MODIFICATION OF BRONZE SURFACE BY SELF-ASSEMBLED MONOLAYERS OF LONG-CHAIN ORGANIC ACIDS

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INTRODUCTION

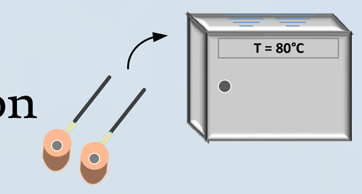
The corrosion protection of the bronze cultural heritage is a special challenge due to the specific conservation and restoration requirements. Since the toxic agents are often used for its protection, it is of great importance to find an efficient, long-lasting, economical and environmentally friendly protection system. One of the possibilities of protection is the modification of the surface by self-assembled monolayers (SAMs) of organic acids. Long-chain organic acids can form SAMs by adsorption of the adhesion group on the surface of the substrate, and long alkyl chains represent a barrier to diffusion of aggressive ions to the metal surface. The final group determines the layer properties.

The aim of this work is to examine the possibility of protecting bronze art from corrosion by SAMs of 16-phosphonohexadecanoic (COOH-PA) acid prepared by different techniques: dip-coating and spraying. The protective properties of such formed monolayers are examined in artificial urban rain (containing 0,2 g/L $NaHCO_3$ + 0,2 g/L $NaNO_3$ + 0,2 g/L Na_2SO_4, adjusted to pH 5 with 2 M H_2SO_4) by electrochemical polarization methods and electrochemical impedance spectroscopy while the structure of the film is determined by Fourier transform infrared spectroscopy.

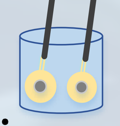
EXPERIMENTAL

SAMPLE PREPARATION

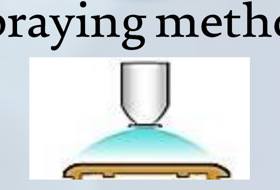
1. Oxidation



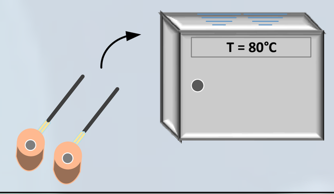
2. COOH-PA film deposition
   a) Dip-coating method



   b) Spraying method

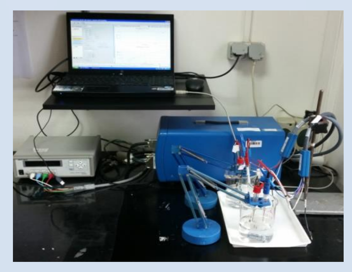


3. Drying



ELECTROCHEMICAL MEASUREMENTS

- Linear polarization
- Tafel extrapolation
- Electrochemical impedance spectroscopy (EIS)



SURFACE STUDIES

- Fourier transform infrared spectroscopy

RESULTS

ELECTROCHEMICAL MEASUREMENTS

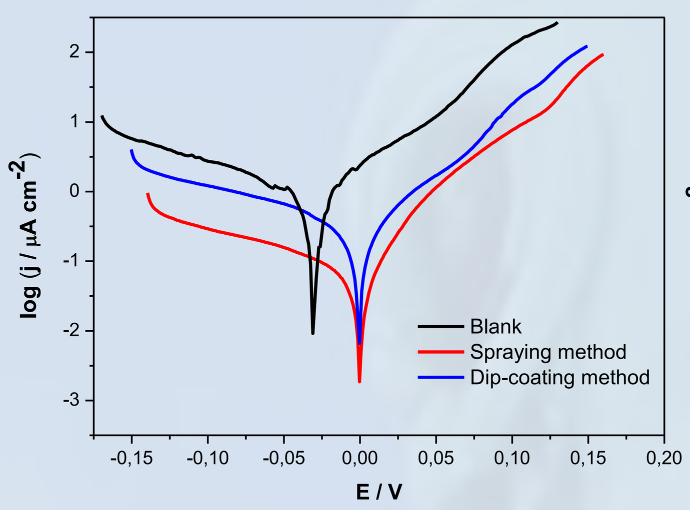


Figure 1. Polarization curves obtained in 0,2 g/L $NaHCO_3$ + 0,2 g/L $NaNO_3$ + 0,2 g/L Na_2SO_4 pH 5 solution for non-treated and COOH-PA treated samples.

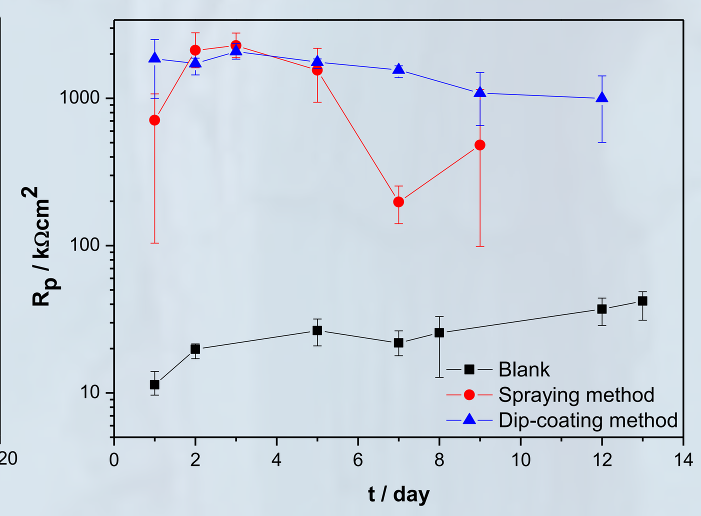


Figure 2. Polarization resistance as a function of immersion time in 0,2 g/L $NaHCO_3$ + 0,2 g/L $NaNO_3$ + 0,2 g/L Na_2SO_4 pH 5 solution for nontreated and COOH-PA treated samples.

Table 1. Corrosion parameters obtained by Tafel extrapolation method.

SAMPLE	E_{corr} (mV)	j_{corr} (μA cm^{-2})	b_a (mV dec^{-1})	$-b_k$ (mV dec^{-1})	Z (%)
Blank	-30,9	0,902	71,7	138,4	-
Dip-coating method	0,5	0,332	70,4	169,6	63,19
Spraying method	-0,2	0,080	43,5	172,8	91,13

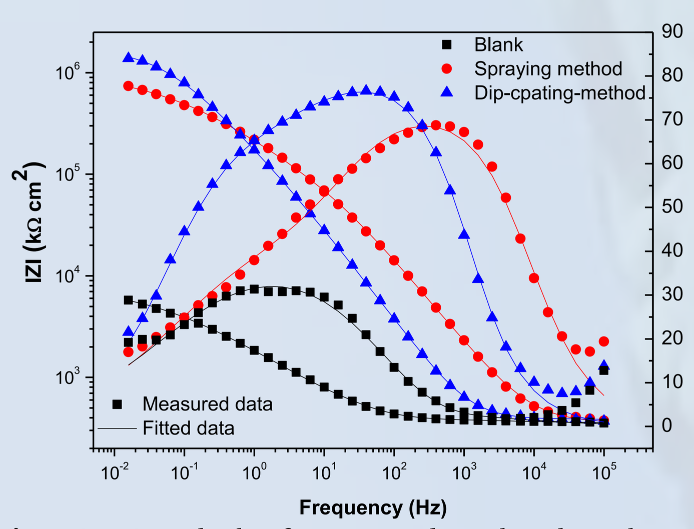


Figure 3. EIS – Bode plots for nontreated sample and samples treated with COOH-PA measured first day in 0,2 g/L $NaHCO_3$ + 0,2 g/L $NaNO_3$ + 0,2 g/L Na_2SO_4 pH 5 solution. Symbols: experimental data; solid lines: modeled data according to electrical equivalent circuits given in Fig. 5.

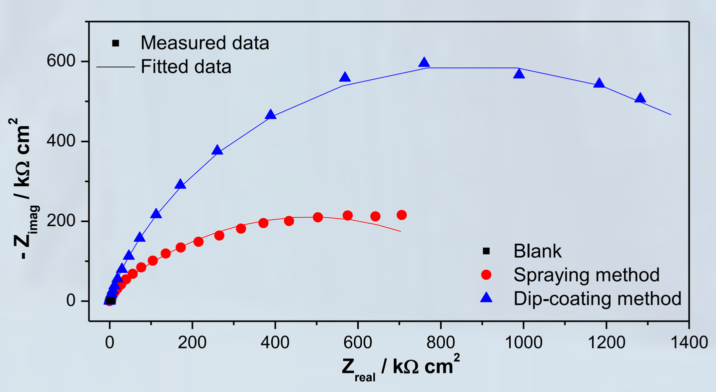


Figure 4. EIS – Niquist plots for nontreated sample and samples treated with COOH-PA measured first day in 0,2 g/L $NaHCO_3$ + 0,2 g/L $NaNO_3$ + 0,2 g/L Na_2SO_4 pH 5 solution. Symbols: experimental data; solid lines: modeled data according to electrical equivalent circuits given in Fig. 5.

Table 2. Fitted EIS data (Q_f – film capacitance, R_f – film resistance, Q_{dl} – double layer capacitance, R_{ct} – charge transfer resistance, n_f, n_{dl} – coefficients describing non ideal capacitive behavior) obtained for blank samples and samples treated with COOH-PA.

	SAMPLE	Q_f / μS sec^n cm^{-2}	n_f	R_f / kΩ cm^2	Q_{dl} / μS sec^n cm^{-2}	n_{dl}	R_{ct}/ kΩ cm^2
1st day of measurement	Blank	212,2	0,50	0,1	4,6	1	7,5
	Dip-coating method	0,8	0,90	158,5	0,8	0,61	1662,0
	Spraying method	0,3	0,83	9,0	1,7	0,50	889,1

SURFACE STUDIES

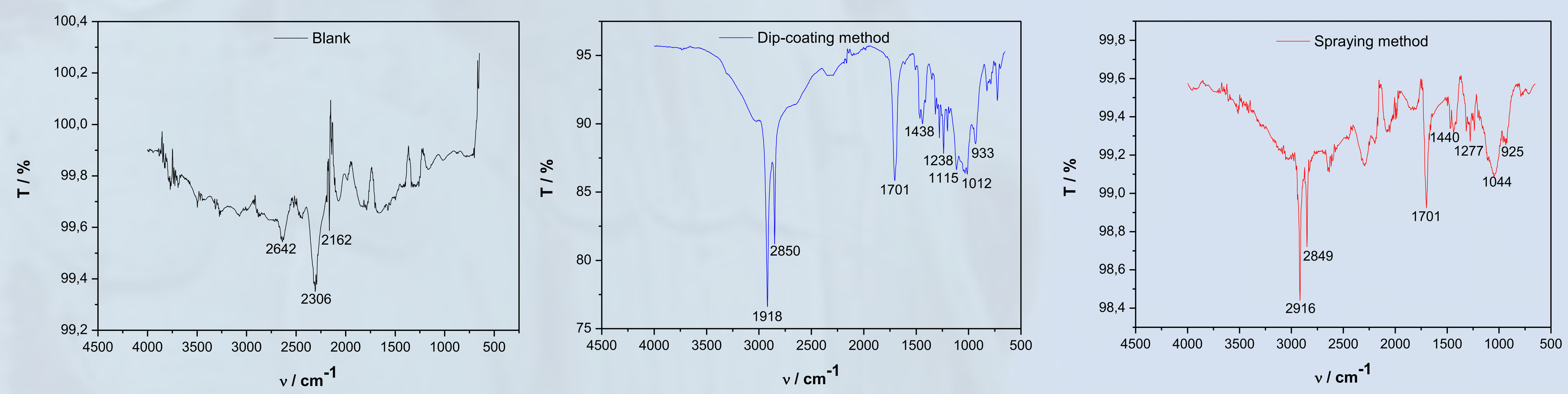


Figure 8. FTIR spectra of non-treated and COOF-PA treated samples prepared by dip-coating and spraying method.

Table 4. Peak values of COOH-PA treated samples prepared by different methods.

	Wavenumber (cm^{-1})	Dip-coating method Wavenumber (cm^{-1})	Spraying method Wavenumber (cm^{-1})
P–O	1150 – 1000	1115, 1012	1044
P=O	1335 – 1150	1238	1277
P–O–H	950 – 900	933	925
$-CH_2$ (sim)	≤ 2850	2850	2849
$-CH_2$ (asim)	≤ 2918	2918	2916
C=O	1820 - 1670	1701	1701
COO^- (sim)	1470 - 1360	1438	1440

A monodentate bonding configuration via single oxygen atom.

Alkyl chain in the film are well ordered with the molecules organized in all-trans configuration on the substrate.

A free carboxyl group.

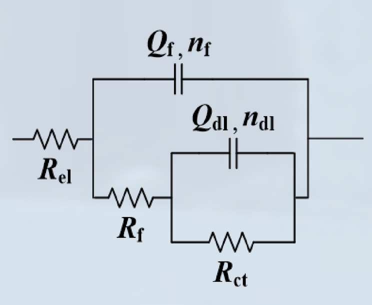


Figure 5. Equivalent electrical circuits used for fitting the EIS data

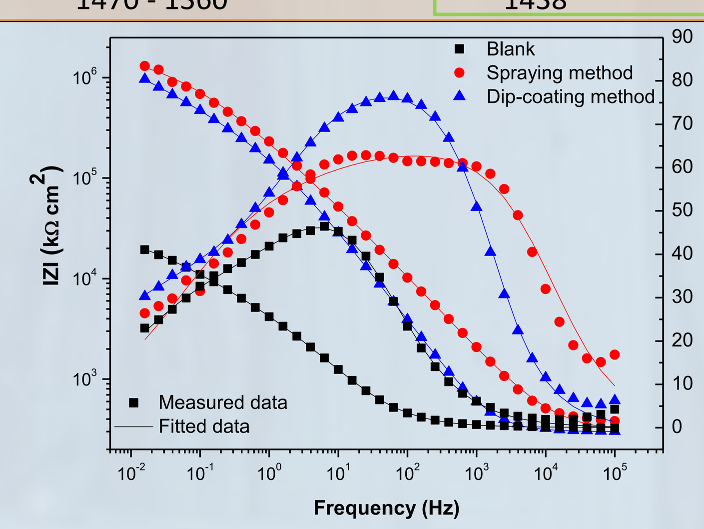


Figure 6. EIS – Bode plots for nontreated sample and samples treated with COOH-PA measured fifth day in 0,2 g/L $NaHCO_3$ + 0,2 g/L $NaNO_3$ + 0,2 g/L Na_2SO_4 pH 5 solution. Symbols: experimental data; solid lines: modeled data according to electrical equivalent circuits given in Fig. 5.

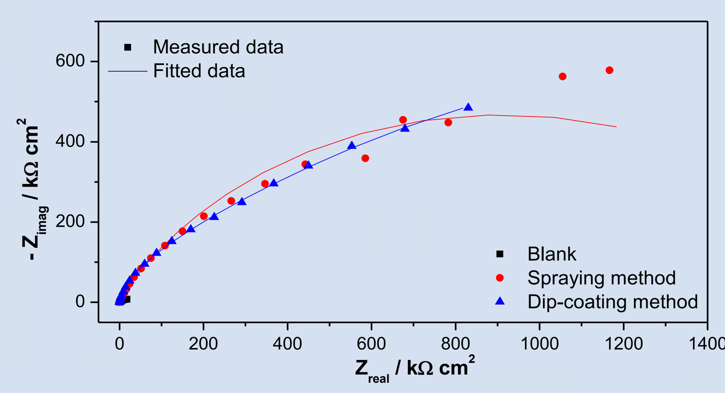


Figure 7. EIS – Niquist plots for nontreated sample and samples treated with COOH-PA measured fifth day in 0,2 g/L $NaHCO_3$ + 0,2 g/L $NaNO_3$ + 0,2 g/L Na_2SO_4 pH 5 solution. Symbols: experimental data; solid lines: modeled data according to electrical equivalent circuits given in Fig. 5.

Table 3. Fitted EIS data (Q_f – film capacitance, R_f – film resistance, Q_{dl} – double layer capacitance, R_{ct} – charge transfer resistance, n_f, n_{dl} – coefficients describing non ideal capacitive behavior) obtained for blank samples and samples treated with COOH-PA.

	SAMPLE	Q_f / μS sec^n cm^{-2}	n_f	R_f / kΩ cm^2	Q_{dl} / μS sec^n cm^{-2}	n_{dl}	R_{ct}/ kΩ cm^2
5th day of measurement	Blank	42,1	0,73	5,6	101,8	0,50	28,38
	Dip-coating method	0,7	0,90	122	2,4	0,50	3189
	Spraying method	0,5	0,78	3,1	0,8	0,50	1921

CONCLUSION

In this work was investigated the possibility of protecting bronze sculptures by modifying the surface of bronzes with SAMs of COOH-PA. Based on the obtained results it is apparent that SAMs significantly contributes to the corrosion protection of bronzes in comparison with the untreated sample. The spraying method, which is also more suitable for commercial use, has demonstrated better properties in the first days of testing. After the fifth day of testing the polarization resistances become smaller in relation to the resistances of the sample treated by the immersion method. The reason for this may be a better formed and arranged film that is generated by the immersion method since molecules have more time to organize into a stable film.