Catalytic properties of nanostructured nickel-containing pectin biopolymers on a glassy carbon surface

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Abstract. Searching for new ways of converting carbon dioxide into value-added products, such as fuels, is a relevant task of our time. Electrochemical reduction of carbon dioxide to carbon monoxide, hydrocarbons and alcohols is considered as one of the main approaches in this area. One of the most advanced approaches is the use of coordination polymers for homogeneous and heterogeneous catalysis of carbon dioxide reduction. We obtained coordination pectin biopolymers with different nickel ions contents (PG-NaNi). The structure and composition of the obtained biopolymers were characterized by such physicochemical methods as IR and ICP-AE spectroscopy. Morphology of PG-NaNi on a glassy carbon surface provides very high surface to volume ratio. Cyclic voltammetry on the modified glassy carbon working electrode in water solution saturated with carbon dioxide shows catalytic properties of PG-NaNi for CO₂ reduction reaction.

1. Introduction

Efficient conversion of carbon dioxide into useful products is an important task of science. The content of carbon dioxide in the atmosphere is constantly increasing due to the extensive use of fossil fuels. Currently its volume fraction in the atmosphere is more than 400 ml/m³ and continues to increase, while in the pre-industrial era it was about 280 ml/m³. The most significant problem at present is the economically feasible conversion of carbon dioxide to monoxide and/or another useful compounds. Electrochemical reduction of carbon dioxide to various products is considered as one of the main approaches to solve this problem.

Selectivity and yield of the electrochemical CO₂ reduction reaction at room temperature strongly depend on the working electrode material, solvent, solvent pH, temperature and CO₂ pressure [1,2]. Direct single-electron reduction of linear CO₂ to the nonlinear anion radical CO₂⁻ occurs at high negative potential -2.21 V vs. SCE with low current density. But multi-electron reduction reactions are possible in the presence of water molecules. These reactions have much less standard electrode potential, for example:

\[
\begin{align*}
\text{CO}_2 + \text{H}_2\text{O} + 2e &= \text{CO} + 2\text{OH} \quad (-0.52 \text{ V}) \\
\text{CO}_2 + 6\text{H}_2\text{O} + 8e &= \text{CH}_4 + 8\text{OH} \quad (-0.25 \text{ V}) \\
\text{CO}_2 + 8\text{H}_2\text{O} + 12e &= \text{C}_2\text{H}_4 + 12\text{OH} \quad (-0.34 \text{ V}) \\
\text{CO}_2 + 9\text{H}_2\text{O} + 12e &= \text{C}_2\text{H}_5\text{OH} + 12\text{OH} \quad (-0.33 \text{ V}) \\
\text{CO}_2 + 13\text{H}_2\text{O} + 18e &= \text{C}_3\text{H}_7\text{OH} + 18\text{OH} \quad (-0.32 \text{ V})
\end{align*}
\]
The values are estimated from thermodynamic data [3], in aqueous media at 25°C with respect to SHE. The standard potentials are conveniently given at pH 7.0, where most of actual CO\(_2\) reductions are measured. You can be seen some more useful products obtained during CO\(_2\) reduction in figure 1.

![Diagram of CO\(_2\) reduction products](image)

**Figure 1.** Main carbon dioxide reduction products.

However, efficient, cheap and stable catalysts are necessary for wide use these reactions. Unfortunately, no catalysts were found that met all the requirements and could be used on an industrial scale.

Many metal complexes are catalysts for the CO\(_2\) electrochemical reduction. At present, three main types of workable complexes can be distinguished [4]: complexes with macrocyclic ligands, diimine complexes, and phosphine complexes. The main problem is their cost and insolubility in the aquatic environment.

Work on the use of metal nanoparticles as catalysts is also underway [5]. However, the high cost of nanoparticles and their agglomeration complicate widespread commercialization.

Coordination polymers with metal ions can be considered as polymerized forms of molecular catalysts. They have several advantages as electrocatalysts - significant design flexibility, high surface to volume ratio and they allow functionalization with multivalent ligands and metal centres. In this work, we propose coordination pectin biopolymers with nickel ions as heterogeneous electrocatalysts for the electrochemical CO\(_2\) reduction reaction.

2. Results and Discussion

Coordination polymers PG-NaNi were obtained as a result of total pectins deesterification with 100% degree of salt formation and its subsequent involvement in complexation [6] (figure 2). The following reagents were used as starting reagents: citrus pectin Classic C-401 manufactured by Herbstreith & Fox (Germany) with 65% esterification degree, nickel chloride NiCl\(_2\) and sodium hydroxide NaOH with 99.9% degree of purity. We synthesized coordination pectin polymers with various substitution degrees of Na ions for Ni(II) - 5, 10, 15, 20, 25%.

IR spectroscopy was used to check the state of carboxy groups in the PG-NaNi polymers. IR spectra were recorded on a Tensor 27 IR spectrometer (Bruker, Germany) with 1 cm\(^{-1}\) resolution in the range 400–4000 cm\(^{-1}\) in KBr pellets. The compounds IR spectra showed the presence of characteristic absorption bands 1610-1625 cm\(^{-1}\) corresponding to the stretching vibrations of the ionic form COO\(^{-}\).
(figure 3), while the absorption band of stretching vibrations of the carboxy or ester group ν(C=O) at 1745 - 1750 cm\(^{-1}\) is absent. So, we were able to achieve complete deesterification of pectin source.

Na and Ni ions were identified in the PG-NaNi acidified aqueous solutions using simultaneous inductively coupled plasma optical emission spectrometer (ICP-OES) model iCAP 6300 DUO by Varian Thermo Scientific Company equipped with a CID detector. Concentration of Na and Ni ions was determined, respectively, by the spectral lines: 588.995 nm and 231.604 nm. It can be seen from the table 1 that part of the Na ions is replaced by Ni ions and their percentage ratio corresponds to the expected.

| Substitution degrees of Na for Ni | 5% | 10% | 15% | 20% | 25% |
|----------------------------------|----|-----|-----|-----|-----|
| Na (mg/l) ±10%                   | 19.4 | 19.3 | 17.8 | 16.4 | 13.7 |
| Ni (mg/l) ±10%                   | 2.28  | 5.93 | 9.93 | 12.7 | 13.4 |

Since results for different PG-NaNi polymers are similar, further we will focus on the results for PG-NaNi with 20% substitution degree of Na with Ni ions.

Our idea was to deposit PG-NaNi on the surface of a glassy carbon (GC) electrode, then to lower the electrode into water saturated with carbon dioxide and try to catalytically reduce CO\(_2\). When water is saturated with carbon dioxide, pH level of the solution greatly decreases (in our conditions, up to pH = 4). This is an undesirable process, therefore pH=7.0 of solutions throughout the entire electrochemical experiments was supported by the addition of small amounts of HCl (≥99.9%) and KOH (≥99.9%). In addition, 0.1 M NaCl (≥99.9%) was added to the water as the supporting electrolyte.

Deposition of PG-NaNi on the GC electrode surface technique was as follows: 7.5 mg PG-NaNi was dissolved in 400 μl mixture of deionized water and isopropyl alcohol (1:1). The resulting solution was placed in an ultrasonic bath for 10 minutes, then was dripped onto the surface of a glassy carbon electrode. After drying in the open air, the modified GC electrode was considered ready for use. An atomic force microscope (MultiMode V) was used to reveal the morphology of PG-NaNi on the GC surface. As you can see in Figure 4, there are fibers of biopolymer PG-NaNi with 40 nm diameter on the GC surface. Fiber agglomeration can be observed in some places (top right in the figure), while single fibers are observed in other places. Such morphology provides a very high surface to volume ratio, and it is very good for a heterogeneous catalyst.

Electrochemical methods able to give the unique information about the electrochemical and subsequent chemical processes [7,8]. Figure 5 shows the results of cyclic voltammetry (CV) on the modified working electrode in water solutions saturated with argon (0 min CO\(_2\) bubbling) or carbon dioxide with different bubbling times. The curves show an irreversible reduction peak with potential E = 1.2 V vs. Ag/AgCl. It can be noted that an increase in CO\(_2\) bubbling time leads to an increase in the
peak current. CV curves with bubbling time over 6 min. do not show an increase in reduction peak current. Worth noting cyclic voltammetry on the unmodified working electrode in water does not show any peaks in this potential range.

![Figure 4](image1.jpg)  **Figure 4.** Atomic force microscope image of the PG-NaNi modified GC surface.

![Figure 5](image2.jpg)  **Figure 5.** CV on the modified GC electrode in water saturated with Ar or CO₂ with different bubbling times.

The foregoing confirms catalytic properties of nanostructured nickel-containing pectin biopolymers PG-NaNi on a glassy carbon surface for CO₂ reduction reaction.

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