The protective properties of graphene oxide coatings functionalized with phosphorus atoms

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Outstanding properties of graphene, like very dense structure, chemical inertness support the anti-corrosion properties, therefore, graphene and its derivatives are more and more applied as protective layers. There are a lot of methods for deposition of thin solid films, including solvent-based techniques (dip coating, spray coating, spin coating), electrophoretic deposition (EPD), or chemical vapor deposition (CVD). However, the last two methods are the most often used. The high temperature and very sophisticated devices cause that CVD becomes an unattractive technique. As an alternative and more promising technique is considered EPD because it is environmental-friendly due to conducting of process at room temperature. Electrophoretically deposited graphene oxide coatings protect from corrosion many metals [1,2]. However, on the other hand, the anti-corrosion properties are determined by electrophoretic deposition parameters and chemical composition. The improvement of the protective properties of graphene oxide coatings can be obtained by properly adjustment of EPD parameters (fewer defects in the structure) as well as the modification of graphene oxide with foreign atoms (enhancement of hydrophobicity).

PREPARATION AND RESULTS

Graphene oxide (GO), reduced graphene oxide (rGO) and phosphorus functionalized reduced graphene oxide (P-rGO) were synthesized by the improved Hummer's method, hydrothermal treatment, and hydrothermal treatment in the presence of different amounts (10, 15, 20 ml) of orthophosphoric acid. After synthesis, graphene precursors of coatings were deposited on the copper substrate by EPD using the following parameters: applied voltage – 15 V, time deposition – 15 s, suspension concentration - -.5 mg ml^{-1}. The structural characteristic of GO and rGO were presented in our previous work [3].

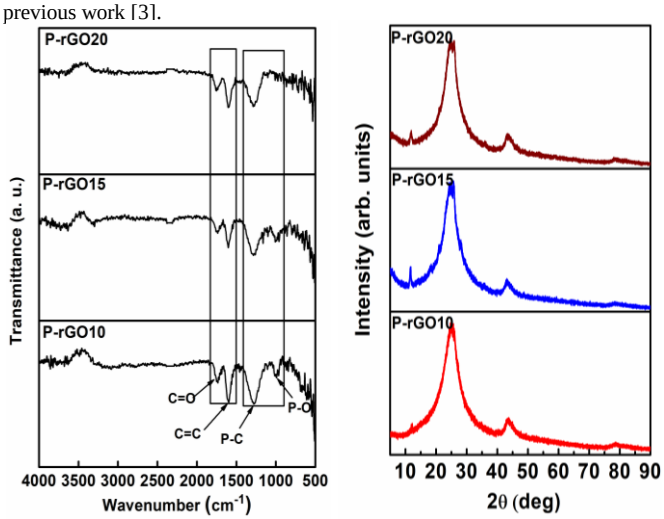

Fig. 1 FTIR spectra (left) and XRD patterns (right) for phosphorous functionalized reduced graphene oxide samples.

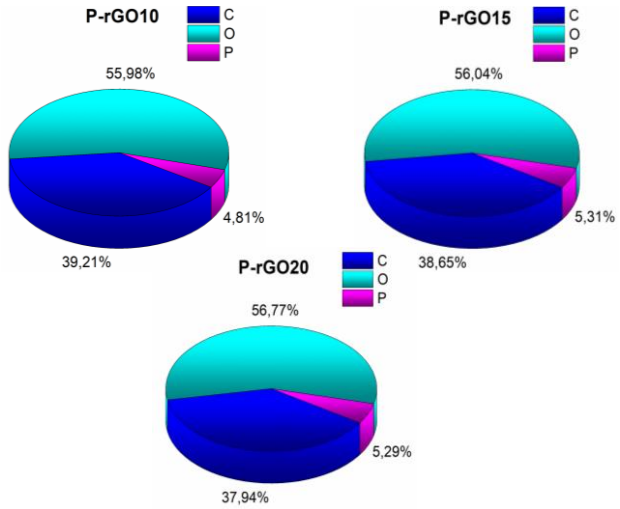

Fig. 2 Chemical composition of phosphorus functionalized reduced graphene oxide samples.

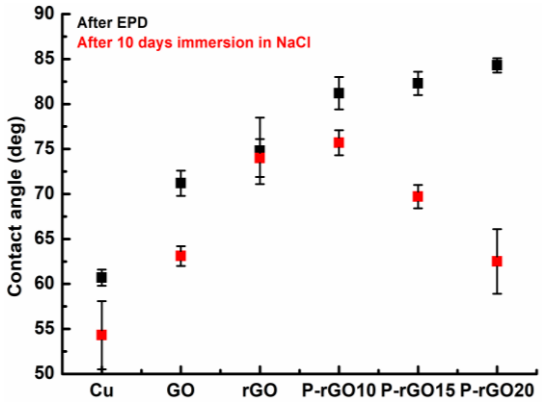

Fig. 3 Contact angle values for coatings: directly after EPD and after 10 days immersion in NaCl.

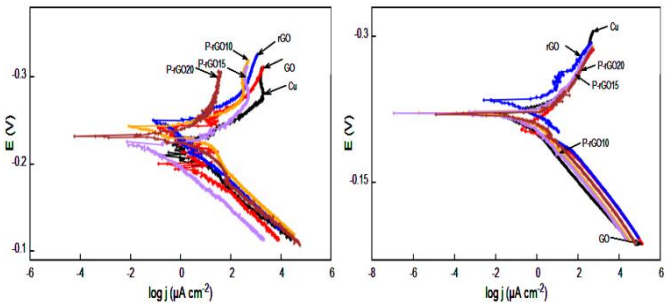

Fig. 4 Polarization curves for bare copper and coatings: measured directly after EPD (left) and after 10 days immersion in 3.5 % NaCl solution (right).

CONCLUSIONS

- FTIR spectra showed, that functionalized graphene precursors of coatings were successfully prepared. It was evidenced by the peaks which can be ascribed to the P-C and P-O groups.
- After hydrothermal treatment of graphene oxide, the interlayer distance (d_{002}) was decreased from 8.5 Å for GO to 3.5 Å for reduced graphene oxide samples. In the case of P-rGO precursors of coatings, d002 increases from P-rGO10 to P-rGO20. This behavior can result from the presence of additional phosphorus groups between graphene layers.
- As can see, phosphorus atom content increases with the amount of added H_3PO_4 reaching the maximum value for P-rGO15. It means that structure of GO was maximally saturated with phosphorus atoms, which simultaneously not causing changes in content for P-rGO20 despite a larger amount of added orthophosphoric acid.
- Morphological analysis showed an intact, defect-free structure.
- P-rGO coatings were less hydrophilic compared to GO and rGO coatings, however, long-term exposure in the saline environment caused a significant reduction of hydrophobic properties.
- This behavior influenced directly the protective properties making P-rGO coatings the most resistant to corrosion, however, after immersion in chloride solution, these properties were substantially reduced.

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