ELECTROCATALYTIC MATERIALS FOR ANODIC OXIDATION OF SULPHITE

PhD Thesis - Abstract
for obtaining the scientific title of doctor at
Politehnica University of Timisoara
in the field of CHEMICAL ENGINEERING
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March 2022

Global energy demand in 2021 has been estimated to increase by 4% over the previous year [1].

Total primary energy supply differs from global final energy consumption, as much of the obtained energy is consumed during the refining process and transportation 44rom the original place of supply to consumers. World final energy consumption refers to that fraction of primary energy that is consumed by end-users (industry, agriculture, transport, etc.) [2].

In 2020, global energy consumption accounted for 31.2% oil, 27.2% coal, 24.7% natural gas, 4.3% nuclear power, 24.7% hydropower and 5.7% other energy sources (solar, wind, geothermal, heat, etc.). Oil, coal and natural gas were the most popular energy fuels [3].

In the new energy economy, clean technology is becoming a major new area for investment and international competition. By 2050, significant growth is expected in the market for manufacturers of electrolysers and fuel cells. Advanced battery cells with an energy density of over 400 Wh/kg, fuel cells, advanced biofuels and synthetic fuels are considered key technologies to reduce pollution [1].

Due to the increasing level of pollution, especially in developed industrial areas, pollution reduction is essential. Human influence on global climate change is widely recognized and close cooperation is needed to improve the quality of the environment. The energy transition to meet climate goals presents both broad challenges and opportunities for societies around the world [3].

Combustion of fuels increases the concentration of sulfur oxides in the atmosphere, which causes an imbalance in the concentration of sulfur on Earth and the use of artificial fertilizers can affect soil fertility, plant growth and soil microbial activities. Sulfuric acid and sulfur dioxide are also released into the atmosphere from oil refining and industrial processing. Sulfur dioxide (SO_2) causes an increase in the temperature and formation of acid rain on Earth [4].

Pollution reduction and green energy production are the main topics in the development plans of many countries around the world. Recently, there has been a significant growth in international agreements and national energy action plans to increase the use of renewable energy due to growing concerns about pollution resulted from energy obtained from fossil fuels such as oil, coal and natural gas [5].

Sulfur dioxide, a gaseous pollutant well known for its harmful effects on the environment and health, is attracting the attention of researchers as a potential source of energy due to the fact that SO_2 can be electrooxidized to produce protons, which subsequently can be reduced, resulting hydrogen gas. SO_2 emissions can therefore be removed in parallel with the production of hydrogen, which can then be used to produce energy without harmful emissions [6,7].

The current method of reducing SO_2 pollution is flue gas desulphurisation, a method in which the sulphite oxidation is one of the essential processes, but it is extremely inefficient in terms of costs [8].

In addition to sulfur dioxide, sulphites resulting as by-products from various industrial processes cannot be stored in the open air due to their harmful effects. An advantageous method of recovery of these compounds is their electrooxidation to stable and more environmentally friendly compounds, such as sulphates, which can be used in various commercial applications [8].

The oxidation process of sulphite is widely used, with huge amounts of sulphite being oxidized annually [9], this process being involved in many chemical and biochemical processes.

In the atmosphere, SO_2 oxidation follows different pathways in which several processes take place in parallel and influence each other. In polluted areas, the oxidation of SO_2 catalyzed by ions or oxides of some transition metals is comparable to the non-catalyzed self-oxidation [10].

Oxygen plays a key role in the oxidation of SO_2 and sulphite in aqueous solutions, many species existing in the solution reacting with dissolved oxygen, some reactions being slow and others fast [9, 11-13].

Due to the wide range of oxidation states that sulfur compounds can have in both sea and ocean water and in the atmosphere, sulphite oxidation plays a key role in a number of microbial metabolic processes [14].

Considering the possibility of using SO_2 emissions as an energy source (through the production of hydrogen, alkaline fuel cells, microbial fuel cells), the researchers focused on the development of materials used to build fuel cells. A few researchers have recently proposed some models of fuel cells that use sulphite as fuel [8, 15–17].

The development of cheap anodes with high catalytic activity for the electrooxidation of these compounds is the biggest step towards the implementation of an efficient system for the valorization of these compounds on a large scale [18]. Currently, the research on electrocatalytic materials for SO_2 or sulphite oxidation is insufficient. The process of electrochemical oxidation of these compounds is unclear, being considered a complex process [19].

Studies to date on this process have shown that the mechanism of electrochemical oxidation of sulphite depends on the catalyst material, the *pH* and composition of the solution and the current density [20,21]. Throughout time, several oxidation mechanisms have been proposed, and due to the complexity of this process there are even some disagreements in the literature [22]. The electrochemical oxidation of tetravalent sulfur compounds, S(IV), which contain oxygen has been studied in more detail in acid solutions.

Studies reported so far have shown that noble metals have the highest catalytic activity for the process of electrooxidation of sulfur dioxide and sulphite. Only a few more recent studies on non-precious materials have been reported [23]. In general, the high costs of precious metals have been reduced by reducing the load of these metals or by alloying them with non-precious metals [24,25].

This study aims to obtain information on the electrochemical characteristics of sulphite in neutral and alkaline media, so as to identify the most suitable electrodic materials to be used in a $Na_2SO_{3\ (aq)}$ / O_2 (air) fuel cell.

This thesis is structured in three parts.

Part I contains ***Chapter 1*** where the current state of research of the sulphite oxidation process is discussed, describing the chemical, electrochemical and bacterial oxidation mechanisms, together with the applications of this process. Materials with a catalytic effect tested to date for sulphite oxidation have also been presented. This chapter includes also a brief overview of existing fuel cells and the fuels used for such devices, as well as the operating principle of an SO_3^{2-} / O_2 fuel cell.

Part II consists of ***Chapter 2***, in which the equipment used in the experimental program is described. This chapter provides an overview of the methods of investigation and characterization applied in this study, as well as a description of the methods of preparing new anodes used for anodic sulphite oxidation.

Part III is intended for experimental studies performed on 9 anodic materials, grouped in 5 chapters. Therefore, ***Chapter 3*** presents the results obtained for the sulphite oxidation on platinum electrode in alkaline and neutral media.

Chapter 4 includes electrochemical and morphological analyzes performed on three nickel-based anodes: smooth nickel, foam nickel and skeletal nickel.

In ***Chapter 5*** the catalytic effect of platinum alloys on the sulphite oxidation in alkaline media has been investigated. Therefore, this chapter includes the description of the preparation method of an anode based on platinum-cobalt alloy deposited on a copper support and the presentation of the results obtained from the electrochemical and morphological analyzes performed on this type of electrode. In addition, anodes based on platinum nanoparticles deposited on a smooth nickel, respectively skeletal nickel support were tested in this chapter.

In ***Chapter 6*** the results obtained for the oxidation of sulphite on a graphite electrode in alkaline media are presented.

Chapter 7 contains the morphological analyzes and the results obtained for the sulphite oxidation on a YCa-114 perovskite in alkaline and neutral media.

Chapter 8 reveals the conclusions and the original contributions achieved through this study.

The original contributions of this study refer to:

- the preparation of an anode based on platinum-cobalt alloy electrochemically deposited with pulsed current on copper support and its use for sulphite oxidation in alkaline media;
- testing of anodes based on platinum nanoparticles on the support of smooth nickel, respectively skeletal nickel for the sulphite oxidation process;
- the use of high-surface-area skeletal nickel and foam nickel electrodes for the sulphite oxidation in alkaline media;
- the use of YCa-114 perovskites (Y0.5Ca0.5BaCo4O7) for the sulphite oxidation process.

Electrochemical oxidation of tetravalent sulfur compounds, S(IV), which contain oxygen, such as $SO_{2(aq)}$, HSO_3^- and SO_3^{2-}, has attracted attention in the development of technologies for hydrogen production, flue gas desulphurisation, fuel cells and food industry [26]. The reaction always takes place on the anodes when applying a certain potential, the most attractive catalysts being precious metals due to their electrocatalytic properties for the oxidation of these sulfur compounds.

Throughout time, several reaction mechanisms have been proposed, but the oxidation process of these compounds is still not clear, being considered a complex transformation. Studies on this process have shown that the mechanism of electrochemical oxidation of sulphite depends on the anodic material, the *pH*, the solution composition and the current density [20,21].

In aqueous solutions, sulphite (SO_3^{2-}) is in equilibrium with bisulphite (HSO_3^-) and sulfur dioxide ($SO_{2(aq)}$). Their composition and concentrations depend on *pH*, as shown in Figure 1. At pH <1.85 sulfur dioxide predominates, while in solutions with pH> 7.2 sulphite ions are mainly present, and between these values mainly bisulphite exists [27].

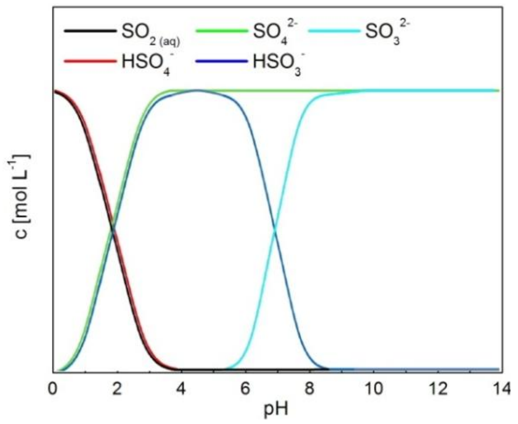


Figure **Error! No text of specified style in document.**. The effect of *pH* on the equilibrium of active species in aqueous solutions.

The oxidation mechanism of sulphites is very complicated, being performed in several steps. In the literature there are two possible reaction mechanisms for the oxidation of sulphite to sulphate in neutral and alkaline media, sulphite radicals being involved in both mechanisms.

The first mechanism describes the oxidation of sulphite ion to sulphate in four stages. Initially, the sulphite ion is weakly adsorbed on the electrode surface and oxidized to a sulphite radical in the next step. Two sulphite radicals combine and form dithionate, which disproportionates into sulphate and sulphite in the final stage of the mechanism. In this case, the rate determining step is reaction (2) [19].

$$SO_3^{2-} \rightleftarrows SO_{3\,(ads)}^{2-} \tag{1}$$

$$SO_{3\,(ads)}^{2-} \rightleftarrows SO_3^{-}{}^{\bullet}{}_{(ads)} + e^- \tag{2}$$

$$2SO_3^{-}{}^{\bullet}{}_{(ads)} \rightarrow S_2O_{6(ads)}^{2-} \tag{3}$$

$$S_2O_{6(ads)}^{2-} + 2HO^- \rightarrow SO_{3(ads)}^{2-} + SO_{4(ads)}^{2-} + H_2O \tag{4}$$

The second mechanism describes the oxidation of sulphite to sulphate through two electron transfer steps. The sulphite radical produced in the first electron transfer step (reaction (2)) is oxidized to sulphate according to reaction (5) [19].

$$SO_3^{-}{}^{\bullet} + 2HO^- \rightarrow SO_4^{2-} + H_2O + e^- \tag{5}$$

In the experimental part of this work is presented the study of the sulphite oxidation process on nine different anodes.

A three-electrode undivided cell connected to SP 150 Bio-Logic potentiostat/galvanostat was used during all measurements The cell was equipped with a working electrode, graphite counter electrodes, reference electrode Ag/AgCl/KCl$_{sat}$ and a nitrogen purging system in order to deaerate the solution before each measurement.

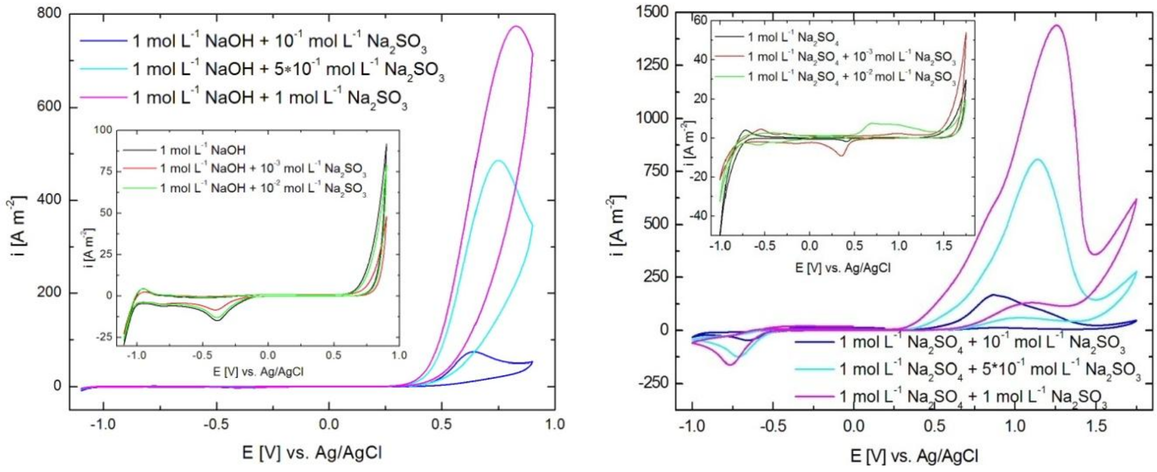
Electrochemical measurements were performed in 1 mol L^{-1} NaOH, respectively Na_2SO_4 in the absence and presence of different concentrations of sulphite (10^{-3}, 10^{-2}, 10^{-1}, $5 \cdot 10^{-1}$ și 1 mol L^{-1}) .

By applying electrochemical analysis techniques, it was possible to highlight the processes that take place at the electrode / electrolyte interface, to identify the potential range characteristic for sulphite oxidation, influence the sulphite concentration in the electrolyte solution, influence the polarization rate and to determine the degree of transformation of sulphite ions. In this regard, cyclic voltammograms were recorded at different scanning rates, between 5-500 mV s^{-1}, while linear polarization curves were recorded at low scanning rate (1 mV s^{-1}) in order to ensure quasi-stationary conditions. Also, the kinetic parameters (anodic transfer coefficient - α and exchange current density - i_o) were determined for the oxidation process of sulphite on each electrode. Electrochemical impedance spectroscopy (EIS) studies were performed using the impedance module of SP-150, in the frequency range from 0.1 Hz to 100 kHz and alternative voltage amplitude of 10 mV. For each spectrum, 60 points were collected, with a logarithmic distribution of 10 points per decade. The experimental EIS data have been fitted to the electrical equivalent circuit (EEC) by CNLS Levenberg – Marquardt method using ZView – Scribner Associates Inc. software. Chronoamperometry, chronocoulometry and chronopotentiometry were applied to determine the efficiency of sulphite oxidation at different potential values.

The surface of the electrodes was analyzed by scanning electron microscopy (SEM) combined with X-ray diffraction spectroscopy (EDX) X-ray diffraction (XRD) for the most electrodes used in electrochemical experiments.

The electrode materials tested in both alkaline and neutral media are platinum and perovskite Y0.5Ca0.5BaCo4O7, while anodes of smooth nickel, foam nickel, skeletal nickel, smooth nickel modified with platinum nanoparticles, skeletal nickel modified with platinum nanoparticles, Pt-Co alloy deposited on copper and graphite were tested only in alkaline media.

The experimental results obtained on platinum electrode in alkaline and neutral media, the sulphite ions are directly oxidized at low anodic polarization, while at advanced anodic polarization the sulphite ions are oxidized indirectly with atomic or molecular oxygen. The participation of atomic oxygen in the oxidation process of sulphite is indicated by the increase of anodic peaks with the increase of sulphite concentration (figure 2).



a) b)

Figure 2. Cyclic voltammograms recorded on the Pt electrode in alkaline (a) and neutral (b) solutions without and with different sulphite concentrations, scanning rate 100 mV s^{-1}.

In addition, the absence of the peak asigned to the reduction of molecular oxygen shows that SO_3^{2-} ions react with the entire amount of molecular oxygen produced on the platinum surface. The optimum potential for sulphite oxidation on a platinum electrode in an alkaline medium is about 0.6 V, and in a neutral medium it is about 1 V.

The kinetic parameters determined by the Tafel slope method show a significant increase in the exchange current density in the presence of sulphite. At the same time, there is a decrease in the charge transfer coefficient α due to the concomitant adsorption of sulphite ions at the electrode/electrolyte interface, equivalent twith the shifting of the reaction plane (inner Helmholtz plane) to the electrolytic solution. When comparing the kinetic parameters determined in alkaline and neutral media, it was found that the values obtained for the exchange current are four times higher in neutral mefia than those obtained in alkaline media. At a moderate anodic polarization, the oxidation process occurs with the formation of atomic oxygen as the rate determining step. Consequently, the generation rate of atomic oxygen is a measure of sulphite oxidation.

The chronoelectrochemical data showed that the potential at which the electrode processes take place depends on the sulphite concentration and that at advanced polarization, the oxidation of sulphite takes place both directly and indirectly with the atomic or molecular oxygen generated at the anode.

Electrochemical impedance spectroscopy confirmed the effect of sulphite concentration on the oxidation rate. The equivalent electrical circuit in Figure 3 was used to fitt the impedance data. The appearance of the Warburg resistive component shows that, at advanced anodic polarization, the process is also influenced by the slow diffusion of sulphite ions.

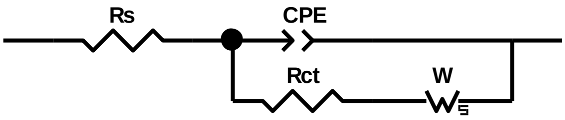


Figure 3. Equivalent electrical circuit for modeling anodic oxidation of sulphite on Pt electrode.

Due to the high price of platinum, the use of new anods with a low platinum content was pursued. Therefore, the experimental program includes the preparation of an anode based on platinum-cobalt alloy electrochemically deposited with pulsed current on copper support. The electrodeposition of the Pt-Co catalytic alloy was performed in an acid solution, the source of platinum ions being the K_2PtCl_4 solution and the cobalt ions from the $CoCl_2{\cdot}6H_2O$ solution. The molar ratio of Pt^{2+} and Co^{2+} ions in the electrolyte solution was 1:20. the optimum conductivity and *pH* stabilization was achieved by adding $1\ \mathrm{mol\ L^{-1}}$ KCl and $5{\cdot}10^{-1}\ \mathrm{mol\ L^{-1}}$ H_3BO_3 to the solution. The pulsed current deposition parameters were $t_{\mathrm{on}} = 20$ ms, $t_{\mathrm{off}} = 100$ ms, $i = 250\ \mathrm{A\ m^{-2}}$ and 20,000 cycles. These are the optimum values for obtaining Pt-Co alloy catalyst particles with nanometric size distribution on the copper support. A type of pulse applied for the deposition of pure alloys or metals, especially for multilayers, is shown in Figure 4.

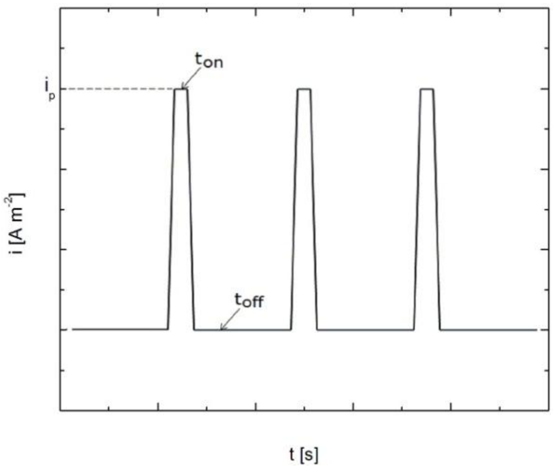


Figure 4. Typical form of current pulses

The structural characteristics, the composition of the alloy deposited on the copper disk and the average size of the alloy crystallites were analized by X-ray diffraction.

Figure 5 shows the XRD spectrum for the Pt-Co alloy, in which the peaks corresponding to the copper (from the support layer) and the $CoPt_3$ alloy can be observed. Pure cobalt was not identified in the structure of the Pt-Co alloy, indicating that cobalt atoms were incorporated into the platinum structure to form the $CoPt_3$ alloy.

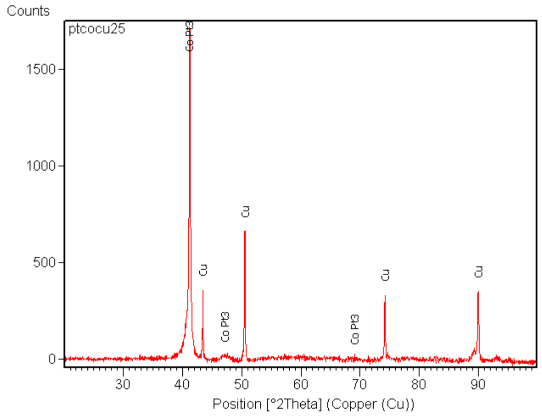


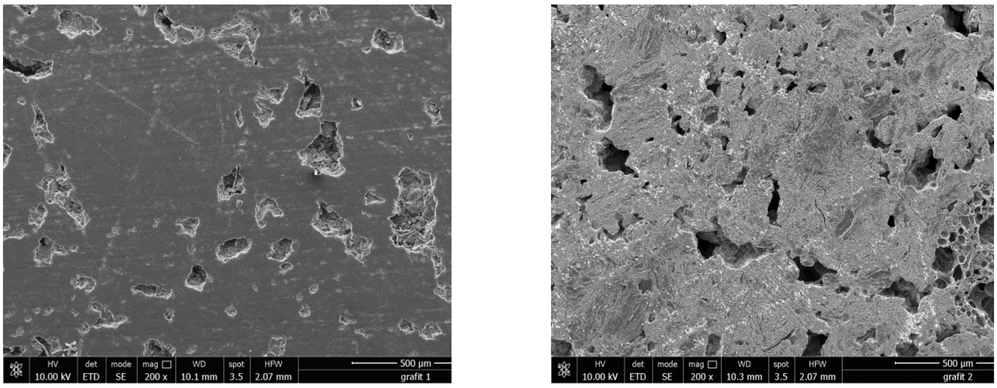
Figure 5. XRD spectrum of copper-deposited alloy.

The results obtained for the sulphite oxidation in alkaline solution on the new electrodes with low platinum content are encouraging. It was found that the optimum potential for sulphite oxidation on the Cu/PtCo electrode is between 0.35 - 0.65 V, and at more positive potential values, the oxidation of SO_3^{2-} ions and the oxygen evolution reaction take place simultaneously.

The anodic oxidation of sulphite ions was studied also on anodes based on platinum nanoparticles deposited on smooth nickel and skeletal nickel, respectively. On the electrodes of Ni-PtNPs and Ni_{sk}-PtNPs it was observed that the optimum potential for sulphite oxidation depends on the sulphite concentration. At advanced anodic polarization, indirect oxidation of sulphite occurs simultaneously with direct oxidation, followed by oxygen evolution reaction. The transformation degree of sulphite ions was found to be almost 7 times higher on the Ni_{sk}-PtNPs electrode compared to Ni-PtNPs. Significant exchange current density values on the three new electrodes (Cu/PtCo, Ni-PtNPs and Ni_{sk}PtNPs) show an important catalytic effect of the electrodes tested for sulphite oxidation.

At the same time, free-platinum electrodes were considered. Therefore, non-precious metals, much cheaper than platinum, were also tested. On nickel-based electrodes (smooth nickel, foam nickel and skeletal nickel) it was observed that the anodic oxidation process of sulphite is mediated by the redox couple $Ni(OH)_2$/NiOOH or $NiOH_{ads}$/NiO_{ads} formed on the active surface of the working electrode. It was found that the optimum potential for sulphite oxidation on the three nickel-based electrodes is between 0.4 - 0.7 V, varying with the change in sulphite concentration. The highest transformation degree of sulphite was obtained on foam nickel electrode, 10 times higher than smooth nickel.

On graphite electrode, a degradation of the electrode surface was observed over time (figure 6). Changes in the electrode surface after electrochemical experiments are likely due to the formation of carbonate ions at advanced anodic potentials.



a) b)

Figure 6. SEM images before (a) and after (b) sulphite oxidation, 200X magnification.

It was found that at low sulphite concentrations, sulphite oxidation is mediated by atomic oxygen adsorbed on the working electrode surface, and at high concentrations ($>10^{-1}$ mol L^{-1}), direct sulphite oxidation occurs simultaneously with indirect oxidation. In addition, the oxygen evolution reaction takes place in parallel with the above-mentioned processes at high current densities.

The kinetic parameters determined by Tafel slope method indicate a one-electron charge transfer process. The exchange current density has a fairly high value, specific for fast load transfer reactions.

Since chronocoulometric curves are quasi-linear dependencies, it can be stated that the efficiency for sulphite oxidation is close to 1. Although the formation rate of oxygenated functional groups on the graphite surface and carbon dioxide evolution is low, the effect on graphite electrode morphology is significant. Over time, the increase of specific surface area promotes sulphite oxidation, but after a longer electrolysis, the graphite electrode should be replaced.

According to the data obtained on perovskite type YCa-114 ($Y_{0.5}Ca_{0.5}BaCo_4O_7$), the optimum potential range for the sulphite oxidation in alkaline media is between 1.0 - 1.75 V, while in neutral media the process followed between 0.5 - 0.75 V, being mediated by the redox couple Co(II)/Co(III). Significant values of the exchange current density confirm a high catalytic effect of the working electrode for the studied process.

Some general characteristics regarding the oxidation of sulphite on all tested anodes were also observed. For example, the calculated kinetic parameters show that the general process is controlled by the charge transfer step. From the chronoelectrochemical data it was observed that an increase in the sulphite concentration stimulates the formation of atomic and molecular oxygen. As expected, the transformation degree of sulphite ions depends on the electrolysis time and the sulphite concentration added in the electrolyte solution. It was found that the efficiency of the oxidation process is influenced by the value of the potential at which this process is performed. On the other hand, the evolution of the open-circuit potential after a certain oxidation time indicates a significant decrease in the concentration of sulphite ions near the anode, which is why the overall process is also controlled by the diffusion of sulphite ions from the solution to the electrode surface.

The electrochemical behavior of SO_3^{2-} suggests that this chemical species can be used as fuel in a SO_3^{2-} / O_2 (air) fuel cell, and the tested anodes proved to be interesting materials, with catalytic properties for both chemical and electrochemical reactions.

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