

Electrochemical Characterization of Bronze Exposed to Outdoor Atmosphere



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The aim of this work was to examine corrosion behaviour of bare and artificial patinated bronzes during exposure to urban outdoor atmosphere. Studies were conducted on copper and two different bronzes in order to evaluate the influence of substrate composition on patina composition and electrochemical behaviour. Additionally, two different patination methods were compared. Corrosion behaviour was examined using electrochemical impedance spectroscopy with gel-electrolyte electrochemical cell. The composition of patina was determined by ATR-FTIR spectroscopy. The obtained results showed that all studied artificial patinas initially decrease the corrosion resistance of copper and bronzes but in time their corrosion resistance improves, and even for certain combinations, artificial patina-bronze corrosion resistance is higher than that of naturally patinated bronze.

Keywords:

patina, copper alloy, atmospheric corrosion, electrochemical methods, ATR-FTIR

Introduction

Copper and its alloys, when exposed to outdoor environment, corrode under the influence of moisture, rainwater and corrosive species in the air. In principle, atmospheric corrosion firstly leads to formation of brown layer of cupric oxides, which then gradually turns black due to the formation of cuprous oxides, and afterwards the greenish-blue layer of patina is formed.^{1,2} Duration of this process, and especially the formation of terminal patina layer, depends on the concentration of various pollutants, such as SO₂, NO_x, or Cl⁻. More polluted atmosphere causes faster formation of corrosion products. In marine atmosphere, corrosion rate is enhanced by the presence of chloride ions, and formation of chloride patina like atacamite Cu₂Cl(OH)₃ is observed. In industrial and urban atmospheres, due to the presence of SO₂, sulphate patina is mainly found in the form of bronchantite Cu₄(SO₄)(OH)₆, antlerite Cu₃(SO₄)(OH)₄ or posnjakite Cu₄(SO₄)(OH)₆·H₂O. Additionally, carbonate patina in the form of malachite Cu₂(CO₃)(OH)₂ or nitrate patina in the form of gerhardtite Cu₂NO₃(OH)₃ are observed.^{1,2} As the natural formation of patina on copper and bronze takes years, artificial patina is commonly applied. This is done for aesthetic reasons, as well as for the protection of the bronze base. Various methods of artificial patination have been developed over time.³ In

practice, the most common methods involve the initial formation of a sulphide layer above which various green patinas are applied. Although the aesthetic value of such prepared patina is clear, practitioners usually fail to examine its composition and protective properties. For that reason, scientific studies have been conducted to reveal artificial or natural patina composition^{4–16} and its protective properties.^{9–16} The influence of bronze composition of patina formation and stability has been examined as well.⁹

Hernandez *et al.*¹⁶ used electrochemical impedance spectroscopy (EIS) to investigate the electrochemical behaviour of copper electrodes coated with two different types of chloride/nitrate artificial patinas in chloride solution and synthetic rainwater. Experiments were performed under continuous and intermittent exposure conditions. Continuous immersion was found to result in gradual dissolution of patina and low protection of copper, while alternating wet/dry cycles resulted in precipitation of a protective corrosion product layer on the pore walls during drying periods, contributing to improved anticorrosion properties. Thus, the usual approach of studying atmospheric corrosion by continuous immersion of bronze samples in artificial rainwater should be avoided. However, for electrochemical measurements, it is necessary to construct an electrochemical cell with some electrolyte that will be in contact with the bronze surface. This presents a practical problem when working on curved and ver-

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tical surfaces, and it may influence the patina chemistry since the electrolyte layer is much thicker than the condensed water layer responsible for atmospheric corrosion. Recently, a new approach has been developed where electrochemical cells with gel electrolytes are used, such as agar^{17,18} and different hydrogels.^{19,20}

The aim of this work was to examine corrosion behaviour of bare and artificial patinated copper bronzes during the exposure to urban outdoor atmosphere. Artificial patina was formed following procedures commonly used in practice in Croatia. The final goal was to compare the properties of such patina with those of naturally formed patina in outdoor atmosphere. Corrosion properties were evaluated by electrochemical impedance spectroscopy measurements with electrochemical cell with agar gel based electrolyte, while the composition of patina was determined with ATR-FTIR spectroscopy.

Material and methods

Sample preparation

Studies were conducted on pure copper (Cu) and two types of bronze samples: CuSn6 (94.15 wt.% Cu and 5.85 wt.% Sn) and quaternary CuSn9Zn2Pb bronze (86.20 wt.% Cu, 9.12 wt.% Sn, 2.10 wt.% Zn, 1.17 wt.% Pb, 0.81 wt.% Fe and 0.32 wt.% Ni). Samples were cut in 5 x 5 cm plates and ground with SiC 80 and 240 grade polishing paper. Afterwards, samples were degreased in ethanol and acetone. Six samples of each studied material were patinated to obtain a brown patina, while three samples of each material were left untreated (blank samples). The metal surface was preheated to approximately 200 °C and then sprayed three times with 1 % potassium polysulphide solution. The surface was then washed with distilled water and lightly rubbed with paper towel to remove loosely adherent patina.

The next step was preparation of green patina above the brown patina. Half of the samples were brushed with 30 % Cu(NO₃)₂ solution and then with 5 % H₂O₂ solution. This treatment was repeated 4 times. Such treated samples are hereinafter referred to as nitrate patina samples (NP). Patination methods previously described were adopted from restoration practitioners.³ The other half of the samples was treated with solution obtained from the local foundry that used this solution for patination of recently installed bronze sculptures. Solution was brushed over the brown patina four times. Such treated samples are hereinafter referred to as artistic patina samples (AP).

All samples were then exposed to outdoor atmosphere, near a busy road in the Zagreb city centre.

Electrochemical cell

Electrochemical measurements were conducted using electrochemical cell with agar based electrolyte – construction of this cell was based on the set-up developed by Ramirez Barat *et al.*¹⁸ It consisted of pseudo-reference electrode and counter electrode made of stainless steel wires (AISI 316L). Artificial rainwater solution was prepared by dissolution of 0.2 g L⁻¹ NaNO₃, 0.2 g L⁻¹ Na₂SO₄ and 0.2 g L⁻¹ NaHCO₃ in deionised water. Solution was additionally acidified with 5 % HNO₃ in order to obtain pH 6.5. The agar-based electrolyte was prepared by dissolving 2.5 % of agar powder in artificial rainwater solution. Agar dissolution was enhanced by heating in microwave oven. The electrolyte was left to cool for a short time before pouring it on the cell, and then left to cool to room temperature until solidification.¹⁸ The exposed area of studied samples was 4.9 cm².

Electrochemical measurements

The electrochemical characterization of copper and bronze samples was conducted using electrochemical impedance spectroscopy. Studies were conducted in a frequency range from 100 kHz to 10 mHz with 10 mV_{rms} amplitude at open circuit potential (E_{oc}).

Spectroscopic and microscopic characterization

The patinas were analysed by ATR-FTIR spectroscopy using a Perkin Elmer Spectrum One FTIR spectrometer, within the scan range from 4000 to 650 cm⁻¹, and with resolution of 0.5 cm⁻¹; the results shown in this paper are averages of 25 scans.

Optical microscopy was conducted using Dino-Lite optical microscope with 50x magnification.

Results and discussion

Electrochemical characterization

Electrochemical characterisation of copper and bronze samples was conducted on freshly prepared samples (after 1 day), and several times during their exposure to outdoor atmosphere. Studies were performed using the electrochemical cell with agar based electrolyte.

Cu samples

Figs. 1a and 1b present EIS spectra of Cu samples, either blank or patinated 1 day after the sample preparation. It can be seen that the impedance modulus at the lowest frequencies for the blank Cu sample is much higher than that of both types of

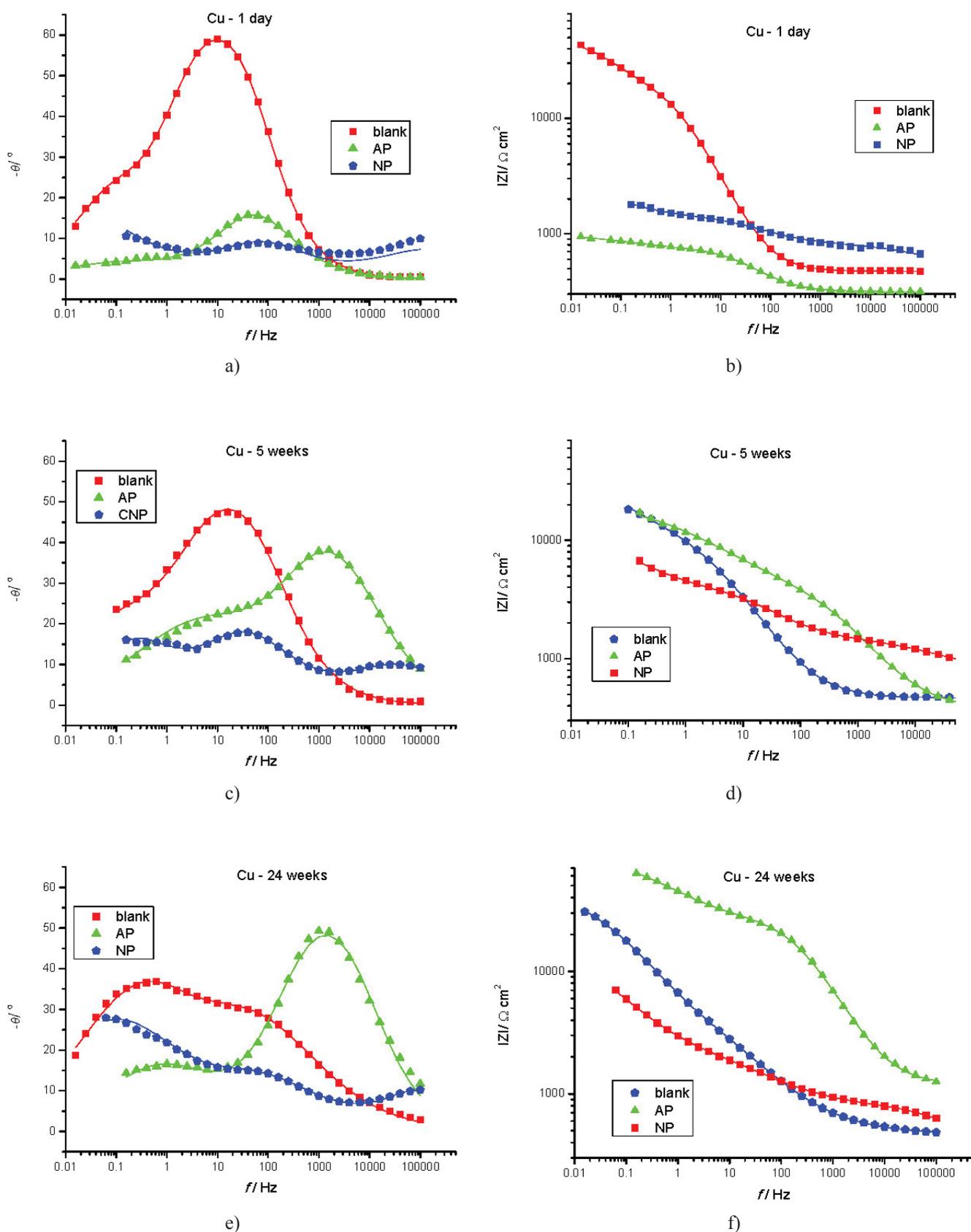


Fig. 1 – Bode impedance plots for blank and patinated Cu samples collected after different periods of exposure to outdoor atmosphere

patinated samples. This can be related to the increase in the active surface area on the patinated samples due to the formation of reactive corrosion species. This reflects in lower phase angle maxima values for patinated Cu compared to blank Cu, which is a typical feature for porous and rough surfaces. Among patinated samples, nitrate patina appears to have better protective properties than the artistic patina. Exposure to outdoor atmosphere for five weeks resulted in the decrease in the impedance of blank Cu sample, and increase in the impedance of both patinated Cu samples (Fig. 1c and 1d). However, the impedance of blank Cu is still significantly higher than the impedance of patinated samples. Prolonged exposure up to 24 weeks (Fig. 1e and 1f) resulted in significant increase in impedance for AP samples, while the impedance of NP and blank Cu samples had not changed much.

In order to better understand observed changes in electrochemical behaviour, EIS spectra were modelled using equivalent electrical circuit models given in Fig. 2. In these models, R_{el} represents electrolyte resistance between working and reference electrode, high frequency data are described by R_{ox} which represents oxide/corrosion products layer resistance, and Q_{ox} which is constant phase element describing capacitive property of surface oxide/corrosion products layer. Medium frequency part of the

EIS spectra is represented by R_{ct} which is charge transfer resistance, and Q_{dl} which is constant phase element describing double layer capacitance. The additional R_F-Q_F loop describes reactive patina layer, where R_F is faradaic resistance associated with the rate of oxidation-reduction processes involving reactive patina layer, and Q_F is constant phase element describing faradic capacitance of reactive patina.¹² For blank Cu and AP Cu samples, two phase angle maxima are observed on all Bode plots, thus a model with two time constants is sufficient to represent EIS data (Fig. 2a). EIS spectra for NP Cu samples exhibit three phase angle maxima: thus, an equivalent circuit with three $R-Q$ loops is needed to adequately describe the obtained spectra (Fig. 2b). Impedance parameters, obtained by fitting experimental data to selected models, are presented in Table 1. For blank Cu sample, decrease in R_{ox} values and increase in Q_{ox} values may be assigned to dissolution of native oxide layer and formation of rougher and less protective layer of corrosion products. However, R_{ox} value remains sufficiently high to provide protection to Cu substrate, which reflects in relatively high values of R_{ct} for all exposure times. On the other hand, AP Cu sample shows initially very low resistance and high capacitive values. Indeed, the value of constant phase element at lower frequencies is too high to be attributed to double layer capacitance, but rather it may be assigned to reactive patina capacitance, thus the equivalent electrical circuit for AP Cu for the first day is presented in Fig. 2c. Significant decrease in capacitance at high and low frequencies accompanied by the increase in resistive elements in time can be explained by transformation of reactive patina into more stable and protective compounds. For NP Cu, EIS data reveal the presence of both stable and reactive patina. Their resistances (R_{ox} and R_F) increase in time, which points to the stabilisation of patina, but the effect is not as dramatic as in the case of AP.

CuSn6 bronze

EIS measurements on CuSn6 bronze samples reveal similar influence of patination on substrate corrosion properties as for Cu substrate (Fig. 3a and 3b). Both AP and NP samples exhibit significantly lower values of impedance modulus compared to the blank sample. In other words, both artificial patination methods initially result in decreased bronze corrosion resistance. The impedance modulus values of patinated samples increase in time with larger increase for NP sample. Impedance parameters for blank CuSn6 samples were determined by fitting the experimental data to model shown in Fig. 2a. As can be seen from Table 2, exposure of bronze to outdoor atmosphere resulted in an increase in oxide

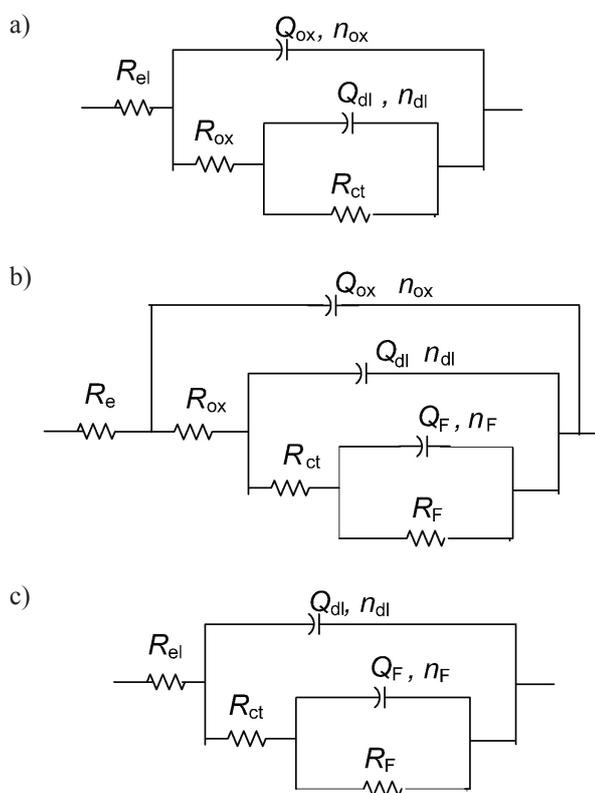


Fig. 2 – Equivalent electrical circuits used for modelling impedance spectra given in Figs. 1, 2, and 3

Table 1 – EIS data for Cu samples

week	$Q_{ox} / \mu\text{Fs}^n \text{cm}^{-2}$	n_{ox}	$R_{ox} / \text{k}\Omega \text{cm}^2$	$Q_{dl} / \mu\text{Fs}^n \text{cm}^{-2}$	n_{dl}	$R_{ct} / \text{k}\Omega \text{cm}^2$	$Q_F / \mu\text{Fs}^n \text{cm}^{-2}$	n_F	$R_F / \text{k}\Omega \text{cm}^2$
blank									
1	10.30	0.83	19.51	81.32	0.66	31.17			
5	12.47	0.75	10.61	74.02	0.54	25.53			
24	38.30	0.51	7.709	27.75	0.64	47.01			
AP									
1				51.41	0.73	0.4343	5759	0.51	0.2617
5	1.443	0.69	4.119	28.41	0.50	16.23			
24	0.1780	0.76	25.88	12.81	0.56	61.95			
NP									
1	2.369	0.52	0.3294	92.40	0.50	0.7327	191.8	0.50	6.470
5	1.778	0.56	0.7787	17.80	0.64	2.975	220.7	0.73	4.891
24	5.000	0.50	0.6359	19.54	0.67	1.020	221.3	0.51	19.02

Table 2 – EIS data for CuSn6 samples

week	$Q_{ox} / \mu\text{Fs}^n \text{cm}^{-2}$	n_{ox}	$R_{ox} / \text{k}\Omega \text{cm}^2$	$Q_{dl} / \mu\text{Fs}^n \text{cm}^{-2}$	n_{dl}	$R_{ct} / \text{k}\Omega \text{cm}^2$	$Q_F / \mu\text{Fs}^n \text{cm}^{-2}$	n_F	$R_F / \text{k}\Omega \text{cm}^2$
blank									
1	18.21	0.78	4.60	92.54	0.51	22.28			
5	26.44	0.50	20.75	38.19	0.50	141.2			
24	9.339	0.72	33.27	14.35	0.69	117.7			
AP									
1				35.83	0.77	0.5104	103.5	0.80	9.031
5	1.255	0.65	1.425	20.14	0.50	2.461	361.9	0.51	13.51
24	14.45	0.50	0.3781	22.26	0.62	1.211	294.2	0.51	8.368
NP									
1	12.18	0.50	0.617	70.88	0.59	0.7424	5381	0.88	0.492
5	49.21	0.50	13.44	127.7	0.72	60.28	278.9	0.78	10.92
24	4.656	0.51	0.809	19.44	0.50	8.071	131.3	0.61	47.94

layer resistance as well as charge transfer resistance, which is an indication of the formation of protective oxide layer. Initial EIS spectrum of AP sample exhibits only two time constants, while spectra obtained after longer exposure to corrosive environment exhibit three time constants. Thus, models presented in Figs. 2c and 2b were used for fitting initial and longer exposure EIS spectra, respectively. Obtained impedance parameters (Table 2) revealed that all resistance values related either to patina (R_{ox} and R_F) or to the substrate (R_{ct}) were lower than those observed for blank CuSn6 bronze. For AP CuSn6 sample, initial substrate and patina layer resistances are higher than for AP Cu sample. However, it appears that for this sample, exposure to outdoor environment resulted in no significant

improvement of the properties of the patina layer. On the other hand, NP sample exhibited very low initial corrosion resistance, but all resistance values increased in time, which is an indicator of the formation of more stable and protective patina layer.

CuSn9Zn2Pb bronze

The third examined substrate was CuSn9Zn-2Pb. Impedance spectra obtained for the blank and patinated samples are given in Fig. 4. As for the two other previously examined materials, patination of this kind of bronze resulted in significant decrease in impedance modulus at low frequencies, i.e. the corrosion resistance of patinated samples was much lower than that of the blank bronze (Fig. 4a and 4b).

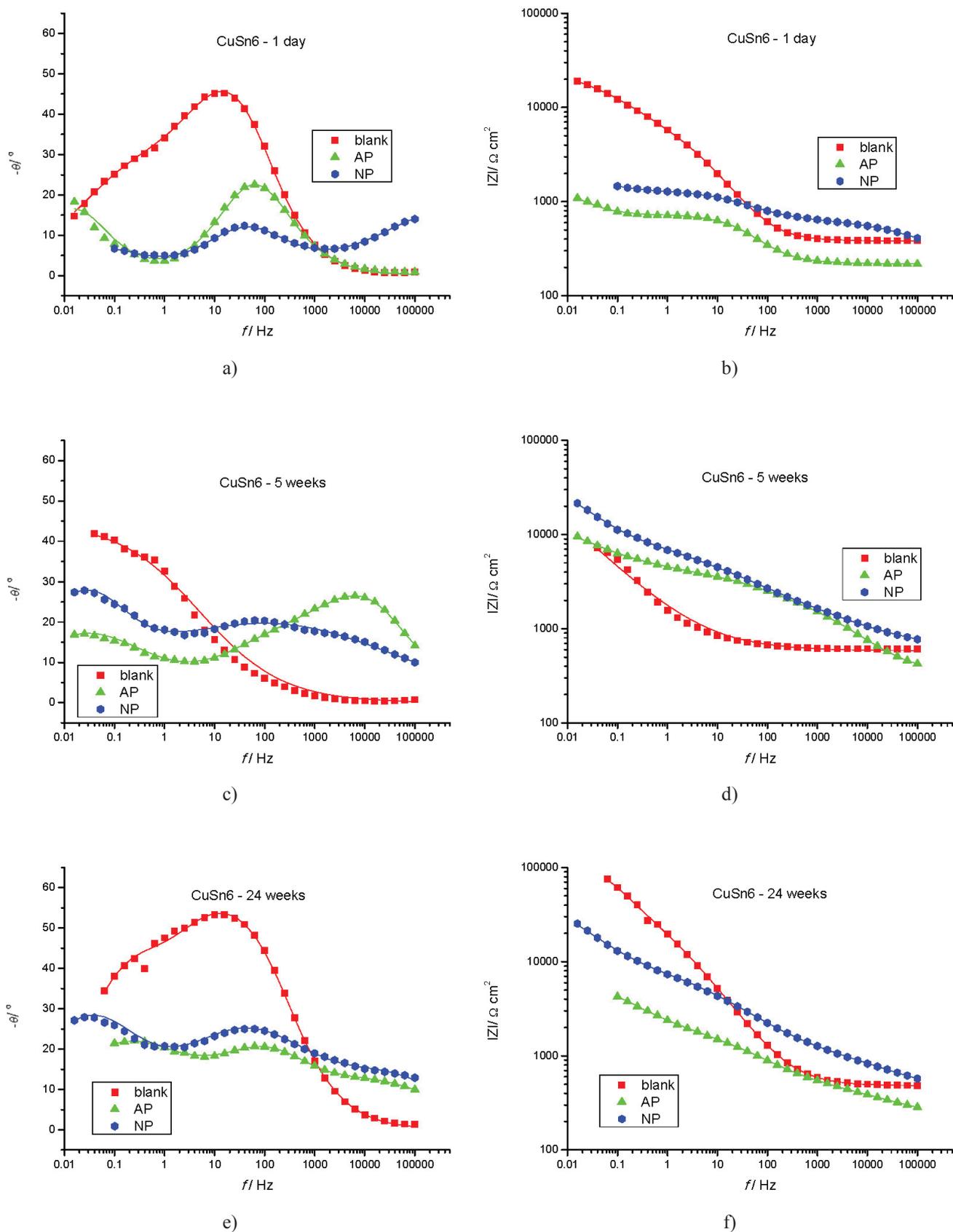


Fig. 3 – Bode impedance plots for blank and patinated CuSn6 samples collected after different periods of exposure to outdoor atmosphere

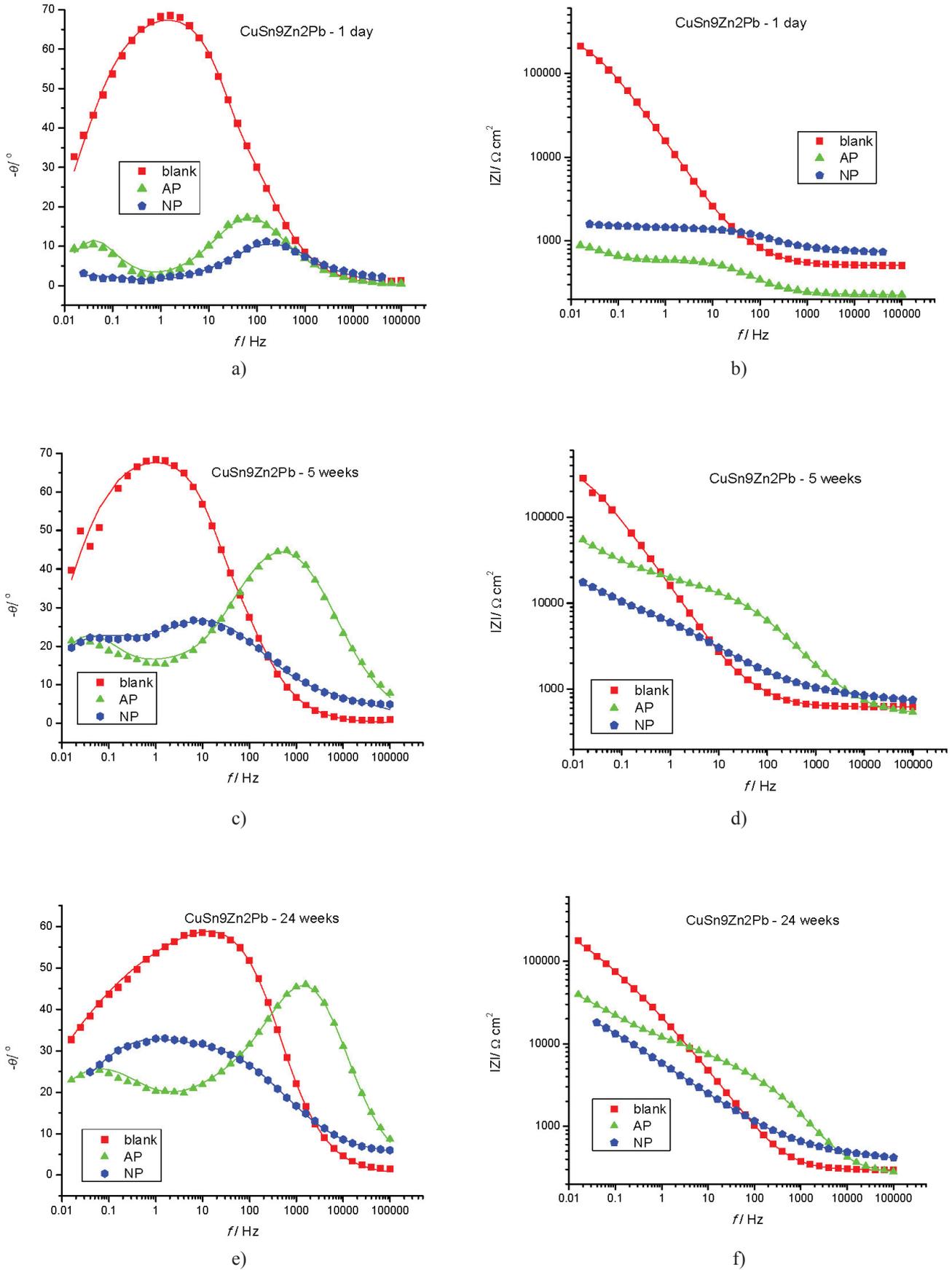


Fig. 4 – Bode impedance plots for blank and patinated CuSn9Zn2Pb samples collected after different periods of exposure to outdoor atmosphere

Very low phase angle values observed on initial EIS spectra for patinated samples indicated high porosity of patina layer. In time, both impedance modulus and phase angle maxima values increased, suggesting that the corrosion resistance of the surface had improved and the patina layer was less porous. EIS spectra were fitted to electrical equivalent circuits shown in Fig. 2a and 2b. Obtained fitting results are given in Table 3. Blank CuSn9Zn2Pb sample appeared to have the highest charge transfer resistance among studied blank samples. This may be related to the alloy composition with higher Sn content and with Zn and Pb included. With exposure to outdoor environment, both R_{ox} and R_{ct} increased as the protective surface layer had formed. Low Q_{dl} values, compared to other blank samples, suggest the formation of protective surface layer that covered bronze substrate and reduced contact between water and bronze. Although CuSn9Zn2Pb bronze appeared to have excellent corrosion properties, patination with either AP or NP resulted in significant decrease in R_{ct} values. Obtained patina layer exhibited high Q_F values, thus it was concluded that patina layer contained high amount of reactive species, especially NP patina. With exposure to outdoor environment, conversion of reactive to a more protective patina layer occurred, which reflected in an increase in all resistance values, especially in the case of AP.

Optical microscopy

Fig. 5 shows optical micrographs of all studied samples after 24 weeks of exposure to outdoor environment. Patina formation is visible on all blank samples. Reddish and black colour of corrosion product is typical for Cu_2O and CuO , respectively. As explained in the Material and Methods section,

the first step in artificial patination was formation of brown sulphide patina. Thus, on all samples, an inner layer of brownish patina was visible. On AP samples, additional light green patina layer was present, while on NP samples, upper patina layer had more bluish appearance.

FTIR spectroscopy

In order to reveal the patina composition, ATR-FTIR measurements were conducted. For blank Cu (Fig. 6a) and CuSn6 samples, almost identical FTIR spectra were obtained after 24 weeks of exposure to outdoor environment; therefore, only spectrum for Cu is presented in Fig. 6. Observed absorption bands indicate the presence of carbonate patina (1542, 1437, 1366, 1096, and 897 cm^{-1}).^{21,22} The strongest absorption bands are observed at 1741 and 1229 cm^{-1} but this was probably due to the presence of organic contaminants, as neither sulphate or nitrate compounds exhibit such strong bands at these wavenumbers. Acetates are often found in outdoor patinas.² As absorption band at 1741 cm^{-1} is typical of C=O stretching, the presence of acetates is quite likely. Unfortunately, IR absorption bands for oxides are at low wavenumbers, so that their existence was not confirmed by FTIR, although they are always found on copper or bronze objects exposed outdoors.^{1,2} For blank CuSn9Zn2Pb sample, FTIR spectrum obtained after 24 weeks of exposure was slightly different from the other two blank samples, but observed absorption bands, (Fig. 6b), can also be attributed to the presence of carbonate patina (bands at 1394 and 1051 cm^{-1}). Both bands are found at lower wavenumbers than for the other two blank samples, which might be an indicator that, instead of copper carbonates, lead carbonates had been formed.²³ Although sulphate patina compounds

Table 3 – EIS data for CuSn9Zn2Pb samples

week	$Q_{ox} / \mu F s^n cm^{-2}$	n_{ox}	$R_{ox} / k\Omega cm^2$	$Q_{dl} / \mu F s^n cm^{-2}$	n_{dl}	$R_{ct} / k\Omega cm^2$	$Q_F / \mu F s^n cm^{-2}$	n_F	$R_F / k\Omega cm^2$
blank									
1	3.338	0.95	0.4323	20.63	0.68	96.02			
5	13.71	0.77	4.516	1.157	1.00	455.7			
24	7.749	0.77	12.39	9.762	0.50	488.8			
AP									
1				54.80	0.72	0.3839	1380	0.95	0.3263
5	1.578	0.68	14.45	29.65	0.59	16.89	74.46	0.75	49.45
24	0.8155	0.77	3.790	21.27	0.53	8.715	64.66	0.55	64.08
NP									
1				21.07	0.63	0.7293	16290	0.70	0.2260
5	1.809	0.55	0.2183	52.25	0.50	13.12	296.9	0.81	13.33
24	5.986	0.52	0.1543	39.45	0.50	6.298	39.28	0.50	30.40

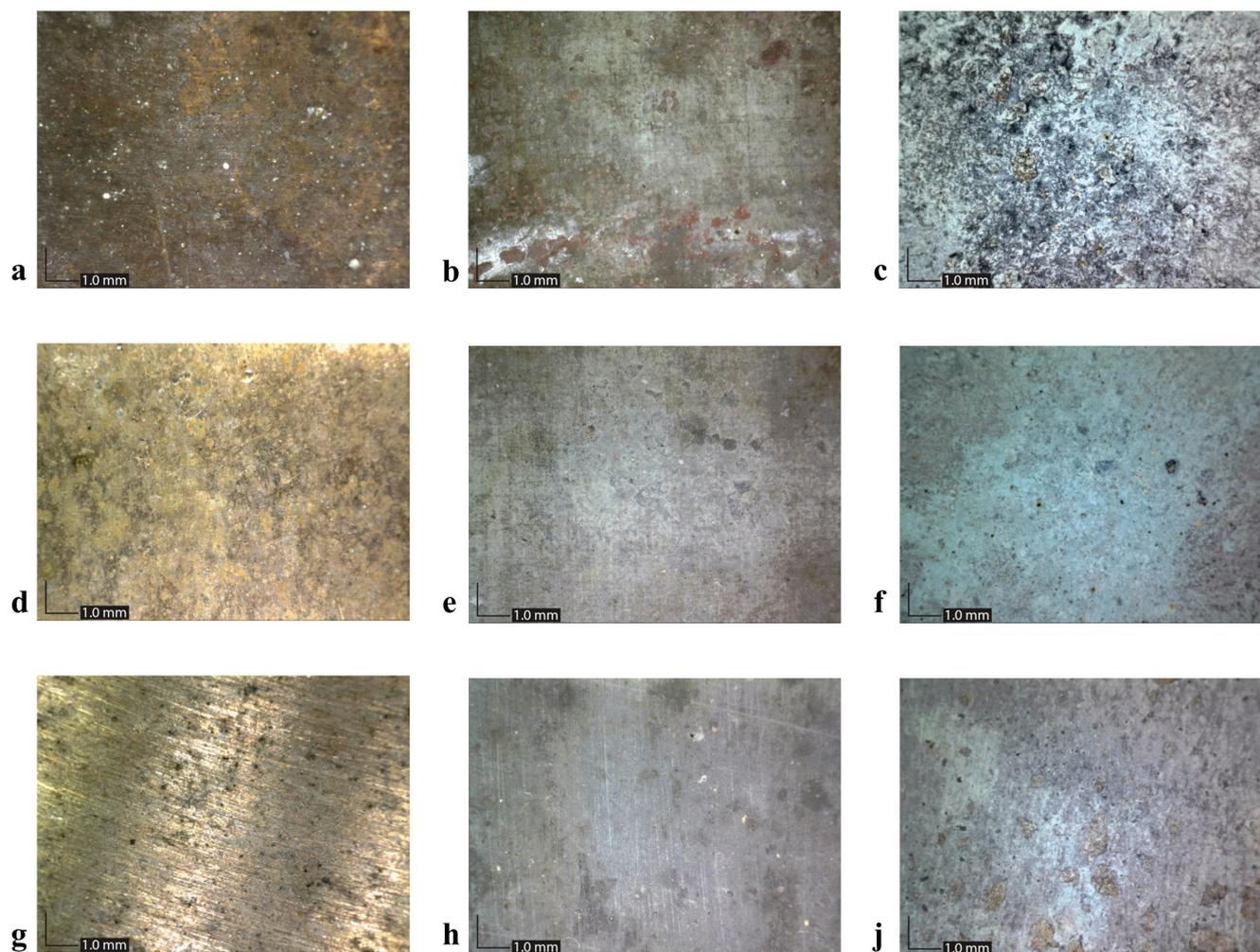


Fig. 5 – Optical microscopy images of studied samples after 24 weeks of exposure to outdoor atmosphere: a) blank Cu, b) AP Cu, c) NP Cu, d) blank CuSn6, e) AP CuSn6, f) NP CuSn6, g) blank CuSn9Zn2Pb, h) AP CuSn9Zn2Pb, j) NP CuSn9Zn2Pb

are commonly found on copper and bronze exposed outdoors, in our work, carbonate patina was observed instead. The possible explanation for this lies in fact that SO_2 concentrations in air have been strongly decreasing in last two decades, unlike CO and CO_2 concentrations. Thus, although the solubility of sulphate compounds is 100 times lower than that of the carbonate patina,² the concentration of SO_2 in air in Zagreb²⁴ is more than 1000 times lower than CO_2 concentration, and formation of carbonates is possible.

For nitrate patina, almost identical spectra were obtained on Cu and CuSn6 samples; therefore, only spectrum for NP Cu is presented in Fig. 6c. All observed absorption bands are typical for copper nitrate patinas, namely gerhardtite.²² It is interesting to mention that ATR-FTIR spectra were also recorded after only 7 weeks of exposure to outdoor environment. The position of absorption bands was almost the same as for 24 weeks, but their intensity decreased in time, suggesting that part of the patina

layer had dissolved. Both oxide and sulphide compounds are difficult to detect with ATR-FTIR, thus it was impossible to determine if transformation of oxide or sulphide patina compounds had occurred. For NP CuSn9Zn2Pb, spectrum (Fig. 6d) is very similar to spectra of other two NP samples. Only small shift of several bands to lower wavenumbers is observed, possibly indicating that not only had copper nitrates formed, but nitrates of other alloying elements as well.

For artistic patina samples, very similar spectra were obtained on all three studied materials. In spectrum of AP Cu sample, recorded 7 weeks after patina formation (Fig. 6e), two bands at 3430, 3321 and 3306 cm^{-1} were observed, typical of hydroxyl stretching bands in chloride patina compound atacamite.²⁵ Bands observed at 1432, 1386, 1095 and 828 cm^{-1} are on the other hand typical of carbonate patina like malachite, while bands 986 and 883 cm^{-1} , in the hydroxyl deformation region are characteristic of atacamite. Thus, mixed carbonate and chlo-

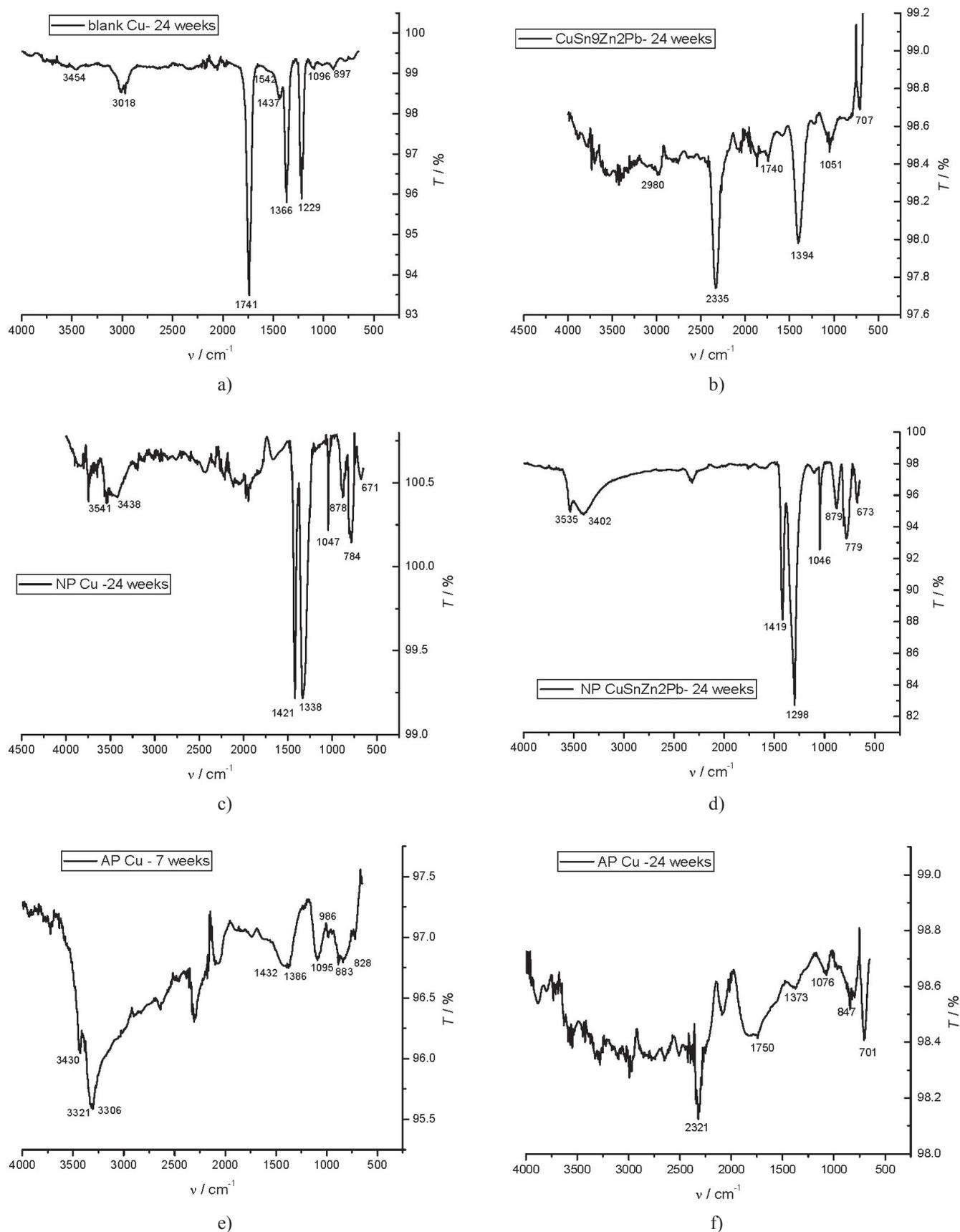


Fig. 6 – ATR-FTIR spectra of studied samples after exposure to outdoor atmosphere

ride patina had formed by using artistic patination solution. After 24 weeks of exposure to outdoor atmosphere (Fig. 6f), bands characteristic for atacamite were not observed, while those characteristic for carbonate patina were still present. Although the formulation of artistic patina solution remained undisclosed, formation of atacamite was an indicator that it contained chlorides that are responsible for low initial corrosion resistance of AP samples. With time, the chloride patina is washed out and more protective carbonate patina is formed. This is in accordance with the results of EIS measurements showing decrease in Q_F with time, which is inversely proportional to amount of reactive patina species.

Conclusions

Results obtained by EIS measurements showed that both examined patination methods resulted in temporary decrease in copper and bronze corrosion resistance, but exposure to outdoor environment led to improvement of corrosion resistance due to the transformation of patina layer. Still, even after 24 weeks of exposure, artificially patinated samples had lower corrosion resistance than blank samples on which natural patina layer had slowly formed. The only exception was AP on Cu, which after 24 weeks showed better corrosion resistance than blank Cu.

Increase in impedance of patinated samples with time is related to dissolution of more reactive patina species and formation of more protective ones, especially in the case of AP containing chloride species.

Comparison of the results obtained on different substrates revealed that, on different copper alloys, the same kind of artificial patination may result in different patina composition and corrosion properties.

ACKNOWLEDGEMENT

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