THE INFLUENCE OF PHOSPHONIC ACID FILM APPLICATION METHOD ON ITS EFFICIENCY IN CORROSION PROTECTION OF CuNi ALLOY IN SEAWATER

Utjecaj metode nanošenja filma fosfonske kiseline na njegovu djelotvornost u korozijskoj zaštiti CuNi legure u morskoj vodi

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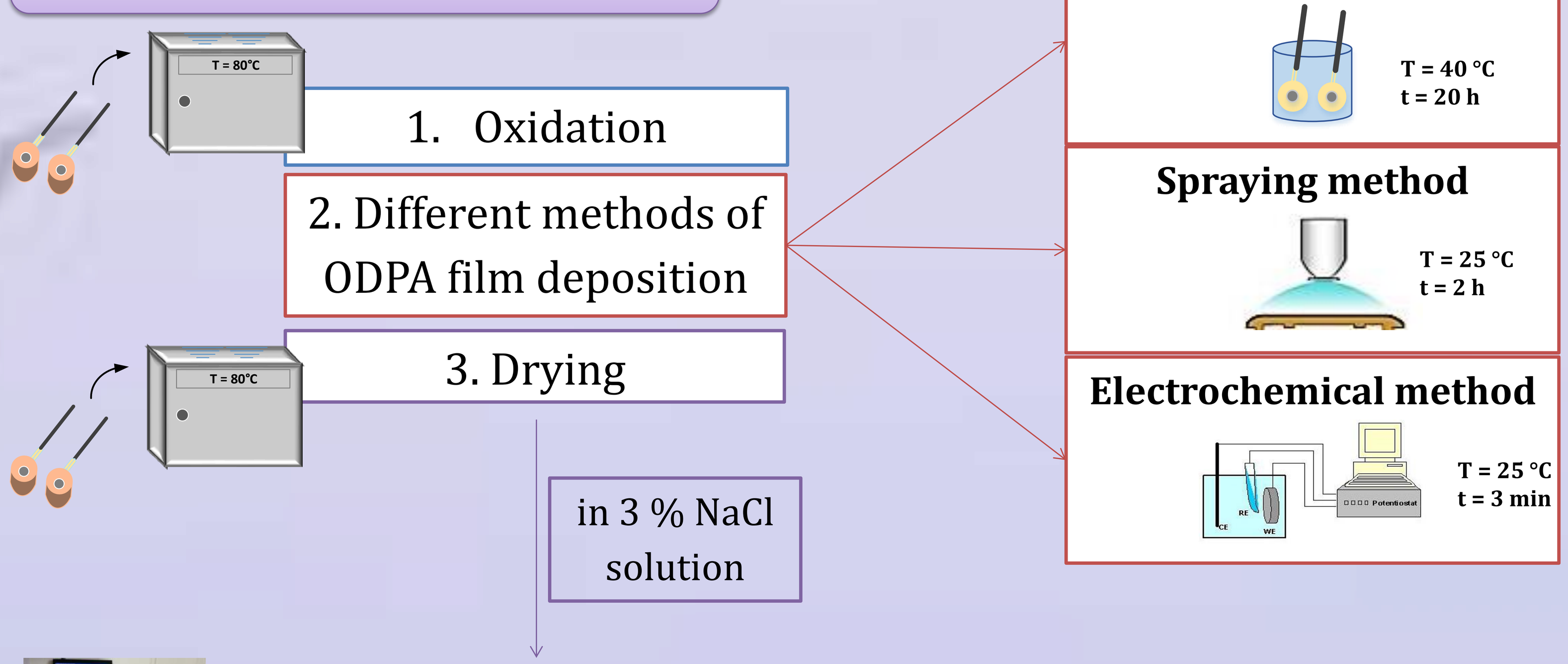
INTRODUCTION

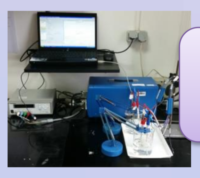
The preparation of self-assembled monolayers (SAMs) on metal or metal-oxide substrates is an important research topic in the field of surface engineering. Reproducible preparation of well-defined and stable monolayers requires appropriate choice of both the self-assembling molecule and the preparation method. Phosphonic acids are a class of molecules particularly known for their spontaneous self-assembly on oxidized substrates. They easily chemisorb on many metals and alloys and show good resistance to hydrolysis. While phosphonic acids have become popular surface modifiers for metal oxides in various fields, especially in the past decade, there is still a lack of consensus on deposition protocols. Very limited study of phosphonic acid SAMs on cupronickel alloy have been performed, mainly with the dip-coating method, which is time consuming, requires high amounts of working solution and is not always practical for application in industry.

The aim of this work is to investigate the possibility of cupronickel alloy protection by self-assembled monolayers of octadecylphosphonic acid (ODPA) prepared by different techniques: dip-coating, electrochemical method and spraying. Each one of these techniques has some advantages: dip-coating method is simple, electrochemical method is less time consuming, but spraying is more practical than the above mentioned methods. The protective properties of such formed monolayers are examined in artificial seawater by electrochemical polarization methods and electrochemical impedance spectroscopy while the structure of the film is determined by contact angle measurements, scanning electron microscopy and Fourier transform infrared spectroscopy.

EXPERIMENTAL

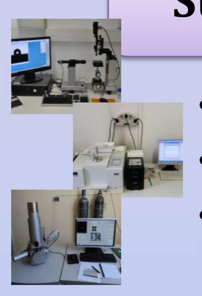
Sample preparation:





Electrochemical measurements:

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



Surface studies:

- Contact angle measurements
- Fourier transform infrared spectroscopy
- Scanning electron microscope

RESULTS

Electrochemical measurements:

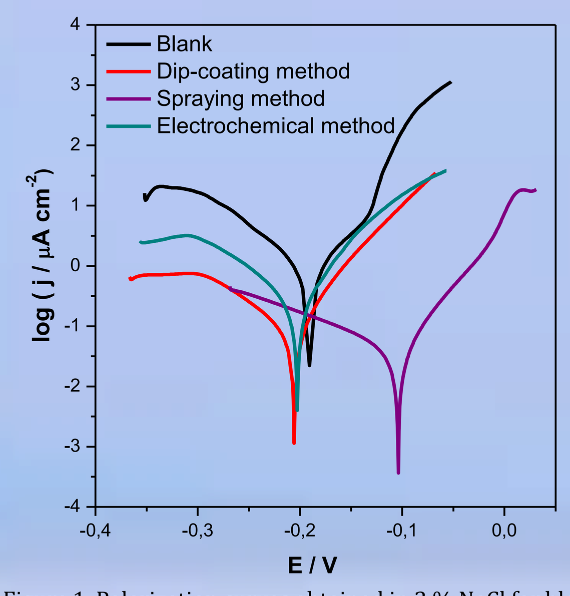


Figure 1. Polarization curves obtained in 3 % NaCl for blank sample and octadecylphosphonic acid treated samples modified with different method of preparation.

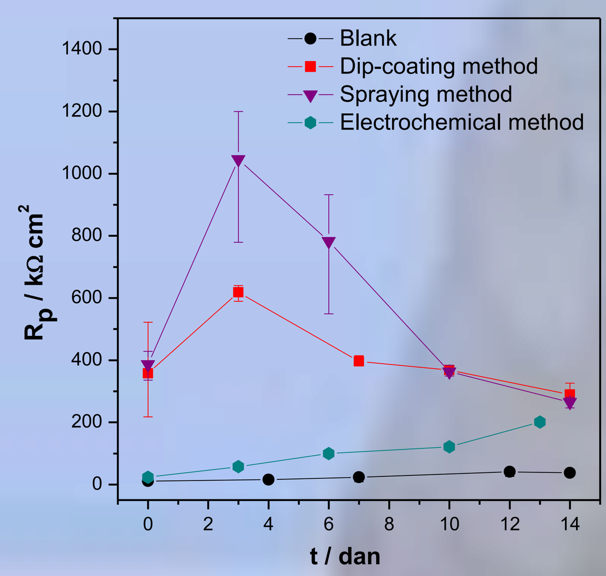


Figure 2. Polarization resistance as a function of immersion time in the sodium chloride solution for nontreated sample (blank) and samples treated with octadecylphosphonic acid by different method of preparation.

Table 1. Corrosion parameters obtained by Tafel extrapolation method.

SAMPLE	E_{corr} (mV)	j_{corr} (μA cm^{-2})	b_a (mV dek^{-1})	$-b_k$ (mV dek^{-1})	Z (%)
CuNi	-177	1,12	78	95	–
Dip-coating method	-207	0,04	43	83	96
Spraying method	-104	0,03	41	91	97
Electrochemical method	-203	0,30	54	92	73

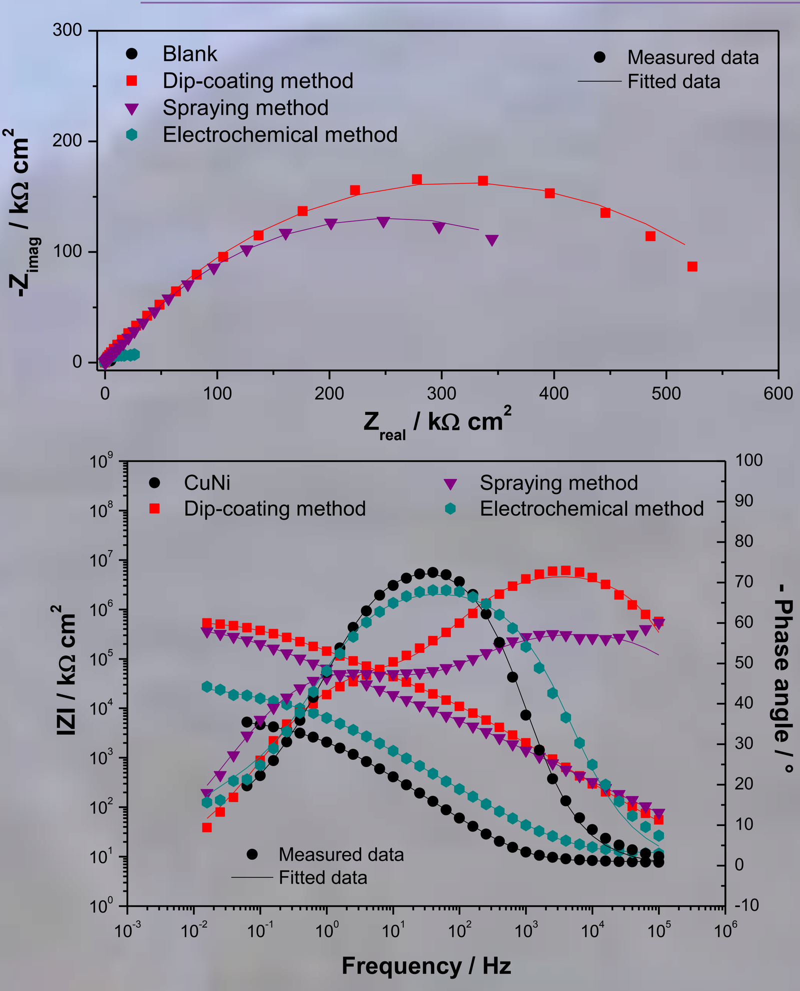


Figure 3. EIS – Nyquist and Bode plots for nontreated sample and samples treated with ODPA by different method of preparation measured after one hour in 3 % NaCl solution. Symbols: experimental dana; solid lines: modeled data according to electrical equivalent circuits given in Fig. 5.

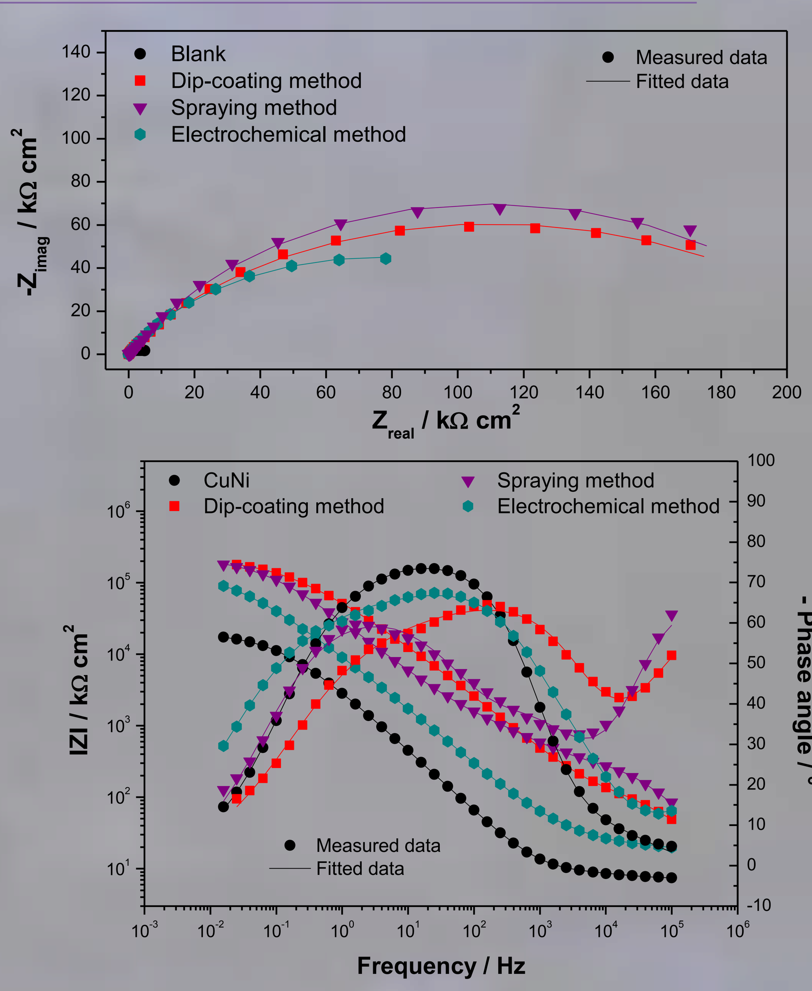


Figure 4. EIS – Nyquist and Bode plots for nontreated sample and samples treated with ODPA by different method of preparation measured last day of measurement in 3 % NaCl solution. Symbols: experimental dana; solid lines: modeled data according to electrical equivalent circuits given in Fig. 5.

Table 2. Fitted EIS data (C_f – film capacitance, R_f – film resistance, C_{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 ODPA.

	SAMPLE	C_f / μF cm^{-2}	n_f	R_f / kΩ cm^2	C_{dl} / μF cm^{-2}	n_{dl}	R_{ct}/ kΩ cm^2
First day of measurement	Blank	50.28	0.87	2.67	482.9	0.5	5.90
	Dip-coating method	0.15	0.82	31.49	1.85	0.58	602.20
	Spraying method	0.38	0.66	18.24	0.09	0.58	486.30
	Electrochemical method	21.85	0.78	14.35	466.8	0.54	23.97

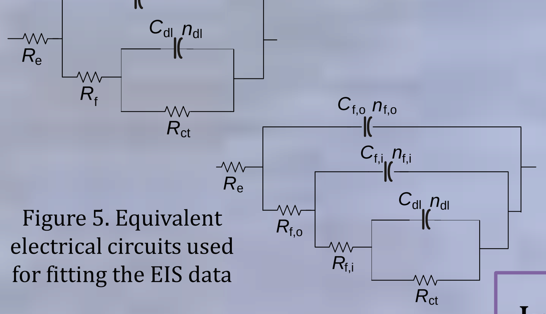
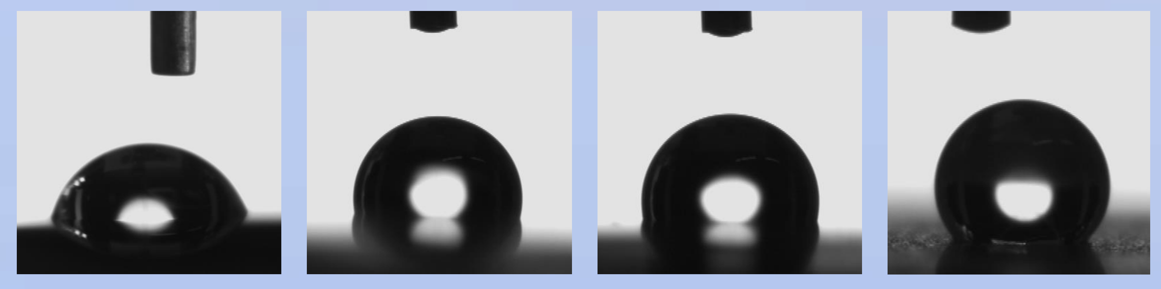


Figure 5. Equivalent electrical circuits used for fitting the EIS data

Table 3. Fitted EIS data ($C_{f,o}$ – outer film capacitance, $R_{f,o}$ – outer film resistance, $C_{f,i}$ – inner film capacitance, $R_{f,i}$ – inner film resistance, C_{dl} – double layer capacitance, R_{ct} – charge transfer resistance, $n_{f,o}$, $n_{f,i}$, n_{dl} – coefficients describing non ideal capacitive behavior) obtained for blank samples and samples treated with ODPA.

	SAMPLE	$C_{f,o}$/ μF cm^{-2}	$n_{f,o}$	$R_{f,o}$/ kΩ cm^2	$C_{f,i}$/ μF cm^{-2}	$n_{f,i}$	$R_{f,i}$/ kΩ cm^2	C_{dl}/ μF cm^{-2}	n_{dl}	R_{ct}/ kΩ cm^2
Last day of measurement	Blank	-	-	-	30.97	0.86	5.53	39.59	0.50	15.21
	Dip-coating method	0.07	0.75	0.15	0.77	0.77	21.12	2.70	0.51	212.20
	Spraying method	0.03	0.90	0.29	0.54	0.72	1.66	5.12	0.72	217.30
	Electrochemical method	0.04	0.58	0.02	1.64	0.92	0.06	13.47	0.77	159.20

Surface studies:



(62 ± 3)° Blank | (107 ± 1)° Dip-coating method | (108 ± 1)° Spraying method | (123 ± 1)° Electrochemical method

Figure 6. Comparison of water contact angles on non-treated and octadecylphosphonic acid treated samples prepared with different methods.

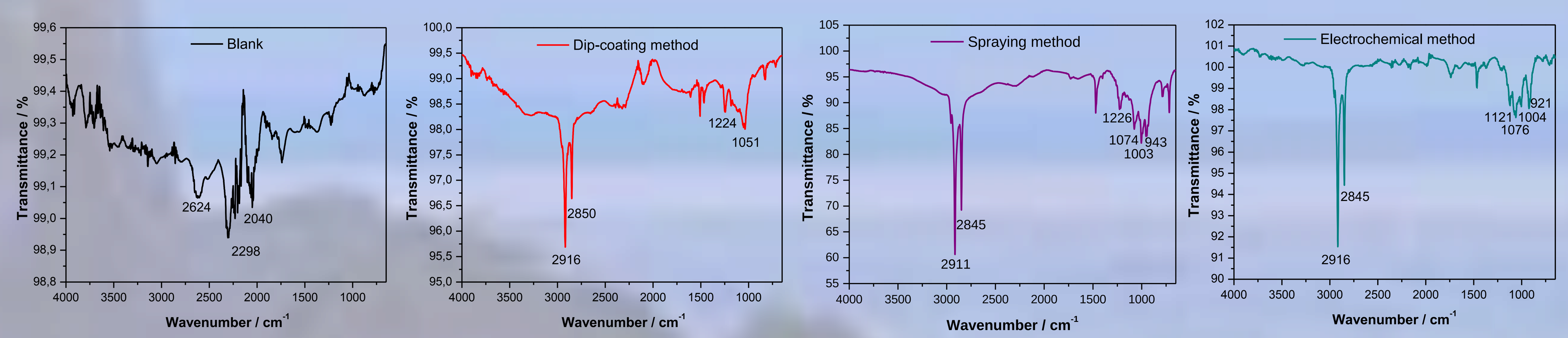


Figure 7. FTIR spectra of octadecylphosphonic acid treated samples prepared by dip-coating, spraying and electrochemical method.

Table 4. Peak values of octadecylphosphonic acid treated samples prepared by different methods.

	Wavenumber (cm^{-1})	Dip-coating method Wavenumber (cm^{-1})	Spraying method Wavenumber (cm^{-1})	Electrochemical method Wavenumber (cm^{-1})
P–O	1150 – 1000	1051	1074, 1003	1121, 1076, 1004
P=O	1335 – 1150	1224	1226	–
P–O–H	950 – 900	–	943	921
$-CH_2$ (sim)	≤ 2850	2850	2845	2845
$-CH_2$ (asim)	≤ 2918	2916	2911	2916

A bidentate bonding configuration via two oxygen atoms.

A monodentate bonding configuration via single oxygen atom.

A tridentate bonding configuration via three oxygen atoms.

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

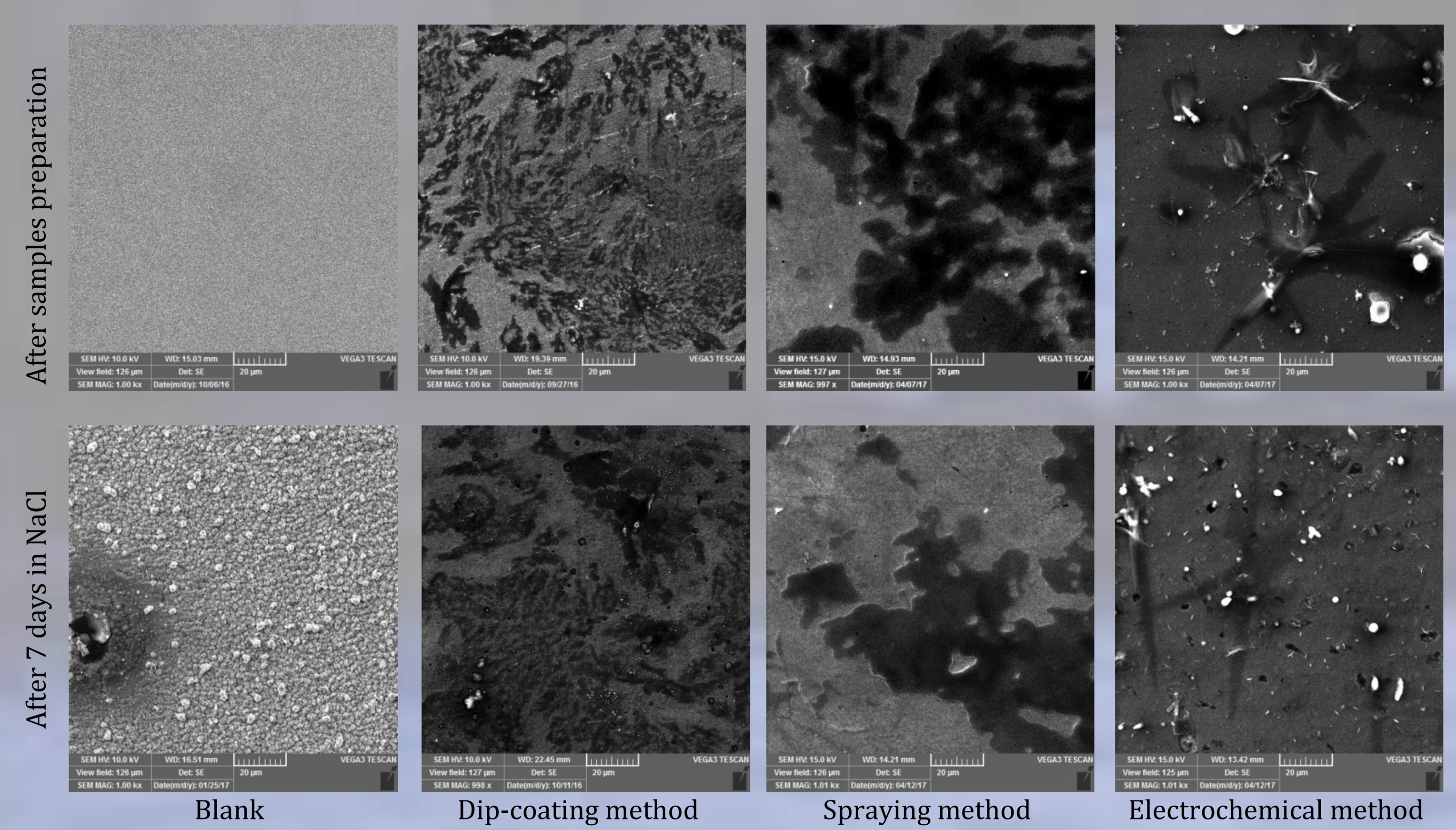


Figure 8. SEM images of non-treated and ODPA treated samples by different methods of preparation before and after exposure to 3 % NaCl solution.

CONCLUSIONS

In this work influence of preparation procedures on protective properties of ODPA SAMs was examined. Although the strongest bonding mode and the most hydrophobic surface was obtained by electrochemical deposition, it was found that the best protective properties are obtained by dip-coating and spraying method. Since, each one of these techniques has some advantages: dip-coating method is simple, electrochemical method is less time consuming, but spraying is more practical than the above mentioned methods, the results of investigations show that by using an adequate preparation method and conditions (temperature, time, applied potential etc.) it is possible to form protective layer of phosphonic acid that significantly reduces cupronickel corrosion rate in seawater.