Electrochemical properties of PrBaCo$_2$O$_6$ electrode in the oxidation of glucose and methyle orange

To cite this article: A M Shalamova and Yu A Glazyrina 2021 IOP Conf. Ser.: Earth Environ. Sci. 864 012025

View the article online for updates and enhancements.

You may also like
- PrBaCo$_2$O$_6$-Sm$_{0.5}$Sr$_{0.5}$CoO$_3$ Composite Oxide as Active Cathode for Intermediate-Temperature Solid Oxide Fuel Cells
  Tatsumi Ishihara, Syuaibatul Islamiyah, Maksymilian Kluczny et al.
- Electrode materials based on complex d-metals oxides for symmetrical solid oxide fuel cells
  Sergey Ya. Istomin, Nikolay V. Lyskov, Galina N. Mazo et al.
- Oxygen Reduction Reaction Kinetics of PrBaCo$_2$O$_6$ As SOFC Cathode
  Nan Zhang, Wenyuan Li and Xingbo Liu
Electrochemical properties of PrBaCo$_2$O$_6$ electrode in the oxidation of glucose and methyle orange

A M Shalamova$^{1,2}$ and Yu A Glazyrina$^1$

$^1$Institute of Chemical Technology, Ural Federal University, 620002 Ekaterinburg, Russia
$^2$Institute of Solid State Chemistry UB RAS, 620990 Ekaterinburg, Russia

kam1995@ya.ru

Abstract. In this work, we investigate the possibility of using double cobaltite with the composition PrBaCo$_2$O$_6$ as an electrocatalyst in the oxidation of organic compounds. A screen-printed carbon electrode modified with the PrBaCo$_2$O$_6$ drop method was investigated as a sensor for glucose. The amperometric signal of this sensor is logarithmically dependent on the analyte concentration according to the equation: $I (\mu A) = 9.485 \cdot \ln (C (\text{mM})) + 17.864 \ (R = 0.9951)$. The limit of detection is 0.52 $\mu$M (at S/N = 3). The linearity range is 0.0-17.5 mM, which corresponds to the physiological values of blood glucose concentration (3.3-5.5 mM). In addition, the possibility of electrooxidation of a refractory organic compound (methylen orange) using a modified electrode was shown.

1. Introduction
The irrational use of non-renewable natural resources (oil, natural gas, and coal) over the past centuries has led to significant problems, such as the global energy crisis and environmental pollution, which prompted the search for clean and renewable energy [1]. The pollution of water bodies and, as a result, the lack of clean drinking water affects people from all over the world. The situation is aggravated by the fact that most hazardous organic pollutants (dyes and pharmaceutical compounds) are bio-refractory, which leads to continuous pollution of the reservoir [2]. There are many methods of water purification such as filtration, osmosis, chlorination, chemical oxidation, and biofiltration. However, these methods are labor-intensive, economically ineffective, complex, and generate harmful by-products. Consequently, it became necessary to create a new effective method that would combine the decomposition of organic substances in water and the production of renewable energy [2].

A fuel cell (FC), in the general case, is a galvanic cell, which consists of two electrodes, on the anode and/or cathode of which a catalyst is located. FC generates electrical energy by converting the chemical energy of compounds (fuel) into electrical energy using various renewable catalysts. In FC, exoelectrogenic microorganisms or semiconductors (electrocatalysts) transfer electrons from the oxidation of substrates to the anode surface. Wherein, electrons flow to the cathode, where various chemicals, such as oxygen [2, 3], can serve as electron acceptors, resulting in the generation of electricity. This technology reflects the trend of waste management and is expected to solve the difficult problem of water and renewable energy deficiency. This concept is used to degradation refractory organic substances such as methyl orange, methylene blue, Congo red [2, 3], rhodamine B, and tetracycline [4].
The aggravation in the quality of drinking water and food products of people around the globe can cause various diseases. Therefore, there is a need to develop new sensors for continuous monitoring of water quality and biological analytes such as glucose, hydrogen peroxide, cholesterol, and others. A promising direction in this area is self-powered biosensors [5]. It is a new type of electrochemical biosensor in which the FC and sensor are combined. The sensor is a three-electrode cell, where sensitivity and selectivity are crucial, and the FC is two-electrode (anode and cathode), and the main focus is on generating open-circuit potential, currents, and maximum current density by improving catalysts, materials, interfaces, and cell designs [6].

Microbial FCs are commonly used as environmental quality monitoring systems. An important feature of microbial biosensors is their duration and stability of operation, as well as high substrate specificity reducing selectivity. Therefore, the first self-powered enzyme biosensors for glucose determination have been developed. This design can be used with other enzymes, but the principle of operation remains unchanged: biological analyte is fuel for the FC. A drawback of enzyme biosensors is the lack of stability due to the internal nature of enzymes, which affects the metrological characteristics of the biosensor, as well as sensitivity to temperature changes, pH, poisonous chemicals, humidity, low reproducibility, and high cost. Consequently, notwithstanding the high sensitivity of biosensors, the current task is to create non-enzymatic sensors with a stable and sensitive response.

Enzyme-free sensors have higher sensitivity, better selectivity, reproducibility, and good stability. There are self-power biosensors based on electrocatalysts for the determination of hydrogen peroxide [7, 8] and glucose [7, 9].

Perovskites with the general formula ABO3 are acknowledged as one of the effective electrocatalysts. These complex oxides are used as catalysts in High-Temperature Electrochemical Redox Reactions, solid oxide FCs, and demonstrate catalytic activity for oxygen reduction reaction (ORR), oxygen evolution reaction (OER), and hydrogen evolution reaction (HER) [10], as well as in relation to glucose [11, 12] and H2O2. These compounds have earned their widespread use due to the successful combination of specific electronic and transport properties [10]. Mainly, the effectiveness of such materials in the above processes is determined by the presence of active centers, the role of which can be played by defects in the electronic and/or crystal structure. Double perovskite is also reported with the formula AA′B2O6–δ. This type of compounds is represented by alternating layers [AO1–δBO2] [A′O] [BO2] and has a higher electronic conductivity due to the different valence of cations [13].

In this work, the possibility of using double cobaltite of the composition PrBaCo2O6 as an electrocatalyst in the oxidation of organic compounds is studied. Analytical characteristics of the electrode modified with the research compound are considered by the example of electrocatalytic oxidation of glucose (as an analyte), as well as the degradation of methyl orange (as a refractory organic compound).

2. Methods
Electrochemical measurements were performed in a standard three-electrode cell for voltammetric measurements: carbon screen-printed electrodes modified with a PrBaCo2O6 suspension (CSPE/PBC) were used as a working electrode; the reference electrode was an Ag|AgCl (3M KCl), Pt-wire was employed as a counter electrode.

An Evolution 201 UV-Visible Spectrophotometer (Thermo scientific®, USA) was used to monitor the methyl orange concentration at 460 nm.

The effectiveness of CSPE / PBC was evaluated by changing the concentration of methylene orange in solution:

\[ MO_{decrease}(\%) = \frac{C_0 - C}{C_0} \times 100\% \]  \hspace{1cm} (1)

where \(C_0\) (initial) and \(C\) (final) of the dye solutions are calculated in mg/ml (\(C_0 = 10\) mg/ml).
3. Results

3.1. Electrocatalytic oxidation of glucose

On cyclic voltammograms (CV), there is a perceptible increase in electrochemical activity with the addition of glucose, which increases with increasing concentration at a wide range of potentials. The obtained CVs are shown in Figure 1a. As it can be observed, there is no oxidation / reduction peak. The signal stabilizes after 2-3 cycles. The working electrode potential is 0.5 V. The recorded chronoamperograms are presented in Figure 1b.

For this electrode, a logarithmic dependence of the current on the glucose concentration is observed in the concentration range of 0-17.5 mM glucose, the regression equation is: \( I (\mu A) = 9.485 \ln(C (\text{mM})) + 17.864 \) (R = 0.9951). The limit of detection is 0.52 µM, it was defined at a signal-to-noise ratio of 3 (S/N = 3).

![Figure 1](image.png)

**Figure 1.** (a) CVs responses of the CSPE / PBC in the absence and presence of 5 mM glucose in a 0.1 M NaOH electrolyte, using 0.1 V/s scan rate; (b) Amperometric response of the CSPE/PBC with serial glucose addition every 30 sec.

3.2. Electrochemical degradation of methyl orange

Organic substances are oxidized by OH radicals arising on the electrode during OER [11, 14]. This reaction can be observed when the current density increases sharply on the oxidation branch of the cyclic voltammogram [14].

Cyclic voltammograms in the presence of methyl orange at the CSPE / PBC electrode are shown in Figure 2a. An increase in the current and a decrease in the potential of the maximum of the reduction current can be observed, which indicates the electrochemical activity of the electrode under study in relation to the oxidation of methyl orange.

![Figure 2](image.png)

**Figure 2.** (a) CVs responses of the CSPE / PBC in the absence and presence of 5 mM glucose in a 0.1 M NaOH electrolyte, using 0.1 V/s scan rate; (b) Amperometric response of the CSPE/PBC with serial glucose addition every 30 sec.

Figure 2b shows the time dependence of MO\(_{\text{decrease}}\) at an imposed potential of 0.6 V. MO\(_{\text{decrease}}\) decreases almost exponentially with time and plateaus after about 60 minutes of electrolysis. Obviously, under the given conditions, complete decomposition of organic matter does not occur. This can be explained by the appearance of a polymer film on the electrode with strong adsorption properties, called the poisoning effect [15].
Figure 2. (a) CVs responses of the CSPE / PBC in the absence and presence of 10 mg/ml methyl orange in a 0.1 M NaOH electrolyte, using 0.1 V/s scan rate. (b) Dependence of MO$_{\text{decrease}}$ on time at an imposed potential of 0.6 V.

4. Conclusion
In this work, a carbon screen-printed electrode modified with PrBaCo$_2$O$_6$ was investigated as a sensor for glucose, and a logarithmic dependence of the current on the analyte concentration was obtained. The linearity range is 0.0-17.5 mM, which corresponds to the physiological values of blood glucose concentration (3.3-5.5 mM). Therefore, this compound can be used as a catalyst for the electrochemical oxidation of glucose. Moreover, this compound promotes the electrooxidation of the refractory organic compound (methylene orange) and can be used as an electrocatalyst for the decomposition of pollutants in fuel cells.

Acknowledgements
The authors appreciate the support of this work within the government assignment № AAAA-A19-119110190048-7.

References
[1] Cai T, Meng L, Chen G, Xi Y, Jiang N, Song J and Huang M 2020 Chemosphere 248 125985
[2] Bai J, Wang R, Li Y, Tang Y, Zeng Q, Xia L and Zhou B 2016 J. Hazard. Mater. 311 51
[3] Zhao K, Zeng Q, Bai J, Li J, Xia L, Chen S and Zhou B 2007 Water Res. 108 293
[4] Yu H, Xue Y, Lu Y, Wang X, Zhu S, Qin W and Huo M 2020 J. Environ. Manag. 254 109738
[5] Han X, Qu Y, Wu J, Li D, Ren N and Feng Y 2020 J. Hazard. Mater. 399 122878
[6] Lv P, Zhou H, Mensah A, Feng Q, Wang D, Hu X and Wei Q 2018 Chem. Eng. J. 351 177
[7] Komkova M A, Karyakina E E and Karyakin A A 2018 Electroanal. 30 607
[8] He L, Zhang Q, Gong C, Liu H, Hu F, Zhong F and Zhang B 2020 Sens. Actuat. B: Chem. 310 127842
[9] Chen Y, Ji W, Yan K, Gao J and Zhang J 2019 Nano Energy 61 173
[10] Deganello F, Liotta L F, Leonardi S G and Neri G 2016 Electrochimica Acta 190 939
[11] He J, Sunarso J, Zhu Y, Zhong Y, Miao J, Zhou W and Shao Z 2017 Sens. Actuat. 244 482
[12] Liotta L F, Puleo F, La Parola V, Leonardi S G, Donato N, Aloisio D and Neri G 2015 Electroanal. 27 684
[13] Yin W J, Weng B, Ge J, Sun Q, Li Z and Yan Y 2019 Energy Environ. Sci. 12 442
[14] Alaoui A, El Kacermi K, El Ass K, Kitane S and El Bouzidi S 2015 Separat. Purificat. Technol. 154 281
[15] Panizza M and Cerisola G 2009 Chem. Rev. 109 6541