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Electrocatalytic activity of sodium copper pectates in oxygen reduction reaction in fuel cells

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Abstract

In this paper, the results of the electrocatalytic behavior of a series of copper sodium pectate complexes with different Cu^{2+} contents (5, 10, 15, 20, 25%) towards the oxygen reduction reaction (ORR) are presented. To investigate the catalytic activity of the studied complexes in ORR, the cyclic voltammograms (CVA) recorded in an oxygen-saturated environment and inert argon gas were compared. Clear reduction peaks are observed in the CVA, confirming the electrochemical activity of the complexes in the oxygen reduction reaction. The kinetics and mechanism of the oxygen reduction reaction on the glassy carbon modified with the complexes in an acidic 0.5 M H_2SO_4 medium were analyzed. The results obtained by cyclic voltammetry at different scan rates show that the ORR on the copper sodium pectate complexes supported on the glassy carbon is diffusion-controlled. The calculation of the number of electrons participating in the electrochemical reaction was carried out. It was found that the best catalyst of the entire series of samples is a sodium pectate complex with a 5% copper content (n = 4). It was noted that the compound is characterized by a large specific surface area. An increase in the amount of copper ions in coordination biopolymers leads to film formation and a decrease in catalytic activity.

Key findings

- Increasing the copper content in the complexes promotes the formation of a film on the surface, which blocks the active centers of the catalyst.
- Electrocatalytic activity of the complexes towards ORR is diffusion controlled.
- ORR on Cu(5%)-NaPG modified glassy carbon proceeds via a more efficient four-electron mechanism.

Accompanying information

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Fuel cell; oxygen reduction reaction; non-platinum electrocatalysts; pectate; coordination biopolymers

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Supplementary information
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1. Introduction

A fuel cell is an electrochemical device that converts the chemical energy of a fuel and oxidizer into electrical energy without combustion. There are different types of fuel cells, each differing in the fuel and electrolyte they use: proton exchange membrane fuel cells (PEMFCs), solid polymer ethanol [1] and methanol [2] fuel cells, solid oxide fuel cells [3], and others. Due to their low operating temperature and silent operation, PEMFCs play a key role in the development of hydrogen energy [4], finding applications in various fields including motor vehicles [5], aviation [6], autonomous power sources, and portable charging devices [7]. The oxygen reduction reaction and hydrogen oxidation reaction (HOR) are direct reactions occurring at the cathode and anode, respectively. ORR is a complex multi-electron electrochemical process. However, the slow rate of ORR leads to low power generation efficiency in PEMFCs [8]. Therefore, one of the important components for the operation of such systems is an electrocatalyst, which promotes the efficient flow of current-generating reactions in fuel cells. Currently, platinum group metal (PGM)-based materials are considered the best ORR catalysts due to their high active surface area and chemical resistance [9]. Due to the slow kinetics of ORR, an even higher platinum loading on the cathode side of the fuel cell is required to accelerate it. The limited availability and high cost of platinum group metals increase the cost of PEMFC, which is the main reason preventing large-scale implementation and development of fuel cells [10]. It is also worth noting that in the corrosive working environment of fuel cells, even platinum-based catalysts are subject to destruction [11, 12]. In this regard, significant progress has been made in the development and research of various high-performance electrocatalysts to solve the above mentioned problems [13].

Many studies use ORR catalysts with lower precious metal content [14]. Particular attention has been attracted by platinum-based alloys [15–17], not only because of the reduced amount of platinum but also because of their high electrocatalytic activity and unique structure [18]. For example, in [19], the authors obtained platinum alloys PtM with various transition metals (M = Ni, Co, Fe, Ti, V, etc.). Stamenkovic et al. revealed the dependence of the catalytic activity of compounds in ORR on the electronic structure of the catalyst surface. A certain shift in the center of the d-zone leads to an increase in catalytic activity. It was also found that Pt_3Co is characterized by the best stability and activity with respect to ORR. Han B. and his colleagues studied the effect of changing the size of nanostructures on the activity of Pt-Ni-based catalysts [20]. The authors also showed that acid treatment leads to exceptional durability of the catalysts. A critical size of 6 nm was found for nanoparticles, defined as the lower limit of particle size for nanoporosity formation. Larger particles have unstable surfaces and thus will be leached from the surface during acid treatment. Finally, annealing after acid treatment was found to significantly improve the stability of the alloy, which contributes to higher catalytic activity in ORR. In [21] the authors reported a high Co (Pt:Co = 66:34) PtCo based catalyst consisting of both small- and large-sized solid particles. The PtCo catalyst was investigated by accelerated pressure testing (AST). PtCo nanoparticles of different sizes exhibited different morphological changes. Small- and medium-sized particles rich in Pt remained almost unchanged, while large-sized nanoparticles containing more Co became hollow shells due to Co leaching from Pt-Co catalysts. Other important aspects affecting the electrocatalysis of ORR alloys are the ratio between Pt and M [22–24] and the different surface structures of nanoparticles [25–27].

Although significant progress has been made in the development and research of various electrocatalysts, achieving a balance between PGM content and high electrocatalytic activity is still an urgent and challenging task. Therefore, replacing PGM-containing catalysts with PGM-free catalysts plays an important role in the large-scale implementation of PEMFCs. Nitrogen-doped transition metal-carbon (M-N-C) materials have great potential as non-platinum electrocatalysts in ORR because of the presence of sufficient active sites for oxygen adsorption and reduction due to their structure [28,29]. The most common catalysts are Fe-N-C [30, 31], Co–N–C [32, 33], Mn–N–C [34, 35]. In [36], Yang et al. prepared a single-atom catalyst supported on iron-nitrogen doped graphitic carbon (SA-Fe/NG) with the addition of an F127 surfactant. The obtained SA-Fe/NG exhibited long-term stability for 5000 cycles. In addition, the SA-Fe/NG catalyst exhibited high catalytic activity toward ORR with the onset (E_{onset}) and half-wave potential ($E_{1/2}$) of 0.9 V and 0.8 V in 0.5 M H_2SO_4, respectively, which were not much inferior to that of the Pt/C catalyst (0.83 V). Han et al. reported a catalyst based on Co embedded in nitrogen-doped hollow carbon spheres (ISAS-Co/HNCS) [37]. A template assisted pyrolysis method was used to prepare ISAS-Co/HNCS. The combination of isolated single Co atoms and hollow carbon support surface provided remarkable redox activity in an acidic 0.5 M H_2SO_4 medium with $E_{1/2} = 0.773$ V. In [38], the authors presented a highly efficient ORR catalyst, which incorporates atomically dispersed single manganese sites bonded to nitrogen on partially graphitized carbon (Mn–N–C). The resulting catalyst demonstrated high stability for 30000 cycles and excellent catalytic activity for ORR ($E_{1/2} = 0.8$ V). In addition, significant progress has been achieved in the study of diatomic catalysts [39,40]. The use of two transition metal centers has improved the catalytic activity and stability. For example, Liu and coworkers [41] developed a catalyst based on two metals Fe and Co modified with sulfur ligands S (Spa-S-Fe, Co/NC). The authors claim that the active site of Co-N_4 and the S ligand connecting the graphite layers can interact with the active site of Fe-N_4, optimizing its d-orbital electronic structure. This helps to improve the adsorption-desorption process of intermediate oxygen compounds and enhance the ORR kinetics. Xu et al. presented a two-component catalyst based on the Fe-Zn metal pair (Fe–Zn–SA/NC) as an alternative to Pt/C [42]. The developed catalyst demonstrated characteristics comparable to platinum catalyst ($E_{1/2} = 0.78$ V in acidic solution) with a fairly long service life.

Recently, coordination biopolymers (pectins) have attracted great interest due to their wide range of properties and bioactivity [43]. Pectins are biopolymers whose main carbohydrate chain consists of α-1.4-linked D-galacturonic acid units. Due to their complex branched structure, non-toxicity, and biodegradability, pectins are of considerable interest for use in various sectors of the food industry [44], pharmacology [45] and catalysis [46,47]. In this paper, we report on the study of a series of sodium copper pectate-based complexes Cu(n%)–NaPG with different Cu^{2+} ion contents as non-platinum electrocatalysts for ORR.

2. Experimental

We considered a batch of 5 catalysts based on copper complexes of sodium pectate as catalysts for the oxygen reduction reaction. Sodium pectate was obtained by adding a solution of NaOH to an aqueous solution of natural pectin. Then, by adding a solution of divalent copper salt to the resulting sodium pectate, metal complexes with varying degrees of substitution of Na^+ by Cu^{2+} were obtained: Cu(5%)-NaPG, Cu(10%)-NaPG, Cu(15%)-NaPG, Cu(20%)-NaPG, Cu(25%)-NaPG [48].

Catalytic ink was then prepared using the obtained complexes. For this, Cu(n%)-NaPG, Vulcan XC-72, and Nafion (10 wt.% solution) were mixed in a ratio of 2:4:5 and dispersed in a solvent for 2 hours. Isopropyl alcohol and deionized water were used as solvents (alcohol:water ratio = 1:1). To measure the catalytic activity in ORR, 20 μl of the prepared ink was applied to the surface of the working electrode and dried at room temperature. All electrochemical measurements of the Cu(n%)-NaPG coordination biopolymers were carried out in a glass three-electrode cell at room temperature in an acidic medium (aqueous solution of 0.5 M H_2SO_4). Cyclic voltammetry curves (CVA) were recorded using an Elins P-20x potentiostat in argon and oxygen. The glassy carbon with a diameter of 3 mm modified with catalytic ink based on Cu(*n*%)-NaPG was used as the working electrode. The reference and auxiliary electrodes were Ag/AgCl and a platinum electrode.

The surface morphology of the complexes was studied by atomic force microscopy on a scanning probe microscope MultiMode V (Veeco) in the tapping mode. Highly oriented pyrolytic graphite (HOPG) was used as a substrate for studying the complexes.

3. Results and Discussions

The electrochemical behavior of electrodes modified with copper complexes of sodium pectate in the oxygen reduction reaction was studied by recording cyclic voltammetric curves in a 0.5 M H_2SO_4 medium saturated with oxygen at room temperature. For comparison, the CVA curves of the complexes were also recorded in an inert argon environment. The results are presented in Figure 1.

The CVA curves of all complexes contain an oxygen reduction peak, which is absent in an argon environment, indicating the electrochemical activity of these complexes with respect to the oxygen reduction reaction.

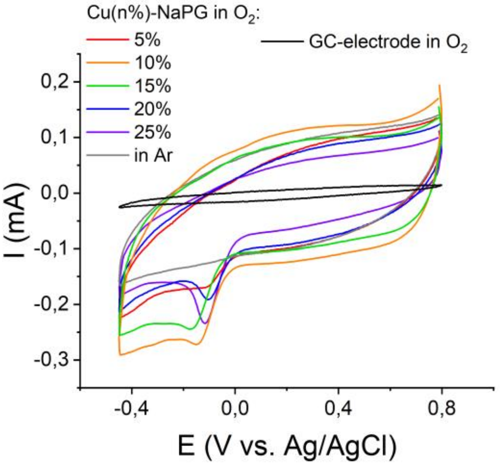

Figure 1 CVA curves of Cu(n%)-NaPG complexes and glassy carbon electrode in a 0.5 M H_2SO_4 medium saturated with O_2 and Ar at a scan rate of 50 mV/s.

To establish the mechanism of the oxygen reduction reaction on copper complexes of sodium pectate, the dependence of the cathodic peak potential E_{pc} (as well as the peak current I_p) on the potential application rate υ in the range of 25–250 mV/s was studied. It turned out that the peak potentials E_{pc} depend on the sweep rate and, with its increase, shift toward more negative values. This trend is maintained for all the studied complexes.

Figure 2 shows the dependences of the cathodic current on the square root of the potential sweep rate for the process of electrochemical oxygen reduction on copper complexes of sodium pectate. It is evident that the cathode peak currents I_p for all complexes increase with the increase in the velocity υ and depend linearly on $\upsilon^{1/2}$, which is confirmed by the determination coefficients R^2. The obtained linear dependence indicates that the oxygen transfer to the electrode modified with copper complexes of sodium pectate is controlled by diffusion.

To confirm that the oxygen reduction reaction is indeed limited by diffusion, graphs (lg I_p) *vs* (lg υ) were also constructed for the studied complexes. Figure 3 shows the obtained linear curves.

It is known that the slope of this linear dependence yields a coefficient called the Semerano criterion, which allows one to establish the limiting stage that determines the nature of the peak cathodic current [49]. The calculated values of the Semerano criterion for the Cu(5%)-NaPG, Cu(10%)-NaPG, and Cu(15%)-NaPG complexes are 0.5. It follows that the process of electrochemical reduction of oxygen on these complexes is indeed limited by diffusion. For the Cu(20%)-NaPG and Cu(25%)-NaPG complexes, the Semerano criterion is 0.62 and 0.64, respectively. A small deviation of the Semerano criterion for these complexes from the theoretical value indicates that a small contribution of the adsorption current is observed due to the adsorption of oxygen on the electrode.

To determine the charge transfer coefficient α in the reaction of electrochemical oxygen reduction on copper complexes of sodium pectate, the Tafel curves were constructed and analyzed (Figure 4).

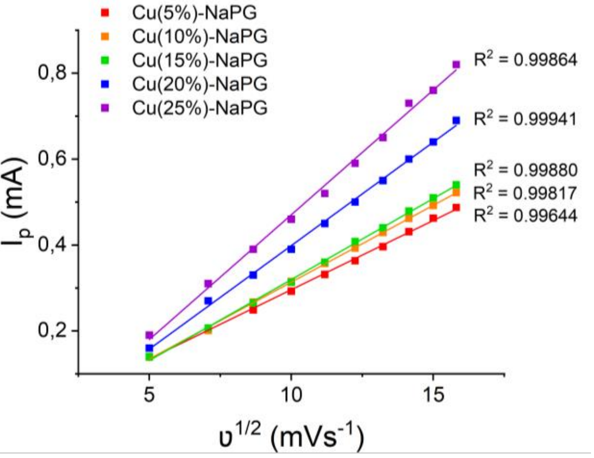

Figure 2 Dependences of the cathode peak current I_p on the square root of the scanning speed $\upsilon^{1/2}$ (25–250 mV/s) for the entire series of Cu(*n*%)-NaPG samples.

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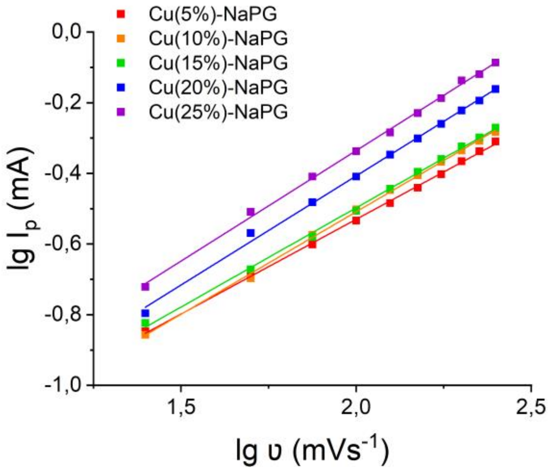

Figure 3 Dependences of the logarithm of the peak current lg I_p on the logarithm of the sweep speed lg υ (25–250 mV/s) for Cu(n%)-NaPG.

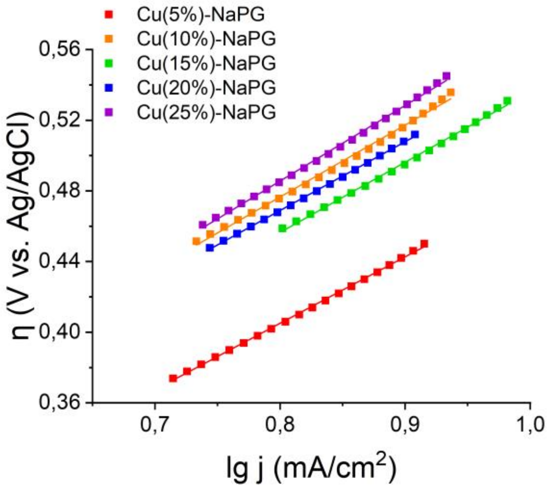

Figure 4 Tafel curves for Cu(n%)-NaPG complexes at a scan rate of 50 mV/s.

The charge transfer coefficients α for the complexes are obtained by the equation: $b = \frac{-2.3RT}{\alpha F}$, where F is the Faraday constant, R is the universal gas constant, T is the temperature, and b is the slope of the function (Figure 4). The calculated average values of α for the studied complexes are presented in Table 1.

In addition, the number of electrons participating in the reaction of electrochemical oxygen reduction was calculated for irreversible processes using the Laviron equation [50]. For this purpose, curves of the peak potential E_p versus the logarithm of the potential sweep rate (lg υ) were constructed for each complex based on the experimental data.

Table 1 Average values of charge transfer coefficient α for Cu(n%)-NaPG.

Complexes	Charge transfer coefficient, α
Cu(5%)-NaPG	0.16
Cu(10%)-NaPG	0.14
Cu(15%)-NaPG	0.15
Cu(20%)-NaPG	0.15
Cu(25%)-NaPG	0.14

As can be seen from Figure 5, a linear dependence of E_p on lg υ is observed for all the complexes. We calculated the value of α from the slope of this dependence. The as-found values of α (Table 1) allowed us to calculate the number of electrons participating in the electrocatalytic reaction of oxygen reduction on copper complexes of sodium pectate. The most efficient was the sodium pectate complex with 5% copper content. The number of electrons for Cu(5%)-NaPG is 4. It follows that oxygen on this catalyst is directly reduced to water. For Cu(10%)-NaPG n is 3.75, for Cu(15%)-NaPG – 3.3, for Cu(20%)-NaPG – 3.52, Cu(25%)-NaPG – 3.59. The data obtained show that O_2 reduction on these catalysts occurs through the formation of intermediate products.

The surface morphology and structure of copper complexes of sodium pectate were studied by atomic force microscopy. An interesting feature was discovered during the microscopic investigations. With an increase in the copper content in sodium pectates, their ability to form films increases. For example, a sodium pectate complex with 5% copper content is characterized by round particles with sizes 30–70 nm, which are located in a thin organic film. The sizes of the most common particles are 50–65 nm (Figure 6).

With further increase in the amount of copper, the complexes already form a dense organic film without inclusions in the form of particles. Apparently, these particles are located inside the organic film. The AFM results are in good agreement with the data of electrochemical studies.

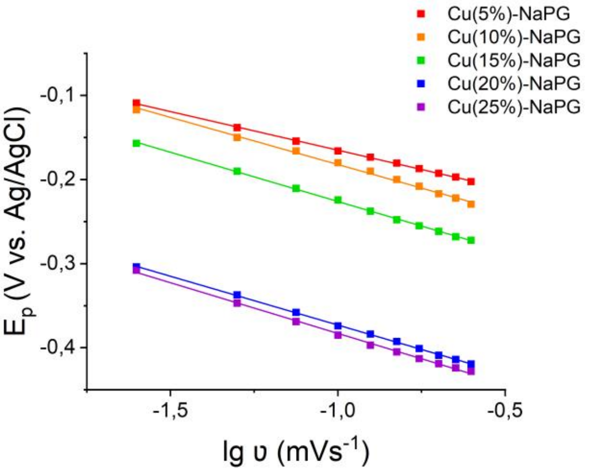

Figure 5 Graphs of the dependence of the cathode peak potential (E_p) on the lg υ (25–250 mV/s) for Cu(n%)-NaPG.

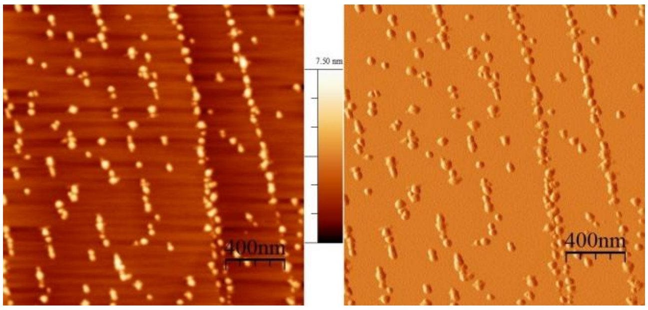

Figure 6 AFM-image of the Cu(5%)-NaPG complex on the surface of pyrolytic graphite: topography (on the left), distribution of the amplitude deviation (on the right).

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The decrease in the number of electrons participating in the electrochemical reaction of O_2 with an increase in the amount of copper in the complexes is apparently associated with the formation of a film that covers the active centers and thereby reduces the efficiency of the catalysts.

4. Limitations

Since electrocatalysts tend to dissolve in acidic environments, their electrochemical stability and durability are important characteristics, which affect the efficiency and service life of electrochemical systems based on them. In the future, it is planned to investigate the stability and long-term degradation of Cu(n%)-NaPG as oxygen reduction electrocatalysts using theoretical and experimental methods.

5. Conclusions

Thus, in this work, several catalysts based on copper complexes of sodium pectate were investigated. Electrochemical studies demonstrated that sodium pectate with 5% copper content Cu(5%)-NaPG can be used as an efficient catalyst since the oxygen reduction reaction on this complex occurs according to the most efficient four-electron mechanism. The dependence of the studied catalysts, performance on the surface morphology of the complexes is shown. It is established that with an increase in the amount of copper, the ability of the complexes to form films increases, which leads to a decrease in the efficiency of the catalysts based on them.

Supplementary materials

No supplementary materials are available.

Data availability statement

The raw/processed data required to reproduce the above findings cannot be shared at this time as the data also forms part of an ongoing study.

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None.

Author contributions

Conceptualization: G.R.N., E.M.L.
Data curation: E.M.L., G.R.N., V.V.K.
Formal Analysis: G.R.N., E.M.L., I.R.N.
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Methodology: E.M.L., G.R.N., I.R.N.
Project administration: I.R.N.
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Software: I.R.N.
Supervision: G.R.N., I.R.N.
Validation: G.R.N., I.R.N.
Visualization: E.M.L., G.R.N.
Writing – original draft: G.R.N., E.M.L.
Writing – review & editing: I.R.N.

Conflict of interest

The authors declare no conflict of interest.

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