Graphene–polypyrrole thin hybrid corrosion resistant coatings for copper

Maido Merisalu \textsuperscript{a,b,*}, Tauno Kahro \textsuperscript{a}, Jekaterina Kozlova \textsuperscript{a}, Ahti Niilik \textsuperscript{a}, Aleksandr Nikolajev \textsuperscript{a}, Margus Marandi \textsuperscript{a}, Aare Floren \textsuperscript{a}, Harry Alles \textsuperscript{a}, Väino Sammelselg \textsuperscript{a,b}

\textsuperscript{a}Institute of Physics, University of Tartu, Ravila 14C, 50411 Tartu, Estonia
\textsuperscript{b}Institute of Chemistry, University of Tartu, Ravila 14A, 50411 Tartu, Estonia

A R T I C L E   I N F O

Article history:
Received 5 October 2014
Received in revised form 22 November 2014
Accepted 19 December 2014
Available online xxx

Keywords:
Anti-corrosion coating
Hybrid protective coating
Large-area CVD graphene
Polymerpyrrole (PPy)
Electrochemical tests
UV radiation exposure

A B S T R A C T

New corrosion-resistant hybrid coatings based on graphene and polypyrrole were prepared and studied. A two-step process was used to fabricate the coatings. First, graphene was grown on a commercial copper foil by chemical vapor deposition (CVD) method. As the coating consisting only from graphene was imperfect, the defects were sealed with polypyrrole using electrodeposition. Corrosion resistance of copper, copper with CVD-graphene coating, and copper with CVD-graphene/polymerpyrrole hybrid coating were tested by immersion in salt water and also studied by open circuit potential measurements of the samples under ultraviolet radiation exposure, linear sweep voltammetry and cyclic voltammetry. The surfaces of the samples were also characterized by different microscopy and Raman spectroscopy methods. Although CVD graphene protected copper against corrosion in a certain extent, immersion tests revealed that the metal corrosion is mainly due to the graphene defects. The hybrid coatings showed much better anticorrosion performance.

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1. Introduction

The present challenge in corrosion prevention is to find the most effective method for different materials favored in certain applications due to their other good properties [1]. In addition, for modern technology it is often demanded that a coating is a multifunctional material, in some cases fully carbon-based materials are preferred [2]. Copper and its alloys are industrial materials that have found different applications, including, for instance, tubes, taps, heat exchangers, containers for different liquids and gases. Unfortunately, these materials tend to be vulnerable to different forms of corrosion [1–5]. For example, pitting corrosion of copper in chloride-containing water is well known [5]. It has also been reported that ultraviolet (UV) radiation (300–450 nm) has an accelerating effect on copper corrosion in dilute chloride aqueous solutions [6]. Traditional wear- and corrosion-resistant coatings are thick, with thicknesses of several to tens of micrometers, but these coatings are not usable in all applications. On metal details with small sizes and/or enhanced precision of dimensions the coating thickness is often strictly limited. Such coatings can be prepared by different physical or chemical vapor deposition methods (PVD, CVD) and they could give a good corrosion resistance on flat and homogeneous surfaces. However, in a number of cases, e.g., for heat exchanger walls thick coatings with heat conductivity much less than copper are unwanted, as well as for the details with sophisticated three-dimensional shapes or for the details with very high precision of dimensions, thick coatings and methods listed above are not efficient enough. In these cases, atomic layer deposition (ALD) method [7–12] might be a promising technology but several important materials, e.g. carbon-based materials, cannot be prepared with this technique.

Graphene (G) is a novel two-dimensional material where carbon atoms form a honeycomb structure. Its possible applications have been intensively studied over the last few years [13–17]. Graphene as many other carbon materials is chemically inert. An ideal graphene sheet is composed of only one atomic layer being, thus, the thinnest material ever produced and studied. At the same time graphene has been proven to be a good diffusion barrier and can be considered as a good ultrathin anticorrosion coating [18]. The corrosion resistance of CVD graphene has been described already [19–22]. On larger areas, however, it is hard to avoid defects in graphene, which often occur on boundaries between different

\textsuperscript{*} Corresponding author at: Institute of Physics, University of Tartu, Ravila 14C, 50411 Tartu, Estonia. Tel.: +372 55597617.
E-mail address: muido.merisalu@gmail.com (M. Merisalu).

http://dx.doi.org/10.1016/j.synмет.2014.12.024
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graphene domains [21]. Each defect in a coating creates a galvanic couple between the anodic substrate and cathodic graphene, causing localized corrosion. Therefore, these defects must be repaired e.g., with a thin carbon-based layer, giving possibility to obtain a continuous defect-free electrochemically homogeneous carbon coating. One method that could be used for repairing the defects in graphene coating is electrochemical deposition of a thin electroactive polymer layer to the sample surface, which mends the defective sites. The polymers can be deposited with different physico-chemical characteristics that depend on the deposition process parameters and substrates used [23].

Electroactive polymers, such as polypyrrole (PPy) and polyaniline (PA), have been mainly studied as corrosion-resistant coatings for different metal substrates, including steel, aluminum and copper [24–28]. There are several positive examples of suppressing the corrosion processes on metals by using conductive polymer coatings but a comprehensive explanation of the electrochemical mechanisms leading to the reduced corrosion rate of metals is still missing [25]. It is known that PPy films can be electrodedeposited from aqueous solutions but PA layers from organic electrolytes, and thus the production of PA films is more complicated and expensive [23]. Our recent investigations of electrodedeposited PPy films showed that it is possible to reduce dopant mobility in the films substantially using bigger (aromatic) organic anions instead of traditional inorganic anionic dopants, e.g., Cl−, NO3−, etc., and applying synthesis parameters that lead to denser packing of the polymer matrix during electrodeposition [29]. On the other hand, only the use of organic dopands does not guarantee the penetration of smaller inorganic anions into the polymer during longer time. It only lowers their diffusion rate in the polymer that was shown by redoxing studies of the polymer [30]. Of course, the existence of oxidizing agents at the polymer–metal interface will cause corrosion of a metal substrate. Therefore, the electroactivity of the polymeric film must be suppressed already in deposition process, which can be done for example by growing ultrathin PPy films from an electrolyte with low concentration of pyrrole [31].

In this work the possibility for improving the corrosion resistance of CVD graphene coating on copper with sealing its defects with electrochemically deposited polypyrrole ultrathin films was studied and demonstrated. The corrosion resistance of the hybrid coatings was tested by immersion in salt solution, linear sweep voltammetry, cyclic voltammetry and open circuit potential measurement of the samples with and without ultraviolet radiation exposure. The coatings were characterized before and after the tests by optical microscopy (OM), scanning electron microscopy (SEM), atomic force microscopy (AFM) and micro-Raman spectroscopy (μRS) methods.

2. Experimental

Graphene was grown on 25 μm thick polycrystalline Cu foils (99.8%, Alfa Aesar) in a laboratory-assembled flow-type CVD reactor [32]. Prior to graphene deposition the foils were treated in 10% acetic acid for 1 h in order to remove the oxide layer and then rinsed in deionized water, acetone (99.5%, Carl Roth GmbH + Co) and isopropyl alcohol (Alfa Aesar). Further pretreatment of the Cu foils was carried out in the CVD reactor. First, the foils were annealed for 30 min at 950–1000 °C in a mixture of H2 and Ar gases (both 99.999%, Linde AGA). The flows of H2 and Ar were set at 130 and 100 sccm, respectively. Immediately after annealing graphene was grown at the same temperature in a gas mixture of 10% CH4 in Ar (99.999%, Linde AGA) supplied at a flow of 40 sccm. The duration of deposition was 20 min. Then the samples were cooled down with a rate of 20 °C/min in Ar environment and used as soon as possible for further experiments.

Pyrrole (Fluka), used for the synthesis of PPy films, was purified by distillation over calcium hydride under vacuum and stored in the dark under Ar atmosphere at low temperature. Polypyrrole was deposited onto graphene in a three-electrode cell having a saturated calomel electrode (SCE) and Pt wire as a reference and a counter electrode, respectively, and a copper foil with or without a graphene coating as a working electrode. The depositions were performed using a potentiostat–galvanostat Reference 600 (Gamry). All potentials were measured versus SCE reference electrode. The area of the working electrode was 1 cm² in all electrochemical measurements.

The graphene sheets with low defect concentrations were coated with polypyrrole for the defect sealing purpose using a pulsed potentio-dynamical deposition method that was based on potential cycling between −400 and 800 mV with an extra-high scanning rate of 10 V/s. Altogether 5000 deposition cycles were applied. All PPy depositions were carried out in 0.1 M oxalic acid aqueous solution with 0.1 M pyrrole addition.

Corrosion tests of a copper foil, the foils with CVD-graphene and with CVD-graphene/polypyrrole hybrid coating were performed in the same three-electrode cell, employing the same potentiostat, and using immersion, corrosion potential measurement, cyclic voltammetry and open circuit potential measurement under UV radiation exposure in naturally aerated 0.5 M NaCl aqueous solution. Before linear sweep and cyclic voltammetry experiments the open circuit potential (OCP) was measured during a stabilization period of 30 min. Immersion tests lasted for 65 h. For cyclic voltammetry experiments, initial potential of −1.1 V, turning potential of 0.5 V, end potential of −1.1 V and potential scan rate of 10 mV/s were used. For linear sweep voltammetry experiments, the initial and end potentials measured versus open circuit potential were −250 mV and 250 mV, respectively, while the potential scan rate was 1 mV/s. In the irradiation experiment the open circuit potential was measured with a frequency of 500 Hz for 5 min. From second to third minute the samples were illuminated with a 405(±10) nm wavelength photodiode through an optical cable, which was transparent for this radiation wavelength. The distance between the opening of the optical cable and tested substrates was 5 mm, resulting an irradiance of 20 μW/cm². To get reliable results in electrochemical tests a new sample was prepared for each test.

Optical microscopy studies were performed with a metallographic optical microscope Eclipse LV150D (Nikon) having Nomarski contrast option as well. High-resolution scanning electron microscopy (HR–SEM) analyses were done by using a dual-beam system Helios NanoLab 600 (FEI), equipped with both electron probe and focused ion beam (FIB), and with energy dispersive X-ray spectrometer (EDX) analyzer INCA Energy 350 having SSD-type X-Max 50 detector (Oxford Instruments). The Slice and View technique was applied by making cross-sections with FIB followed by imaging with HR–SEM. Raman studies with lateral resolution of 2 μm were made with an inVia Raman microscope-spectrometer (Renishaw).

3. Results and discussion

3.1. Corrosion behavior of copper and copper with CVD-graphene

Raman spectroscopy (Fig. 1) and scanning electron microscopy (Fig. 2) studies of CVD graphene coatings on copper and transferred graphene on Si/SiO2 substrates, showed that graphene covered the substrates continuously. The graphene coating consisted mainly from a monolayer but some regions had also two or more graphene layers, and it had, especially on copper, only a small number through-coating defects. This conclusion was made on the basis of the measured Raman spectra and mapping data analysis: in most
of areas of the Cu/G coating the Raman spectra were like the one given in Fig. 1, line 2 having relatively intense and narrow 2D peak.

Further, based on the work of Ferrari et al. [33] and on our own experience we know that after transferring the CVD-graphene from copper foil onto a Si/SiO\textsubscript{2} substrate one could have just a similar spectrum as in Fig. 1, curve 3, which is typical for monolayer graphene [34]. Secondly, the correlative studies of the graphene samples with HR-SEM and \(\mu\)-Raman mapping showed that in the SEM image most of the contrast of different graphene areas is caused by crystalline blocks of copper substrate underneath the graphene, and only small contrast changes indicate the change in the number of graphene layers, accordingly the steps in the thickness of a graphene film. As we know from the Raman measurements that the coating is mainly monolayer graphene, thus only the small darker areas that can be seen in Fig. 2 belong to the bi- or few-layer graphene. On the other hand, also SEM study confirms the Raman analysis data that the whole copper surface is covered with ultrathin carbon coating, otherwise in the uncovered regions the copper surface must be covered with natural oxide layer, and in the SEM images there must appear remarkable contrast between these oxidized copper regions and others, covered with graphene and having beneath bare copper surface. Such type of defects with no covered with graphene areas with submicrometer dimensions were found in SEM study only in a few places.

After immersion tests, the copper foil without coating showed signs of uniform and pitting corrosion (Fig. 3a). Most of the surface became tarnished, which indicated occurring of general corrosion (see also discussions related to Fig. 4). Additionally, localized corrosion pits were easily detectable by OM as dark points inside a brighter area while the last area was as smooth as the initial copper surface (inset of Fig. 3a). Since the pits were mostly evenly distributed on the substrate surface, they were likely initiated by the copper defects that could have been decorated by impurities. The samples that were coated with graphene showed better performance in the immersion tests (Fig. 3b) but after 65 h immersion in salt solution the solution reached metal and caused noticeable delamination of graphene layer in several, probably defective points of graphene coating (see the right inset of Fig. 3b). After appearance of graphene delamination the immersion test was stopped. Depending on the duration of exposure, the area of copper directly exposed to the salt solution showed different stages of pitting and/or general corrosion (see insets of Fig. 3b). The same kind defects were formerly observed in the graphene coating also by Chen et al. [21].

Comparison of linear sweep voltammograms (Tafel plots) for bare and graphene coated copper electrodes (Fig. 4a) showed that due to graphene coating the rates of anodic reactions (copper oxidation that leads to partly passivation of its surface) and cathodic reactions (reduction copper oxide that formed due to exposure to oxygen in air) as well as the current density of corrosion (\(j_{\text{corr}}\)) decreased markedly (Table 1). It should be noted however that Tafel approximation only gives rough estimation of the corrosion current densities of copper and graphene coated copper since in both cases pitting corrosion occurs and diffusion of oxidants may be slowed by corrosion products. However, the significant decrease in corrosion current density suggests that the

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**Fig. 1.** Raman spectra of Cu/G/PPy (curve 1), Cu/G (curve 2) and Si/SiO\textsubscript{2}/G coatings (curve 3).

**Fig. 2.** SEM image of a typical continuous graphene coating on Cu foil.

**Fig. 3.** OM images of (a) Cu foil and (b) Cu foil with graphene coating, both after 65 h immersion in salt solution. Inset in the part (a) shows an area marked with white rectangle with bigger magnification. Insets in the part (b) show OM (left) and SEM (right) images of the coating with higher magnification.
graphene coating was of sealing type. At the same time the corrosion potential \( E_{\text{cor}} \) of a graphene-coated copper had shifted to more cathodic values compared with \( E_{\text{cor}} \) of bare copper by \( \approx 60 \text{ mV} \). The reason for that is not clear yet but the same effect was described in the work of Kirkland et al. [20]. However, in that work it was observed for the graphene coating on nickel a shift of \( E_{\text{cor}} \) in opposite direction, to more anodic values. The authors marked that one of the possible reasons of the different behavior of graphene on copper and nickel can be the difference in the electrical conductivity of the underlying substrates as the conductivity of copper is more than 4 times better in comparison of that for nickel. Correspondingly, different influence of the conductance inhomogeneity of the graphene coating is modulating the surface conductivity of the samples. Anyway, the authors declared that the effect must be studied further. The values of \( j_{\text{corr}}, E_{\text{cor}}, \) current density of reduction \( J_{\text{red,max}} \) and current density of oxidation \( J_{\text{oix, max}} \) determined in this work are given in Table 1.

To understand better the corrosion mechanism of the samples also cyclic voltammetry experiments were carried out (Fig. 4b) and equilibrium of redox reactions of copper in water with chlorine addition was analyzed. Using calculated E-pH diagrams for copper in a neutral aqueous solution of NaCl with pH 6.8, temperature \( T = 25^\circ \text{C} \), normal pressure, chlorine concentration between 0.2 and 1.0 M, and copper concentration between 10–6 and 10–5 mol/l one can expect in anodic sweep \( \approx 500 \pm 500 \text{ mV} \) the following copper oxidation reactions going on [35,36]:

\[
\text{Cu(s)} + 2\text{Cl}^- \rightarrow \text{CuCl}_2^2^- + e^-, \ E = -364 \text{ mV},
\]

\[
\text{CuCl}_2^2^- \rightarrow \text{Cu}^{2+} + e^- + 2\text{Cl}^-, \ E = +144 \text{ mV}
\]

and/or

\[
4\text{CuCl}_2^2^- + 6 \text{OH}^- \rightarrow \text{CuCl}_2 + 3\text{Cu(OH)}_2 + (\text{s}) + 4e^- + 6\text{Cl}^-,
\]

\[ E = +212 \text{ mV} \]

Now if the pH moves a little more to basic direction \( \approx 7.2 \), e.g., locally near the electrode, there could be obtained a local copper oxidation reaction:

\[
\text{CuCl}_2^2^- + \text{H}_2\text{O} \rightarrow \text{Cu}^{2+} + 2\text{H}^+ + 2\text{Cl}^- + e^-, \ E = +138 \text{ mV},
\]

where the \((\text{s})\) denotes the solid depositing phase.

The last Reactions (3) and (4) are quasi-reversible, whereas the depositing layers inhibit further metal corrosion process.

During the back sweep Reactions (1) and (2) are fully, and (3) and (4) partly reversed. In addition, oxygen reduction that produces \( \text{OH}^- \) groups is going on, while intermediate peroxide could be involved in the reaction [37]. Thus, the anodic peak is connected with dissolution of the copper substrate. In this process, the chloride ions take actively part forming either copper chloride species or mixture of copper dichloride and hydroxide, from which the latter partly passivates the substrate. The cathodic peak is oppositely caused by reduction of mostly \( \text{CuCl}_2^2^- \) that was created at anodic potentials in the first sweep.

Adding the graphene coating to the substrate decreases a little the heights of both anodic and cathodic peaks (Fig. 4b, curve 2). Therefore, the graphene coating improves somewhat the corrosion resistance of the sample as it blocks chloride ions from reaching the copper. Similar reduction of the copper oxidation/reduction peaks for graphene coated copper samples was described in the work of Ambrosi, et al. [38].

Open circuit potential measurements and following microscopy studies showed that under the exposure of UV radiation the sample potential showed a cathodic pulse and the uncoated copper severely corroded; Fig. 5a and d. The same test for graphene coated copper sample showed that during the first pulse of the radiation a minor change in potential could be observed in the open circuit potential measurement (Fig. 5b). At the second and third pulse of UV radiation, the potential change increased each time. This is related to the increasing of exposed area of bare copper due to the delamination of graphene (Fig. 5e). Thus, under the UV radiation the delamination of graphene was accelerated.

Summarizing the effect of CVD graphene coating on copper corrosion we can say that only an ideal, defect-free graphene-coating can protect the metal. Unfortunately currently it is not possible to prepare mono- and even few-layer graphene without defects, and thus corrosive substances reach the substrate surface and create a galvanic couple of copper and graphene.

Thus, the only way to improve the graphene coating quality is to try to repair the defects in it, e.g., by adding to the coating a thin polymer layer or preventing the creation of a galvanic couple by modifying either graphene or the exposed copper in the defect regions.

### 3.2. Polyppyrrole deposition on non-continuous and continuous CVD-graphene

A potential method to seal defects in a graphene coating is the electrochemical deposition of polyppyrrole, which has previously been used alone as a corrosion-resistant coating on metals [24–27]. First, it was needed to study the polymer deposition behavior on graphene perfect and defective sites. For this purpose, a partly

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**Table 1**

<table>
<thead>
<tr>
<th>Sample</th>
<th>( E_{\text{cor}} ) (0.5 h)</th>
<th>( E_{\text{cor}} ) (65 h)</th>
<th>( j_{\text{corr}} )</th>
<th>( j_{\text{red,max}} )</th>
<th>( j_{\text{oix,max}} )</th>
</tr>
</thead>
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<tr>
<td>Cu</td>
<td>247</td>
<td>270</td>
<td>1.6</td>
<td>23.8</td>
<td>26.0</td>
</tr>
<tr>
<td>Cu/Gr</td>
<td>303</td>
<td>274</td>
<td>0.3</td>
<td>17.7</td>
<td>22.4</td>
</tr>
<tr>
<td>Cu/Gr/PPy</td>
<td>120</td>
<td>205</td>
<td>6.2</td>
<td>5.9</td>
<td>9.4</td>
</tr>
</tbody>
</table>

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Fig. 4. Results of electrochemical potentiodynamic corrosion tests of Cu, Cu/Gr and Cu/Gr/PPy samples in salt solution: (a) graphs of linear sweep voltammetry (Tafel plots); (b) graphs of cyclic voltammetry (CV plots).
non-continuous graphene sample having large areas of both separate islands and continuous graphene was used and covered potentiodynamically with polypyrrole changing the potential between 0.4 and 0.8 V. As can be seen from image in Fig. 6, there is a brighter area (I) in the polymer coating that had graphene islands that were clearly separated from each other (see left inset). In the darker region (II) the islands had grown together forming continuous coating (see right inset). Since polypyrrole was deposited preferably on graphene instead of bare corroding copper, it helped visualizing graphene islands by OM, and also SEM studies confirmed that there was no graphene between the islands (image not given). In addition, polypyrrole was deposited on the edges of graphene islands a little faster forming over there mound like borders of the coating that move slowly over the borders of graphene island during the growth of the polymer coating. Now if the distance between the graphene islands is short enough the PPy coating can grow together forming a continuous layer with thicker stripes on the graphene defects that can be distinguished in the right inset in Fig. 6, and even better in Fig. 7a and in the left inset there. Thus, the electrochemical repairing of graphene defects with thin PPy layer has certain limits for the dimensions of the defects.

Next, polypyrrole was deposited by the pulse deposition (fast potentiodynamic) process onto almost continuous graphene that was prior CVD grown onto the Cu substrate (Fig. 7). Pulse deposition was chosen due to the following reasons. First, after

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**Fig. 5.** Measured potentials during open circuit potential measurements under brief exposure of UV radiation and SEM images: (a, d) for copper, (b, e) for copper with graphene coating, and (c, f) for copper with graphene/PPy hybrid coating.

**Fig. 6.** Photo image of a Cu sample covered with inhomogeneous graphene coating followed by potentiodynamic deposition of polypyrrole onto the sample (areas I and II); the right side is polymer-free (area III). In the left and right insets OM images are given from areas I and II with higher magnification.
each anodic growth step the new polymer layer is reduced during cathodic sweep, thus, is also densified. Second, at anodic synthesis potentials at the substrate-solution interface a lot of H\textsuperscript{+}-ions is generated that turn the environment locally very acidic, and the graphene layer may be damaged, the pulse growth method helps to lower proton concentration near the electrode.

The hybrid graphene-PPy coatings were carefully investigated by OM and SEM–FIB. The studies showed that PPy had been uniformly deposited on defect-free graphene areas and stitch together the defects of graphene, see Fig. 7a and inset I there. Further cross-section images were made in three characteristic sites – at a smooth area (image not given), at the copper crystals interface (inset II) and at a small defect (inset III), which all were coated/sealed with thin polypyrrole film. In the first site the polymer coating had a constant thickness and no defects were present. The cross-section image made at the copper crystals interface showed that the coating had followed the copper substrate and no defect was present. The third cross-section image that was taken at the “spider”- like thicker polypyrrole formation, revealed a defect in the substrate, which was sealed by polypyrrole. The last defect was initially caused by an imperfect copper substrate – in the places like that graphene, having a negative thermal expansion, could be locally deformed and even broken. Therefore, polypyrrole had deposited on the exposed edges of graphene and eventually sealed the defect.

The Raman studies of the obtained coatings were complicated, as the thin polypyrrole layer on graphene was rapidly heated by focused laser radiation and tended to burn away. Therefore, the radiation intensity was tuned down to 5\% of its normal intensity, which still allowed getting Raman spectrum with only a short exposure time but both characteristic peaks of polypyrrole and graphene (G and 2D peaks are characteristic of defect free
graphene) appeared in the spectrum. Fig. 1, top curve 1, showing that graphene was not destroyed during the PPy deposition.

3.3. Corrosion resistance of CVD-graphene/polypyrrole hybrid coatings on copper

Linear sweep voltammetry experiments were performed after the Cu/G/PPy samples had stabilized in the solution for 30 min. As can be seen in Fig. 4a, the corrosion potential, $E_{corr}$, of graphene-polypyrrole-coated copper had shifted to more anodic values vs. the one of bare copper, inversely to the Cu/Gr sample studied before. At the same time corrosion current density, $I_{corr}$ of the sample with the hybrid coating had even higher value compared to the $I_{corr}$ of Cu/G sample (Table 1). It must be pointed out that the PPy deposition pulses, including the final pulse, ended at cathodic potential. Therefore, the polymer was in reduced state in the fresh hybrid coating. During the anodic sweep of linear sweep voltammetry PPy film was gradually oxidized and its conductivity increased. For that reason the $I_{corr}$ was higher than for bare copper.

In this stage, however, the corrosion rate of Cu/G/PPy samples does not describe the corrosion speed of copper but first of all characterizes the oxidation of polypyrrole, which at the same time preserves the copper from corrosion also in defective areas of graphene. The cyclic voltammograms given in Fig. 4b affirm this statement as both oxidation and reduction current peaks for the hybrid coating are remarkably lower than the ones for bare copper and Cu/Gr samples, and at ~0.4 V it is clearly seen the start of the rise of the polymer oxidation peak, see graph 3.

During the immersion test for 65 h the $E_{corr}$ value of the hybrid coating starting from more anodic values shifted to more cathodic value towards the one of bare copper substrate. It is known that in a water solution PPy can absorb up to 50 vol% of water during long-term stay there, accompanying remarkable swelling, especially during oxidation [23]. Now if the solution contains chlorine anions they can diffuse into the polymer and finally reach the surface of copper producing corrosion of the substrate. Thus, on defective sites, PPy-s main function is significantly slowing the diffusion of corrosive species from the electrolyte to the metal. In addition, the PPy layer helped to prevent the delamination of the graphene layer fixing the borders of graphene at the defective sites (Fig. 5c).

Open circuit potential measurements and following microscopy studies showed a better performance of Cu/Gr/PPy samples under UV radiation exposure too (Fig. 5c and f). During illumination the sample potential changed pulse-like but the change was similar also on the second pulse of the radiation. Therefore, the photo-active area of the substrate did not increase during the UV illumination, thus no delamination of the coating occurred.

Images of the hybrid coating taken after immersion in the salt solution during 65 h are depicted in Fig. 7b. Both OM and SEM images showed that the coating withstood the test, while the area that was coated only with CVD graphene failed completely; compare areas I and II, and the corresponding insets. In the cross section image (inset Ic) one can see that in places where the coating is locally not connected with the substrate, e.g., because of graphene expansion during cooling down after synthesis, the metal surface could be corrosion free, as it appeared under the left-side gather, or slightly corroded as happened under the right-side one.

Further improvement of both the quality of CVD graphene and the corrosion resistance of the polymer can improve the anticorrosion properties of studied hybrid coating.

4. Conclusions

In this work, to our best knowledge, the possibility to enhance corrosion resistance of CVD-graphene coating on Cu substrate by using electrochemically deposited top-layer of polypyrrole for repairing the defects in graphene was studied for the first time. The samples Cu/Gr/PPy with the ultrathin hybrid coating and for comparison with the graphene coating were thoroughly studied by OM, SEM, FIB and μRMS methods and analyzed with electrochemical methods like open circuit potential, linear sweep and cyclic voltammetry. In addition, the coatings were tested by immersion in 0.5 M NaCl solution for 65 h and with short-time UV radiation exposure.

The studies and testing results showed that the new ultrathin hybrid coating withstood the tests well. Its corrosion resistance behavior was complex and time-dependent. The copper substrate surface was mainly protected by graphene but in the defect sites of graphene, intense galvanic corrosion of copper started and led to destruction of the graphene coating. Repairing the defects with the PPy top-layer improved the situation significantly. In the salt solution, the PPy layer can, first, passivate the small areas of bare copper at the defect sites of graphene due to oxidation of the PPy. After some time the polymer is fully oxidized and it will work as passive layer caking the small defects of the graphene, thus counteracting to diffusion of corrosive species and markedly reducing the corrosion rate of the substrate. Galvanic couples between graphene and copper in graphene defects were also removed as both graphene and its defects were fully sealed by homogenous polypyrrole. The polymer top layer also slows down delamination of the coating during corrosion in the case of artificially created defects as it adhered to the graphene sublayer. It was also discovered that polypyrrole intensively deposits on the graphene defects while on continuous graphene the deposition is uniform as. This made the microscopic defects clearly visible under optical and scanning electron microscopy studies and more importantly visualized graphenes continuity in macroscopic scale for naked eye observations.

Acknowledgements

Special thanks to Jaan Aarik for the fruitful discussions, to Raivo Jaaniso, Alma-Asta Kissler and Peeter Ritslaid for technical assistance. This work was supported by the Estonian Ministry of Education and Research (project IUT2-24), Estonian Centre of Excellence TK117, European Social Fund (Grant MIT1) and European Regional Development Fund (project 3.2.1101.12-0026).

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