7, the coating defect, revealed by a localized decrease of the current in the SECM map, didn't increase in dimension during the exposure time to the electrolyte solution. This result is consistent with other long time EIS measurements already performed [10], which showed a constant impedance modulus even over longer periods of immersion in the aggressive electrolyte (up to 3 weeks).

In order to confirm this behaviour, the SECM measurements were performed in two areas for each sample and on different samples of the same formulation.

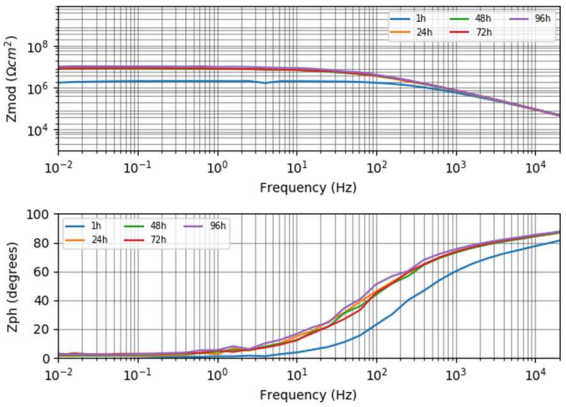

Fig. 3 - EIS spectra for 15 wt% TEOS hybrid coating.

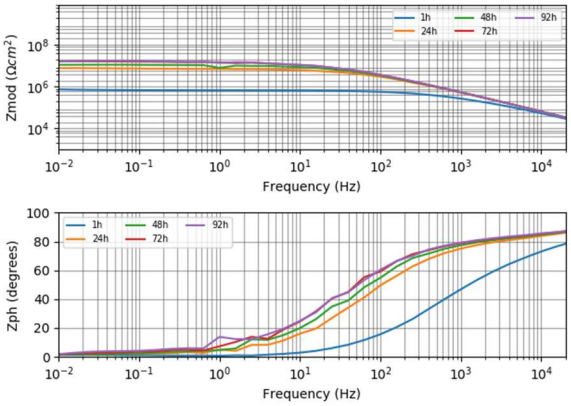

Fig. 4 - EIS spectra for 30 wt% TEOS hybrid coating.

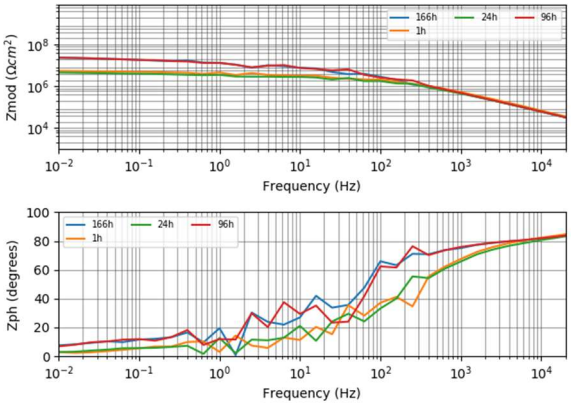

Fig. 5 - EIS spectra for Graphene Oxide hybrid coating.

Even if the SECM measurement is localized in a small area and therefore could be susceptible of punctual modifications of the coating surface (often the coating is not completely homogeneous), a good agreement between the results obtained by means of the different tests was found.

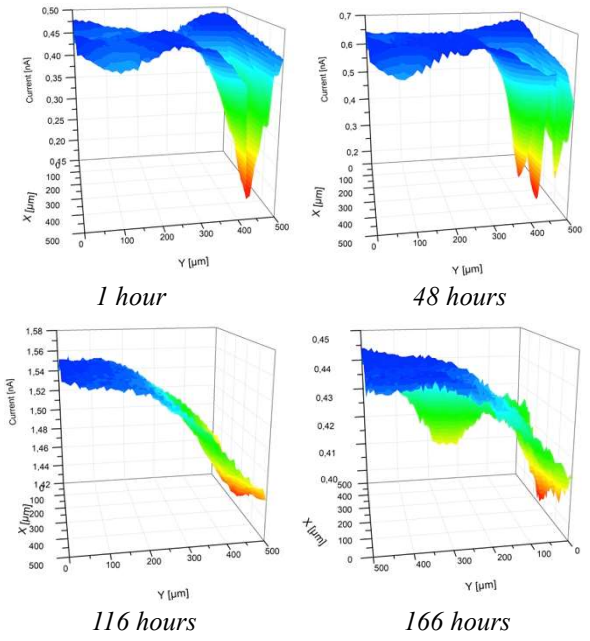

Fig. 6- SECM graphs for 15 wt% TEOS sample

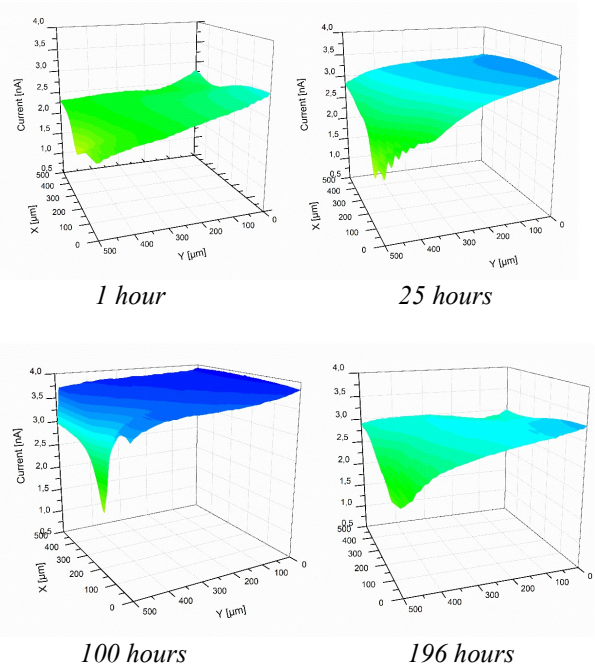

Fig.7-SECM graphs for 0,05wt%Graphene Oxide sample

IV. CONCLUSIONS

Aim of this study was to characterize the corrosion resistance behaviour of two novel hybrid coatings with possible applications in protection of cultural heritage. Electrochemical tests carried out over one week of immersion in an electrochemical cell gave interesting results. All coatings exhibited a good protective behaviour for the metallic substrate, as highlighted by the EIS tests. None of the coatings degraded during the measurements.

SECM measurements, allowed one to observe that coatings containing graphene oxide had a better performance. For the graphene loaded coatings, the presence of defects, probably due to the coating realization process, was better withstood by the coating, as the defect size did not increase during exposure. On the contrary, the defect size increased for coatings containing TEOS.

These results are a promising starting point for further studies on these kind of hybrid coatings for protection of metallic artefacts.

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