Protection of Copper Surface With Phytic Acid Against Corrosion in Chloride Solution

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Dedicated to the memory of Prof. Dr. Marija Kosec.

Abstract

Phytic acid (inositol hexaphosphate) was tested as a corrosion inhibitor for copper in 3% sodium chloride. Phytic acid is a natural compound derived from plants, it is not toxic and can be considered as a green inhibitor. Electrochemical methods of linear polarization and potentiodynamic polarization were used to study the electrochemical behaviour and evaluate the inhibition effectiveness. To obtain the optimal corrosion protection the following experimental conditions were investigated: effect of surface pre-treatment (abrasion and three procedures of surface roughening), pre-formation of the layer of phytic acid, time of immersion and concentration of phytic acid. To evaluate the surface pre-treatment procedures the surface roughness and contact angle were measured. Optimal conditions for formation of phytic layer were selected resulting in the inhibition effectiveness of nearly 80%. Morphology and composition of the layer were further studied by scanning electron microscopy, energy dispersive X-ray spectroscopy and X-ray photoelectron spectroscopy. The layer of phytic acid with thickness in the nanometer range homogeneously covers the copper surface. The obtained results show that this natural compound can be used as a mildly effective corrosion inhibitor for copper in chloride solution.

Keywords: Copper, phytic acid, chloride solution, corrosion, corrosion inhibitor

1. Introduction

Copper has a high thermal and electrical conductivity, resistance to micro-organisms and good mechanical properties.[1] Moreover, it forms many alloys, which increases its use in industry and in daily life. Pure copper exhibits a good corrosion resistance at the atmospheric conditions, but in many aggressive media the corrosion rate increases. For example, in chloride solutions uniform and pitting corrosion may occur, as chloride ions accelerate dissolution of copper.[2] One of the important ways to protect metals against corrosion is the use of corrosion inhibitors. Up to date, mainly organic molecules which contain heteroatoms have been investigated as inhibitors. A coordinative bond between heteroatoms and copper modifies the surface resulting in the formation of protective surface layer. The most widely used inhibitors such as azoles and amines have shown a high level of inhibition.[3] However, some of these compounds are at high price, or are toxic and should be thus use with restriction. Due to these reasons, contemporary research is dedicated to search for new, environmentally friendly reagents available at reasonable price.

Phytic acid is in chemical structure inositol hexaphosphate (IP$_6$), with a molecular formula $C_6H_6[OPO(OH)_2]_6$. It contains six phosphates with 12 replaceable protons (Fig. 1) and expresses highly pH dependent chelating properties, so it is able to interact with many metal ions, such as Cu^{2+}, Zn^{2+} and Fe^{2+}.[4,5] It may be assumed that the interaction between phytic acid and copper would lead to the surface modification and, consequently, to the surface protection.

Phytic acid is a natural compound derived from plant sources. It can be found in cereals, nuts, seeds, corn,
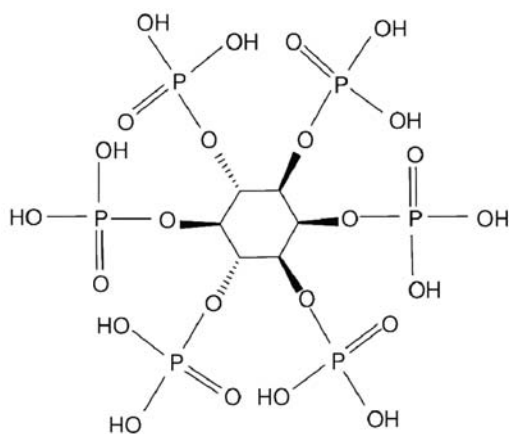
Figure 1. The structure of phytic acid (inositol hexaphosphate, IP$_6$).

wheat, rice and soybeans.[6] Hitherto is this compound used as a cleansing agent, water treatment agent, food additive and cosmetic additive.[4,7] Phytic acid is a non-toxic and environmentally friendly reagent. Moreover, it is soluble in water and available at low cost.[8,9] Due to these properties phytic acid and its salts have recently attracted interest as potential corrosion inhibitors on different metals.[4–15] Phytic acid extract from rice bran inhibited corrosion of copper almost to 95%.[10] The inhibition effect was the highest at the concentration of 5 mg/L IP$_6$, as determined from the weight-loss measurements. In addition to the electrochemical methods, Shen et al. used surface enhanced Raman scattering to investigate the composition of copper surface in 3% NaCl containing IP$_6$.[11] Formation of self-assembled monolayers was achieved on roughened surfaces obtained through oxidation-reduction process. Namely, in order to enhance subsequent adsorption of IP$_6$, in majority of studies the surface roughening in KCl[4,5,13–15] or H$_2$SO$_4$[11] were used. In some studies no surface roughening was used prior immersion in IP$_6$ solution.[8,9]

Phytic acid acted as a cathodic inhibitor with values of ΔG_{ads} close to –40 kJ mol^{-1} indicating that chemisorption may be the operative mechanism.[11] The binding of Na phytate on copper was determined using Raman spectroscopy and electrochemical methods in 0.1 M KCl.[5] The chemical adsorption was proposed to occur through two phosphate groups leading to the inhibition effectiveness (IE) of 41.2%.[5] Na phytate achieved high inhibition in 0.1 M NaOH (ca. 90%).[7] Phytate was shown to promote the formation of the cuprous species, but strongly inhibited the subsequent oxidation to cupric corrosion product. The inhibition effectiveness was strongly dependent on NaOH concentration.[7] In domestic water, the IE value of copper corrosion was dependent on the type of the phytate salt; the IE for Ca and Mg salts was 90%, but that of Na phytate only 65.3%.[12] Electrochemical studies performed on silver electrode showed that IP$_6$ can form dense monolayers and protect silver in acidic and in alkaline condi-

tions.[13] Further, phytic acid is able to interact with brass[4] and cupronickel (copper-nickel alloy).[14,15]

The aim of this work was to consider the use of phytic acid as an inhibitor of copper corrosion in chloride solution. In order to stimulate the adsorption of phytic acid at the copper surface, three different surface roughening procedures were examined. In the first set of experiments the electrochemical measurements were carried out directly in 3% NaCl solution containing phytic acid. In the second set of experiments, the sample was first immersed in the solution of phytic acid, and then electrochemical measurements were performed in 3% NaCl solution. The corrosion parameters and inhibition effectiveness were deduced from electrochemical polarization measurements. Surface roughness, contact angle, surface morphology and composition were analysed using confocal microscope, tensiometer, scanning electron microscope, energy dispersive X-ray spectrometer and X-ray photoelectron spectrometer.

2. Experimental

2. 1. Materials and Chemicals

Working electrode used for electrochemical measurements was copper (purity 99.9%) purchased in the shape of 2 mm-thick foil (Goodfellow, Cambridge, UK). Samples were cut into the shape of discs with diameter 15 mm. Electrode was first abraded on SiC papers under water stream up to 4,000-grit (Struers Labo-Pol-5), rinsed with water, ultrasonically cleaned with ethanol and dried by a stream of nitrogen gas. All experiments were performed on freshly prepared copper surface.

Electrochemical measurements were performed in 3% sodium chloride (Carlo Erba Reagenti, p.a. quality). Phytic acid was supplied by Acros organics (purity 50%), H$_2$SO$_4$ (96%) by Carlo Erba Reagenti, HNO$_3$ (65%) by AppliChem, and KCl by Sigma Aldrich. Solutions were prepared using Milli-Q deionized water with the resistivity of 18.2 MΩ cm at 25 °C (Millipore, Billerica, MA).

2. 2. Surface Pre-treatment

To increase the surface roughness three procedures on freshly abraded copper electrodes were performed - two types of oxidation-reduction cycle (ORC) and etching:

(i) oxidation-reduction cycle was performed electrochemically in 0.1 M KCl. Sample was subjected to potential cycle between –0.4 and 0.4 V vs. saturated calomel electrode (SCE) with a potential scan rate of 30 mV/s and then hold at the final potential for 5 seconds.[5] This procedure was repeated three times. This procedure was denoted as "ORC in KCl".

(ii) oxidation-reduction cycle was performed elec-

trochemically in 2 M H_2SO_4. Sample was pola-
rized with a potential scan rate of 30 mV/s from
–0.55 V up to the potential at which the current
reached the value of 215 mA/cm^2.[11] This proce-
dure was denoted as "ORC in H_2SO_4".

(iii) etching was performed by immersing the sam-
ple into 10% HNO_3 for 30 seconds. This proce-
dure was denoted as "etching in HNO_3".

Following the roughening step the surface was al-
ways rinsed with distilled water and dried.

2. 3. Formation of Layer of Phytic Acid

Two procedures were used to form the layer of phyt-
ic acid on abraded surface (without roughening step) and
roughened copper surface. The first comprised the immer-
sion of the electrode directly in 3% NaCl solution contai-
ning various concentrations of phytic acid (0.01, 0.05, 0.1,
0.5 and 1 mM) as inhibitor. Immersion time was up to 6
hours followed by electrochemical measurements. Second
procedure included the pre-treatment the electrode, i.e.
immersion of the sample into solution of various concen-
trations of phytic acid (0.01, 0.1 and 1 mM) for various
immersion times (1, 4, 6 and 8 hours) to form the protec-
tion layer. The sample was then transferred into another
cell to perform electrochemical measurements in 3%
NaCl solution.

2. 4. Electrochemical Measurements

Electrochemical measurements and oxidation-re-
duction cycles were performed in a three-electrode cell
(volume 1000 mL, Autolab, Metrohm Autolab, Utrecht,
The Netherlands). Copper sample as working electrode
was embedded in a Teflon holder with the area exposed to
solution of 0.95 cm^2. Saturated calomel electrode (SCE, E
= 0.250 V vs. SHE) was used as a reference electrode and
carbon rod served as a counter electrode.

A Parstat potentiostat/galvanostat model 263A
(PAR) controlled by PowerSuite software was used for
ORC and electrochemical measurements. Before the elec-
trochemical measurement, the sample was allowed to sta-
bilize at the open circuit potential (E_{oc}). Linear polariza-
tion was then performed using a potential scan rate of
0.167 mV/s in potential range ± 10 mV with respect to the
stabilized value of E_{oc} to obtain the polarization resistance
(R_p). The value of R_p was determined as the slope of the
current vs. potential curve. Potentiodynamic curve started
250 mV more negative with respect to E_{oc} in the anodic
direction with a potential scan rate 1 mV/s up to 0.8 V.
The values of corrosion potential, E_{corr} and corrosion cur-
rent density (j_{corr}) were deduced by the analysis of the Ta-
fel region. Measurements were repeated at least twice and
the results presented are the mean values. Inhibition effec-
tiveness, IE, of the samples immersed into IP_6 solution
was calculated according to the equation:

$$IE(\%) = \frac{j_{corr(bare)} - j_{corr(mod)}}{j_{corr(bare)}} * 100 \qquad (1)$$

where $j_{corr(bare)}$ and $j_{corr(mod)}$ is corrosion current density for
bare surface and surface modified by phytic acid.

2. 5. Surface Analysis

Surface roughness (R_a) was determined using a con-
focal optical microscope (Axio, CSM 700, Zeiss). 3-D
profiles were measured using an objective of 50× magnifi-
cation. The vertical resolution was 0.05 μm, and the scan-
ning range 10 μm. The results are expressed as average
surface roughness, R_a, as the average of the absolute value
of height Z(x,y) in the measurement length, l, of the
roughness curve in x and y direction.[16] The value of l was
1 mm.

A tensiometer Krüss DSA 20E 20 (Krüss GmbH,
Hamburg, Germany) was used for contact angle measure-
ments (CA) of water drop on copper surface. The measu-
rements were carried out at room temperature. Contact
angles were determined based on the image of the deioni-
zed water drop on the sample surface using Drop-shape-
analysis software which enables the fitting of the water
drop on the surface and allows a precise determination of
the contact angle value. Each contact angle value is the
average of at least three measurements made on different
locations of the same sample.

For surface analysis a field emission scanning elec-
tron microscopy (FEG-SEM; Joel JSM-7600F) equipped
with energy dispersive X-ray spectroscopy (EDS, Oxford
Instruments, INCA) were used. Further, X-ray photoelec-
tron spectroscopy (XPS) was performed with a TFA
Physical Electronics Inc. spectrometer using mono-chro-
matized Al Kα radiation (1486.6 eV) and a hemispherical
analyser. The measurements were conducted at three dif-
ferent take-off angles (detection angle) with respect to the
surface plane, 15°, 45° and 75°. Information closer to the
surface is obtained at small angles, whereas at large an-
gles information closer to the inner interface with the bulk
is obtained. The energy resolution was 0.5 eV. Survey
scan spectra were recorded at a pass energy of 187.85 eV,
and individual high-resolution spectra at a pass energy of
29 eV with an energy step of 0.1 eV.

3. Results and Discussion

3. 1. Corrosion Measurements in 3% NaCl Solution Containing Phytic Acid

The effects of the concentration of phytic acid (IP_6),
the pre-treatment of the surface and immersion time at the
E_{oc} on the copper corrosion 3% NaCl were investigated.
First, measurements were carried out on abraded copper
surface. Linear polarization (Fig. 2) and potentiodynamic

curves (Fig. 3) were measured following the stabilization at the E_{oc} for six hours (denoted as t_{stab}). Electrochemical parameters (R_p, E_{corr}, j_{corr}) and inhibition effectiveness (IE) deduced from electrochemical measurements are presented in Table 1.

During stabilization at the E_{oc}, the potential shifted in the negative direction within the first 1000 s and then remained approximately constant. Copper sample in NaCl solution without IP$_6$ inhibitor achieved the most negative value of E_{oc} (Table 1). The highest polarization resistance and, consequently, highest resistance to uniform corrosion, exhibited the sample immersed in the solution containing 0.05 mM phytic acid (Fig. 2). It is noteworthy that R_p and j_{corr} values were not completely correlated, i.e. high R_p values were not always followed by low j_{corr} values, probably due to the insufficient protection of the surface by IP$_6$ molecules once the surface was polarized to cathodic direction. Further, in NaCl solution without inhibitor the copper sample exhibited only slightly lower R_p value than the sample immersed in 0.05 mM phytic acid; samples immersed in solutions containing other concentrations of IP$_6$ exhibited lower R_p values.

Polarization curves in 3% NaCl solution with and without addition of IP$_6$ (Fig. 3) showed typical shape characteristic for chloride solution.[17] Cathodic reaction in the vicinity of E_{corr} is related to the reduction of oxygen. In neutral chloride solution, anodic reaction is formation of cuprous ions followed by the formation of the main initial corrosion product cuprous chloride (CuCl).[2] CuCl reacts to produce cuprous oxide reflecting in the formation of plateau in the range from –0.3 to –0.2 V (Fig. 3). The mechanism of cuprous oxide production in the presence of chloride ions is usually taken as precipitation reaction.[2] At potentials more positive than –0.2 V the current density increases again leading to the formation of anodic peak at 0 V due to the formation of CuCl. The current minimum denotes the maximum surface coverage with cuprous chloride. CuCl species do not attain the sufficient protection and the current density progressively increases resulting in the formation of cupric ions.

In the presence of IP$_6$ the value of E_{corr} is shifted to more positive values up to 40 mV. The shape of the curve changed; the current density in the cathodic branch decreased, and in the anodic branch the current plateau disappeared. At potentials more positive than –0.2 V the presence of inhibitor did not affect the shape of the curve significantly. Decreased values of j_{corr} resulted in the
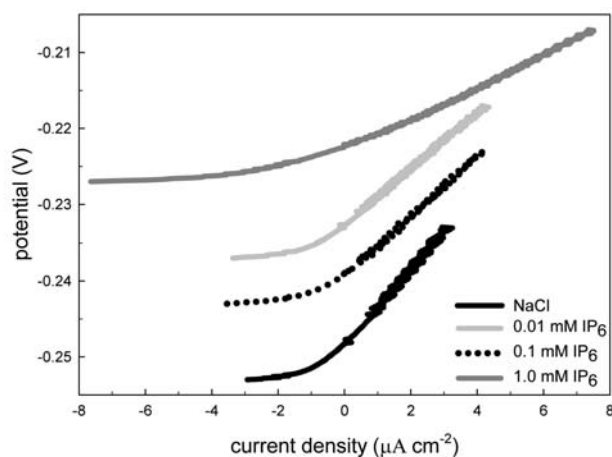

Figure 2. Linear polarization curves recorded for abraded Cu in 3% NaCl, and in 3% NaCl with the addition of different concentrations of phytic acid (IP$_6$). dE/dt = 0.167 mV/s, t_{stab} = 6 h.
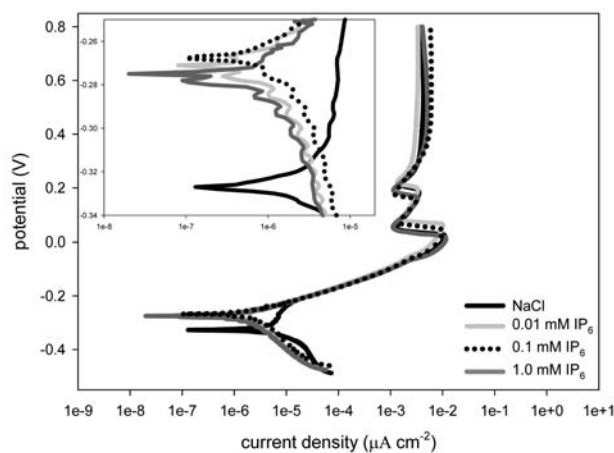

Figure 3. Potentiodynamic polarization curves recorded for abraded Cu in 3% NaCl, and in 3% NaCl with the addition of different concentrations of phytic acid (IP$_6$). dE/dt = 1 mV/s, t_{stab} = 6 h.

Table 1. Electrochemical parameters (open circuit potential, E_{oc}, polarization resistance, R_p, corrosion potential, E_{corr}, corrosion current density, j_{corr}, and inhibition effectiveness, IE) deduced for abraded Cu in 3% NaCl, and in 3% NaCl containing different concentrations of phytic acid (IP$_6$). The sample was stabilized at the E_{oc} for 6 h.

solution	E_{oc} (mV)	R_p (Ω cm^2)	E_{corr} (mV)	j_{corr} (µA cm^{-2})	IE (%)
NaCl	–246	3900	–326	4.30	
0.01 mM IP$_6$	–231	3145	–271	1.72	60.2
0.05 mM IP$_6$	–245	3988	–278	1.56	63.7
0.1 mM IP$_6$	–236	3085	–275	1.51	64.9
0.5 mM IP$_6$	–234	2631	–279	1.95	54.7
1.0 mM IP$_6$	–219	1483	–227	2.00	53.5

IE values between 53.5% and 64.9% depending on the IP_6 concentration (Table 1). The highest IE value was achieved at 0.1 mM; it is noteworthy that the inhibition effect was high already at 0.01 mM (60%), and decreased at IP_6 concentrations higher than 0.1 mM (53.5% at 1 mM).

Next, the effect of surface pre-treatment was examined. Surface roughness and contact angle were measured. The Cu sample abraded using 4,000-grit SiC paper has the R_a value of 49 nm (Table 2). All three roughening procedures increased the R_a value, which was the lowest after etching in HNO_3, and highest after ORC in KCl. The values of contact angles were higher for roughened samples than for abraded samples.

Table 2. Surface roughness, R_a, and contact angle, CA, for abraded Cu sample, and Cu samples roughened using different roughening procedures.

Pre-treatment	R_a (nm)	CA (°)
Abraded Cu	49	57.7
ORC in KCl	332	61.2
ORC in H_2SO_4	126	78.6
Etching in HNO_3	91	67.0

Abraded sample exhibited only lines due to grinding procedure (Fig. 4a). Etching resulted in the increased roughness of 91 nm, but grinding lines, although deeper, were still visible. In contrast, ORC procedures produced rough surface with R_a 126 nm in H_2SO_4 and 332 nm in KCl (Table 2). Grinding lines were no longer visible.

Abraded Cu sample showed approximately three time smaller values of j_{corr} in the presence of 0.1 mM IP_6 (IE = 65%) in NaCl solution (Fig. 3, Table 3). The sample roughened by etching in HNO_3 achieved similar results (IE = 64%) as a non-roughened (abraded) sample in the IP_6 solution, while sample roughened by ORCs resulted in slightly lower IE values (55.8% and 55.4%) (Fig. 5, Table 3). Thus, as the roughening of the surface did not significantly affect the electrochemical parameters it can be concluded that under the conditions of immersion in NaCl solution containing IP_6 the adsorption of inhibitor is not additionally stimulated by surface pre-treatment. In contrast to surface pre-treatment, immersion time at the E_{oc} has a significant role for the protection of the surface. Prolongation of immersion time from 1 h to 6 h decreased the value of j_{corr} from 2.31 to 1.51 $\mu A\ cm^{-2}$ (Table 3).
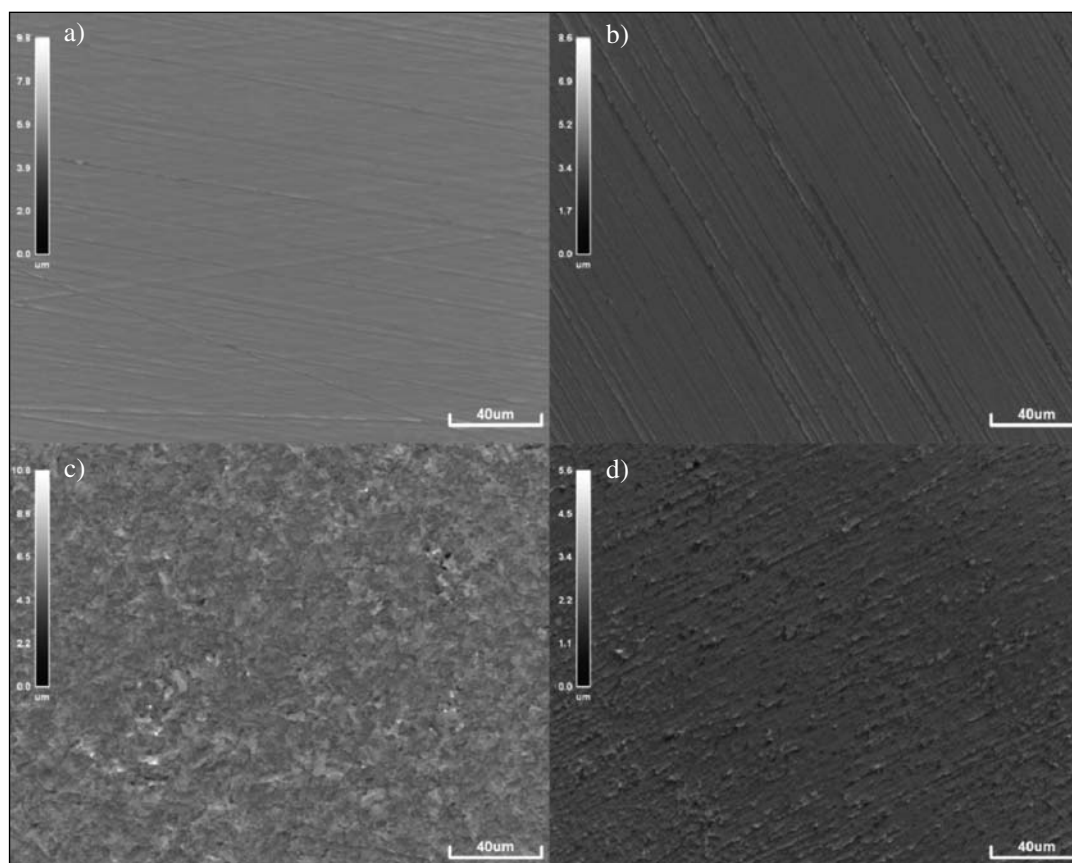

Figure 4. Topographic pictures for (a) abraded Cu sample, and Cu samples roughened using different procedures: (b) etching in HNO_3, (c) ORC in KCl, and (d) ORC in H_2SO_4.

Table 3. Electrochemical parameters (open circuit potential, E_{oc}, polarization resistance, R_p, corrosion potential, E_{corr}, and corrosion current density, j_{corr}, and inhibition effectiveness, IE) deduced for abraded Cu sample, and Cu samples subjected to different roughening procedures. Measurements were performed in 3% NaCl containing 0.1 mM phytic acid (IP$_6$). $dE/dt = 1$ mV/s. The samples were stabilized at the E_{oc} for $t_{stab} = 1$ h and $t_{stab} = 6$ h.

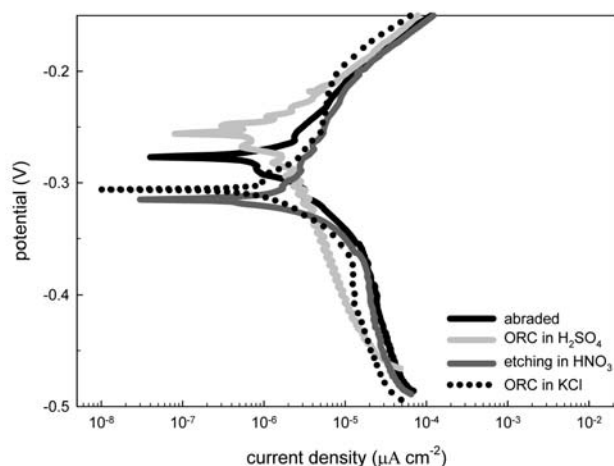| Treatment / solution	t_{stab} (h)	E_{oc} (mV)	R_p (Ω cm^2)	E_{corr} (mV)	j_{corr} (μA cm^{-2})	IE (%)
abraded / NaCl	6	–246	3900	–326	4.30	–
abraded / NaCl + IP$_6$	6	–236	3085	–275	1.51	64.9
ORC in KCl / NaCl + IP$_6$	6	–227	1987	–270	1.91	55.8
ORC in H$_2$SO$_4$ / NaCl + IP$_6$	6	–228	2286	–269	1.84	57.4
etching in HNO$_3$ / NaCl + IP$_6$	6	–236	3319	–273	1.55	64.0
abraded / NaCl	1	–243	3573	–277	1.86	–
abraded / NaCl + IP$_6$	1	–225	1937	–265	2.31	–

Figure 5. Potentiodynamic polarization curves recorded in 3% NaCl for abraded Cu and Cu samples roughened by different procedures. $dE/dt = 1$ mV/s, $t_{stab} = 1$ h. Prior to measurements samples were immersed to 0.1 mM solution of phytic acid (IP$_6$) for 4 h.

3. 2. Corrosion Measurements in 3% NaCl Solution With Previous Immersion of the Sample in Phytic Acid

The purpose of the following experiments was to examine whether prior immersion of copper sample in IP$_6$ solution affects the subsequent behaviour in NaCl solution. The 0.1 mM was determined as an optimal IP$_6$ concentration (Table 1). First, copper surface was only abraded and not additionally roughened (Fig. 6). Polarization measurements are compared for the sample immersed into solution of 3% NaCl containing 0.1 mM IP$_6$ for 6 h, and for the sample immersed in 0.1 mM IP$_6$ for 6 h, transferred to 3% NaCl and immersed for 6 h. Therefore, the samples differed only in the pre-formation of the layer in IP$_6$ solution prior exposure to NaCl solution. Under these conditions, i.e. at non-roughened copper surface, previous immersion into IP$_6$ solution did not result in the improvement of corrosion resistance in NaCl solution as the curve was similar to that of abraded Cu sample in NaCl solution.

In contrast, after 6 h immersion in NaCl solution containing IP$_6$ the j_{corr} value decreased (Fig. 6). From the cathodic part of the potentiodynamic curves it is also evident that IP$_6$ act as the cathodic inhibitor.

In order to check whether roughening the copper surface prior immersion to IP$_6$ solution would improve the results, samples were subjected to three different sample pre-treatments and then immersed in 0.1 mM IP$_6$ solution for 4 h. Following the stabilization at E_{oc} for 1 h, potentiodynamic curves were recorded in 3% NaCl solution (Table 4). The values of IE achieved by different pre-treatments were as follows: 7% for etching in HNO$_3$, 29% for ORC in KCl, and 57% for ORC in H$_2$SO$_4$. The latter pre-treatment thus resulted in the highest value of IE and was chosen as optimal for further experiments. The ORC procedure in KCl including three repetitive cycles resulting in an extensive surface roughening seems not to be suitable for adsorption of phytic acid molecules.

The comparison of the values of IE deduced from electrochemical measurements (Table 4) with surface properties (Table 2, Fig. 3) indicates that increased roughness
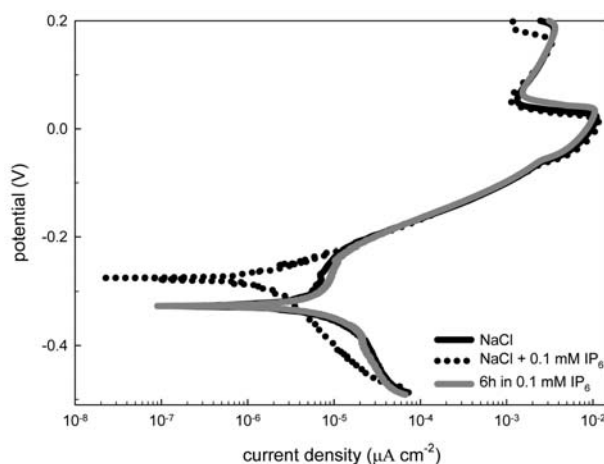

Figure 6. Potentiodynamic polarization curves recorded for abraded Cu samples in 3 % NaCl, in 3% NaCl containing 0.1 mM IP$_6$, and in 3% NaCl after 6 h immersion in 0.1 mM IP$_6$ solution. $dE/dt = 1$ mV/s, $t_{stab} = 6$ h.

Table 4. Electrochemical parameters (open circuit potential, E_{oc}, polarization resistance, R_p, corrosion potential, E_{corr}, corrosion current density, j_{corr}, and inhibition effectiveness, IE) deduced for abraded Cu sample and Cu samples subjected to different roughening procedures. Measurements were performed in 3% NaCl solution. $dE/dt = 1$ mV/s, $t_{stab} = 1$ h. Prior measurements the samples were pre-treated in 0.1 mM phytic acid (IP_6) for 4h.

Treatment	E_{oc} (mV)	R_p (Ω cm^2)	E_{corr} (mV)	j_{corr} (μA cm^{-2})	IE (%)
abraded	−243	3573	−277	1.86	−
ORC in KCl	−248	8502	−303	1.33	28.7
ORC in H_2SO_4	−225	4004	−255	0.80	57.0
etching in HNO_3	−247	5881	−313	1.73	6.9

resulted in the formation of more protective layer which exhibit also increased hydrophobicity. The samples subjected to ORC in H_2SO_4 exhibited the highest values of IE, so this procedure may be optimal as a surface pre-treatment.

Next, the effect of time of immersion (1, 4, 6 and 8 hours) in IP_6 solution on the inhibition effectiveness was investigated in order to select the optimum conditions. Electrochemical parameters are summarized in Table 5. The sample immersed in IP_6 solution for 6 hours had the best resistance against corrosion as it achieved the highest R_p and the lowest j_{corr} values. Once the optimal conditions were determined high R_p values were correlated with low j_{corr} values indicating that the surface was protected under the conditions of open circuit and under polarization. Further, the values of E_{oc} and E_{corr} are more negative compared to abraded Cu. The related IE value was 77%. As samples immersed into IP_6 solution for shorter or longer immersion times exhibited lower IE values, the immersion time of six hours seems to be an optimum value for the IP_6 concentration of 0.1 mM.

For the selected conditions the optimal concentration of the inhibitor was investigated. Potentiodynamic curves recorded for bare Cu sample, and Cu samples pre-treated for 6 h in solutions of phytic acid of different concentrations (0.01, 0.1 and 1 mM) showed that the concentration 0.1 mM resulted in the lowest values of current density (Fig. 7). The related IE value was 77%; lower and higher concentration achieved worse IE values (47% for 0.01 mM and 54% for 1 mM). It should be noted that higher concentration of phytic acid may affect local pH at the
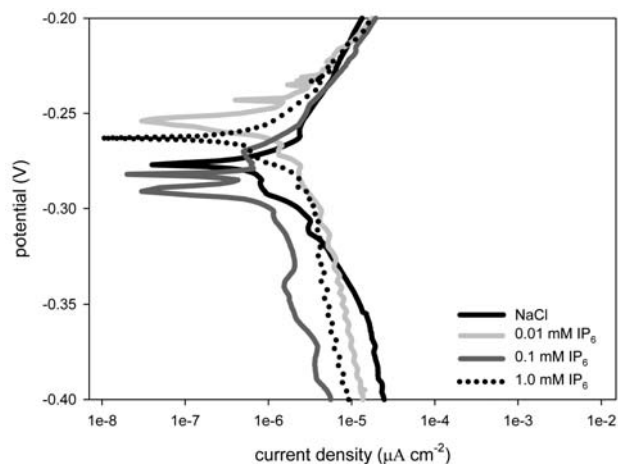
Table 5. Electrochemical values deduced from polarization measurements in 3% NaCl solution for Cu samples roughened by ORC in H_2SO_4 and immersed in 0.1 mM phytic acid (IP_6) for different immersion times, t_{imm}. Measurements were performed in 3% NaCl solution. $dE/dt = 1$ mV/s, $t_{stab} = 1$ h.

t_{imm} (h)	E_{oc} (mV)	R_p (Ω cm^2)	E_{corr} (mV)	j_{corr} (μA cm^{-2})	IE (%)
NaCl	−243	3573	−277	1.86	
1 h in IP_6	−214	2454	−254	1.01	45.5
4 h in IP_6	−225	4004	−255	0.80	57.0
6 h in IP_6	−253	7407	−287	0.43	76.9
8 h in IP_6	−215	2330	−255	0.93	50.1

Figure 7. Potentiodynamic polarization curves recorded in 3% NaCl solution for Cu sample roughened by ORC in H_2SO_4 and immersion for 6 h in solution of phytic acid (IP_6) of different concentrations. $dE/dt = 1$ mV/s, $t_{stab} = 1$ h.

electrode surface and thus alter the electrostatic forces responsible for adsorption of IP_6.

3. 3. Morphology and Composition of Layers Formed in Phytic Acid

Morphology of the surface layers formed on abraded and roughened Cu surface after immersion for 6 h in 0.1 mM solution of IP_6 was analysed by SEM (Fig. 8). Roughened sample was subjected to ORC in H_2SO_4. For abraded sample no formation of the surface layer could be observed after immersion in IP_6 solution (Fig. 8a), and only grinding marks could be noticed. The immersion of roughened sample in IP_6 solution resulted in the formation of surface layer which homogeneously covered the surface as grinding marks could no longer be observed (Fig. 8b). This result confirms the electrochemical results (Fig. 6) that surface pre-treatment was necessary to achieve bonding between metal surface of molecules of phytic acid and formation of protective layer. The layer formed on roughened surface in phytic acid exhibited larger contact angle than that formed on abraded Cu surface,
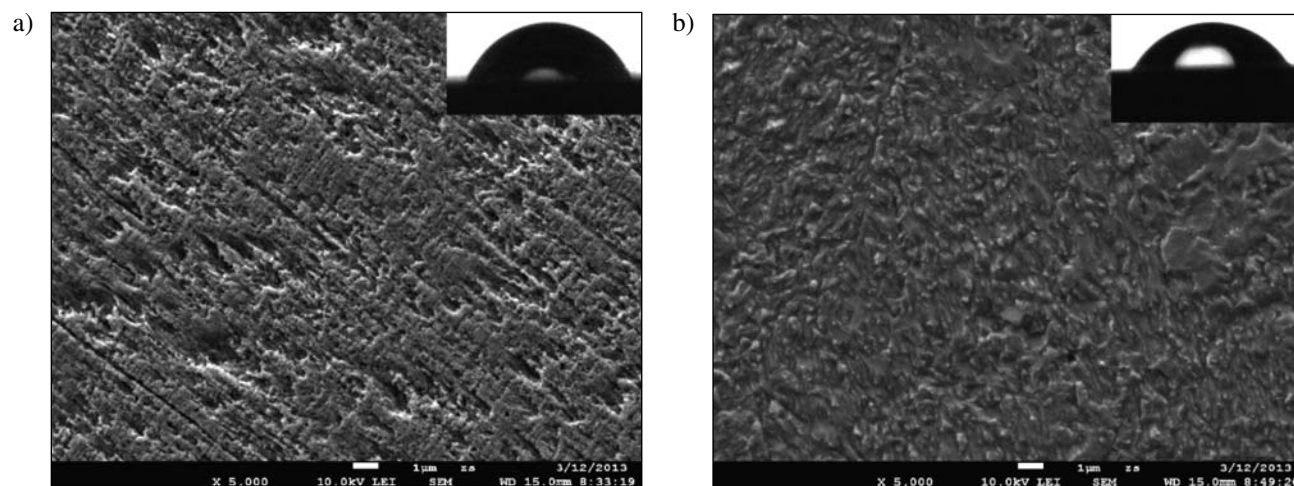
a)   b)

Figure 8. SEM images and images of water drop during contact angle measurements (inset) of Cu surface after immersion for 6 hours in 0.1 mM solution of phytic acid (a) abraded Cu; (b) roughened by ORC in H_2SO_4.

i.e. CA = 71.4° on roughened and CA = 65.7° on abraded surface (Fig. 8, inset). Values obtained did not differ significantly from those obtained on bare surface, i.e. CA = 78.6° on roughened and CA = 67.0° on abraded surface (Table 2).

    For both samples the EDS analysis identified only signal of copper. As the depth of the EDS analysis is approximately 1 μm, we can assume that the layer formed in phytic acid is thinner; therefore, signals of phosphorus and oxygen related to phytic acid could not be identified by EDS. To prove the formation of protective layers, XPS with the analysis depth of approximately 10 nm was explored.

    Survey XPS spectrum recorded at the surface of Cu sample immersed for 6 h in 0.01 mM IP_6 solution identified the presence of copper, oxygen, phosphorus and car-

Figure 9. Survey spectra of the surface layer formed on roughened copper surface after 6 hours immersion in 0.1 mM phytic acid. Take-off angle 45°. The composition deduced from survey spectrum is given in inset. Surface was roughened by ORC in H_2SO_4.

bon (Fig. 9). The presence of phosphorous confirms that the molecule of phytic acid has interacted with copper surface and formed a surface layer. As the ratio P:O in phytic acid is 1:4, the expected content of oxygen would be around 10 at.% if only phytic layer would be present at the surface. As the measured oxygen content is over 30 at.% it may be assumed that copper oxide is formed along with the layer of phytic acid molecules. The content of carbon expected from the atomic ratio in IP_6 should not exceed that of phosphorus, so we can conclude that the vast majority of measured carbon is related to adventitious carbon.

    High resolution spectra were recorded to analyse the presence of various chemical species at the surface. The position of Cu $2p_{3/2}$ peak is at the binding energy, E_b, of 932.8 eV, in accordance with literature data for Cu and Cu_2O (Fig. 10a). Copper and cuprous compounds cannot be differentiated in Cu 2p spectra due to the small chemical shift.[18] The presence of cupric species is noted by the satellite peak approximately 10 eV above the main Cu $2p_{3/2}$ peak. The absence of the peak proves that cupric species are not present the surface (Fig. 10a). In order to differentiate between copper and cuprous species Auger peak in the XPS spectrum is used (Fig. 10b). Auger $[Cu(L_3M_{4,5}M_{4,5})]$ spectra of Cu and Cu_2O are significantly different and allow them to be differentiated.[18] The metal shows an Auger peak centred at a binding energy, E_b, of 568.2 eV, while in Cu_2O this peak is centred at E_b of 570.6 eV.[19] Each of the Auger peaks can be deconvoluted using four peaks.[18] The Auger peak of the sample immersed in phytic acid showed both peaks, at 568.0 eV and 570.8 eV (Fig. 10b) proving the presence of copper and cuprous oxide species. The peak at lower E_b, 565.5 eV, is related mainly to Cu. The intensity of peaks related to Cu metal (at 565.5 eV and 568.0 eV) decreased with decreasing take-off angle, i.e. from interface with metal substrate to la-
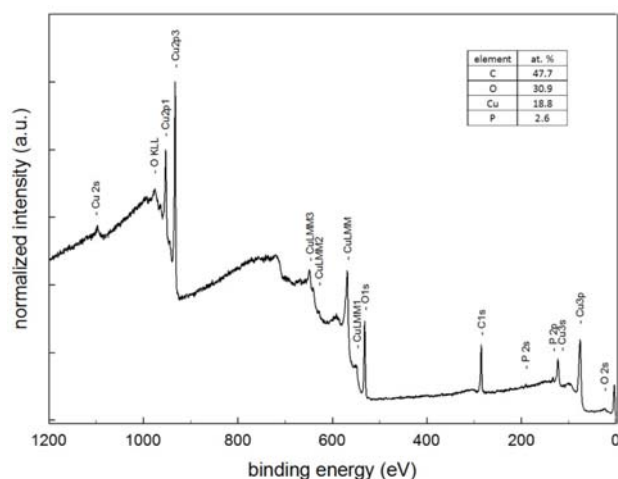
yer surface, indicating that cuprous species (at 570.8 eV) are mainly present at the surface layer.

The O 1s peak was centred at 531.5 eV at take-off angle of 45° (Fig. 10c). This peak comprises contribution from different oxygen species: O^{2-} (E_b from 530.1 to 530.3 eV), hydroxide, OH^- (E_b from 531.4 to 531.6 eV) and water, H_2O (E_b from 532.3 to 532.5 eV). In the presence of phosphorus (Fig. 9) the presence of phosphate species, PO_4^{3-} should be considered which are located at slightly higher E_b range than OH^- species, i.e. from 531.6 to 533.0 eV.[20] The shape and position of the O 1s spectrum (Fig. 10c) indicates that the surface layer formed comprised oxide, hydroxide and phosphate species. The intensity of peak related to species at 532.4 eV related to phosphate increased at smaller take-off angle, indicating that these species are enriched at the layer surface.

The phosphorus 2p spectrum should theoretically be a non-resolved doublet with $2p_{1/2}$ and $2p_{3/2}$ components at ΔBE of only 0.8 eV.[20] At smaller and larger take-off angles the shape of the peak changed indicating that the distribution of different phosphorus species across the layer.[21] At take-off angle of 45° the peak was centred at 133.4 eV. In phytic acid, phosphorus may be bonded to carbon (C–P), single-bonded to oxygen (P–OH) and double-bonded to oxygen (P=O). At larger take-off angle, i.e. closer to interface with substrate, another peak is observed at 133.8 eV. Further, in the case of binding with copper surface, it can also be bonded to oxygen of cuprous oxide. Detailed deconvolution of XPS signal is beyond the scope of this work as at this point of investigation it was important to prove that phytic acid is bonded to copper surface.

Angle resolved XPS analysis represents a non-destructive method of surface profiling analysing the surface depth of approximately 10 nm. Spectra recorded at close to layer surface (15) and closer to interface with metal (75°) are similar indicating that the layer thickness is in the range of 10 nm.
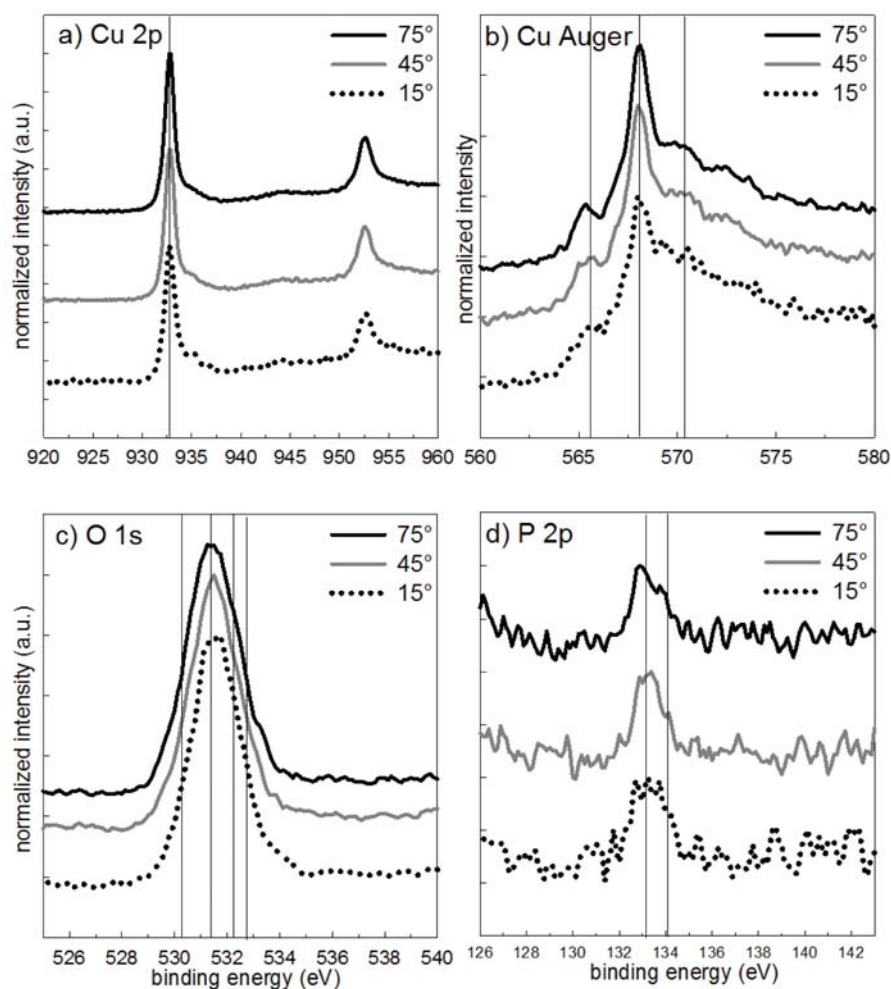

Figure 10. High resolution XPS spectra (a) Cu 2p, (b) Cu Auger, (c) O 1s, and (d) P 2p, of the surface layer formed on roughened Cu samples electrode after immersion in 0.1 mM phytic acid for 6 hours. Surface was roughened by ORC in H_2SO_4. Spectra were recorded at different take-off angles (15°, 45° and 75°). Vertical lines denote the position of reference species.

4. Conclusions

Corrosion protection of copper in 3% NaCl was investigated with electrochemical and surface analytical techniques. Phytic acid was selected as a "green" corrosion inhibitor due to its availability from plants, non-toxicity and reasonable price. Present study proves that its use as corrosion inhibitor is justified but only when used under optimal preparation conditions which were tested in details.

When adding phytic acid directly to NaCl solution, the roughening of the sample surface can be omitted as a pre-treatment. Compared to roughened surface, abraded surface achieves better inhibition effectiveness when immersed for sufficient immersion time and at sufficient acid concentration. At optimal conditions, 6 h immersion time and 0.1 mM concentration, the corrosion was reduced for 65% compared to bare surface. Potentiodynamic measurements show that phytic acid acts as a cathodic inhibitor.

When sample is pre-treated in solution of phytic acid before exposure to chloride solution, surface roughening is necessary. Optimal conditions were achieved for surface roughened by oxidation-reduction cycle in 2 M H_2SO_4, immersion time of 6 h and concentration of phytic acid of 0.1 mM. The layer formed under these conditions at copper surface achieved inhibition effectiveness of 77% when exposed to chloride solution.

SEM analysis confirmed that surface roughening was required to achieve the bonding between copper surface and phytic acid and the formation of homogeneous layer. This layer shows higher contact angle than bare copper surface. Due to small thickness of the layer formed it was necessary to use X-ray photoelectron spectroscopy to analyse the surface composition. The bonding of phytic acid to the copper surface is proved by the presence of phosphorus peak. Copper surface is covered by a cuprous oxide layer. Therefore, when bonded to the surface, phytic acid is bonded to Cu_2O. The thickness of the layer formed is nanometer sized.

5. Acknowledgements

6. References

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Povzetek

Raziskali smo inhibicijo korozije bakra s fitinsko kislino (inozitol heksafosfat) v 3 % natrijevem kloridu. Fitinska kislina je naravna spojina pridobljena iz rastlinskih virov in jo lahko zaradi svoje nestrupenosti označimo kot zeleni inhibitor. Z uporabo elektrokemijskih metod linearne polarizacije in potenciodinamske polarizacije smo študirali elektrokemijsko vedenje ter ovrednotili inhibicijsko učinkovitost. Z namenom, da bi dosegli optimalno korozijsko zaščito, smo spreminjali naslednje eksperimentalne pogoje: predpripravo površine (brušenje in trije postopki povečanja hrapavosti), način tvorbe plasti fitinske kisine, čas potopitve in koncentracijo fitinske kisline. Vpliv postopkov predpriprave površine smo ocenili z merjenjem hrapavosti in kontaktnih kotov. Pri izbranih optimalnih pogojih tvorbe plasti fitinske kisline smo dosegli skoraj 80 % inhibicijsko učinkovitost. Morfologijo in sestavo zaščitne plasti smo analizirali z vrstično elektronsko mikroskopijo, spektroskopijo energijske porazdelitve rentgenskih žarkov ter rentgensko fotoelektronsko spektroskopijo. Ugotovili smo, da plast fitinske kisline z debelino do 10 nanometrov homogeno prekrije bakrovo površino. Rezultati raziskave so pokazali da to naravno spojino lahko uporabljamo v praksi kot relativno učinkovit inhibitor korozije bakra v kloridni raztopini.