IOSUD - Universitatea Politehnica Timişoara
Şcoala Doctorală de Studii Inginereşti

ANODIC OXIDATION OF SULFITES IN NEUTRAL AND ALKALINE MEDIUM ON NON-NOBLE MATERIALS

PhD Thesis – Abstract

for obtaining the scientific title of doctor at
Politehnica University of Timișoara
in the field of CHEMICAL ENGINEERING
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December, 2024

The doctoral thesis was developed during the doctoral activity within the Laboratory of Electrochemistry, Corrosion and Electrochemical Technologies, Department of Applied Chemistry and Inorganic Compounds and Environmental Engineering of Politehnica University Timișoara.

The proposed research topic follows current trends in identifying new energy sources that limit environmental pollution by using anodes based on non-noble materials for sulfite/oxygen (air) fuel cells with anion exchange membranes.

Climate change recogistered in recent decades has drawn researchers' attention to the possible irreversible consequences on our planet. The widely shared opinion among them is that, in addition to the natural causes of global warming (volcanic eruptions, variations in ocean stream, the shift of the Earth's magnetic poles, solar storms, earthquakes, etc.), anthropogenic activities also make a major contribution.

The latest data showes that the last decade (2011–2020) was the warmest on record. In 2019, for example, the average global temperature was 1.1°C higher than in the pre-industrial period. Calculations show that the current rate of increase in global warming due to anthropogenic activities is 0.2°C/decade [1].

The European Commission, through its Climate Action Department, has warned that an increase in average temperature of 2°C compared to the pre-industrial period will have a serious impact on nature, as well as on the health of the planet's inhabitants. At the same time, the probability of catastrophic climate phenomena will increase [1]. The dramatic consequences of climate change refer to the melting of glaciers and polar ice caps - followed by the flooding of large areas of inhabited land, drought and excessive rainfall, the desertification of large regions of the globe, floods and tsunamis [2-5].

The main cause of accelerated climate change is greenhouse gases, including carbon dioxide, nitrous oxide, methane, and fluorinated compounds. Carbon dioxide is considered to have the most pronounced effect, with concentrations now 48% higher than in the pre-industrial period (1750) [6]. The carbon dioxide content in the atmosphere is systematically monitored at the Mauna Loa Observatory in Hawaii, which for November 2024 indicates a value of 423.85 ppm CO_2 in the atmosphere [7].

It can be seen that, since 1960, the increase in carbon dioxide content has increased dramatically, from about 300 ppm to over 400 ppm, currently.

The increase in carbon dioxide content in the atmosphere is mainly due to the burning of fossil fuels: coal, petroleum derivatives and natural gas. Also, the chemical industry makes an important contribution to the increase in carbon dioxide emissions into the atmosphere, especially through ammonia and methanol production facilities. Also, large quantities of carbon dioxide are released into the atmosphere in the process of producing hydrogen through methane pyrolysis or coal gasification. Cutting down trees also has a negative effect by reducing the amount of carbon dioxide absorbed in the photosynthesis process. Under these circumstances, the nations of the planet have mobilized in concerted action to limit the increase in average temperature, as well as its effects on human civilization. Significant in this regard is the Paris Agreement, initiated in 2015, which has as its main objective to maintain the current trend of average temperature increase below 2°C above pre-industrial levels and to continue efforts to limit it to 1.5°C. The agreement entered into force in November 2016, when the condition of being ratified by at least 55 countries responsible for at least 55% of greenhouse gas emissions was met. All European Union countries have ratified the agreement and have committed to continuing financial support for emission reductions in developing countries [9].

One of the goals of achieving the main objective of the Paris Agreement is to implement, by the middle of the 21st century, the concept of net zero greenhouse gas emissions, which will require an extraordinary financial effort [10]. The first activity in favor of achieving this objective is the replacement of fossil fuels with renewable sources: solar energy, wind energy, hydropower - including wave and tidal energy, geothermal energy, biomass energy, to which is added the chemical energy stored in galvanic cells and fuel cells powered by carbon-free fuels.

In order to reach zero carbon dioxide emissions by 2050, a series of actions are necessary to be completed by 2030, including: increasing the share of solar and wind energy by 3.5 times; phasing out energy produced by burning coal; maintaining the natural gas exploitation and transport infrastructure for energy security; increasing sales of electric vehicles to 50% of the total; making buildings more energy efficient; increasing sales of heat pumps for buildings by 50%; financing research and development activities for the capture and sequestration of carbon dioxide; developing and optimizing gas and electricity transport and distribution capacities [11].

According to the European Commission strategy, hydrogen will become a mainstream fuel by 2030. The EU's priority is to develop clean, renewable hydrogen produced by water electrolysis, using mainly wind and solar energy, as this is the option most compatible with the EU's long-term climate neutrality objective [12].

Unfortunately, currently, the largest amount of hydrogen is obtained from natural gas, liquid hydrocarbons and coal, industrial processes that simultaneously result in large amounts of carbon dioxide - 5.5 t CO_2/ t H_2 in the case of methane pyrolysis, respectively 11 t CO_2/ t H_2 - in the case of coal gasification. Only 4% of the hydrogen produced worldwide is obtained by water electrolysis, the price of electrolytic hydrogen being 3-4 times higher than that obtained by methane pyrolysis. Because of this, generating electricity in fuel cells using electrolytic hydrogen is very expensive.

Under these conditions, researchers' attention has been focused on the use of sulfur compounds, such as hydrogen sulfide, sulfur dioxide, and sulfites, as fuel in fuel cells. This outlook is encouraging, given that these combinations are available in large quantities. Moreover, sulfur dioxide and sulfites result as waste in a number of industrial processes.

When evaluating the ab initio electromotive force of a fuel cell based on sulfur compounds, it is useful to use Latimer diagrams (figure 1) [13].

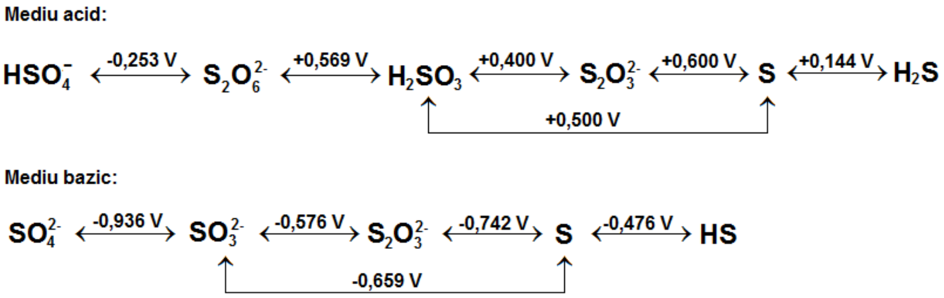

Figure 1. Latimer diagram for sulfur compounds.

For example, in basic medium, at pH = 14, the standard potential of the sulfite/sulfate redox couple is -0.936 V, while the standard potential of the O_2/HO^- couple is +0.401 V [14]. Therefore, the standard electromotive force of a sulfite/oxygen fuel cell is 1.337 V.

Analyzing the data available in the specialized literature, our research was oriented towards evaluating the electrochemical behavior of sulfites in neutral and alkaline environments, in order to identify the possibilities of using it as a fuel in sulfite/oxygen (air) fuel cells.

The general objective of the doctoral thesis is to research the electrochemical behavior of sulfite in neutral and alkaline environments on different electrode materials, in order to identify an efficient electrocatalyst for a sulfite/oxygen (air) fuel cell.

To achieve the general objective of the thesis, the following activities were carried out:

- Analysis of the electrochemical behavior of sulfites on non-noble materials.
- Determination of kinetic parameters that characterize the anodic oxidation process of sulfites by the potentiodynamic polarization method.
- Determination of charge transfer resistance for the anodic oxidation process of sulfites by electrochemical impedance spectroscopy.
- Study of the possibilities of using various materials with electrocatalytic properties for the anodic oxidation of sulfite in solutions with neutral and alkaline pH.
- Testing of inexpensive anodes with high catalytic activity for the electrooxidation of SO_2 or sulfite.
- Study of the electrochemical behavior and stability of the various materials used in the thesis, in a wide potential range, in different neutral and alkaline electrolytic media.

This thesis is structured in three parts.

Part I includes Chapter 1, which describes the oxidation process of sulfur dioxide and sulfites in aqueous solutions, describing the chemical and electrochemical oxidation mechanisms.

Also, the catalytic materials tested so far for sulfite oxidation were presented. This chapter also includes a brief presentation of the different types of anodes used in existing fuel cells and the fuels used for such devices.

Part II consists of Chapter 2 which describes the methodology and equipment used in the experimental program. This chapter provides an overview of the investigation and characterization methods applied in this study, on the anodes used for the anodic oxidation of sulfite.

Part III is dedicated to experimental studies carried out on 5 anode materials, grouped into 4 chapters. Therefore, in chapter 3 the results obtained for the oxidation of sulfite on graphite electrode in neutral environment are presented.

Chapter 4 includes electrochemical analyses performed on lead electrodes in a neutral environment.

In Chapter 5, the catalytic effect of stainless steel alloys on the oxidation of sulfite in neutral and alkaline environments was investigated. Therefore, this chapter includes the presentation of the results obtained from electrochemical analyses performed on two types of electrodes (Incoloy 800 and AISI 420).

Chapter 6 presents the results obtained for the oxidation of sulfite on a bright nickel electrode in an alkaline medium.

Chapter 7 concludes this study by outlining the conclusions and highlighting the original contributions made in the experimental program.

The elements of originality of the doctoral thesis refer to:

- the use of base metals as anodes for the oxidation of residual sulfites obtained in various industrial branches;
- determination of the kinetic parameters of the anodic oxidation process of sulfites in neutral or alkaline medium;
- determination of optimal oxidation potentials of sulfites and the degree of transformation by chrono-amperometric and chrono-coulometric methods.

Sulfur dioxide is very soluble in water. For example, at 0°C, 68.6 volumes of SO_2 dissolve in one volume of water [17], which is almost 20 g SO_2/100 g water. As the temperature increases, the solubility of SO_2 decreases. A small part of the dissolved sulfur dioxide reacts with water, forming sulfurous acid (1.1).

$$SO_2 + H_2O \rightleftarrows H_2SO_3 \qquad (1.1)$$

The acid formed dissociates in two steps with the formation of hydrogen sulfite (1.2) and sulfite (1.1) ions.

$$H_2SO_3 \rightleftarrows HSO_3^- + H^+ \qquad (1.2)$$

$$K_1 = 1,5\cdot10^{-2} \quad [16]$$

$$H_2SO_3 \rightleftarrows SO_3^{2} + H^+ \qquad (1.3)$$

$$K_2 = 1,1\cdot10^{-7} \quad [15]$$

The lower the pH of the solution, the more the reaction equilibria (1.1 – 1.3) are shifted to the left. Shifting the pH towards higher values leads to a decrease in the concentration of dissolved sulfur dioxide. Figure 1.1 highlights the stability of the chemical species of the sulfur dioxide/hydrogen sulfite/sulfite system as a function of the solution pH [17].

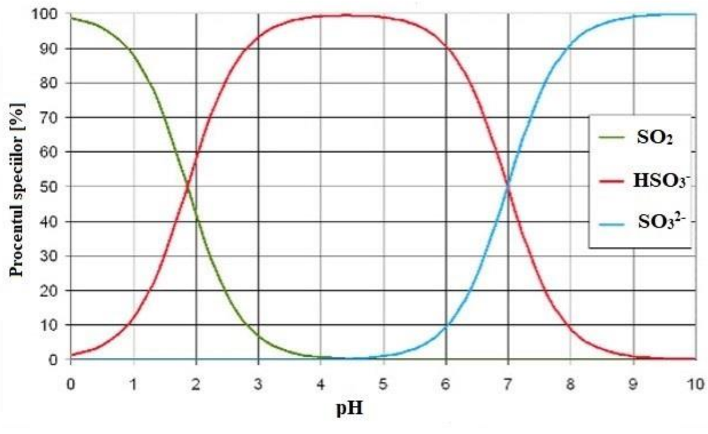

Figure 1.1. Sulfur dioxide/hydrogen sulfite/sulfite equilibrium in aqueous solution.

From figure 1.1 it can be seen that as the pH of the solution increases from 0 to higher values, the hydrogen sulfite concentration increases until reaching the maximum value, at a pH of approximately 4.5. At this pH value, practically only hydrogen sulfite is found in the solution. As the pH increases further, the hydrogen sulfite concentration begins to decrease, while the sulfite concentration increases. At pH greater than 10, only sulfite ions exist in solution.

The evaluation of the electrochemical behavior of sulfur dioxide/sulfite solutions must take into account the equilibrium that is established between the chemical species present in the solution, as well as the fact that these species have a reducing character. As shown above, from the Latimer diagrams, it can be seen that the redox potentials involving sulfur dioxide, hydrogen sulfite and sulfite species are more negative than the redox potential of oxygen O_2/H_2O, at the same pH value. This is why sulfur dioxide and sulfites can be used as anodic depolarizers in the production of hydrogen by water electrolysis.

The proposed mechanisms for anodic oxidation processes are classified into two distinct categories: direct oxidation on the electrode surface by electron transfer from the chemical substrate to the electronic conductor or indirect oxidation through an intermediate generated at the electrode.

An anodic electron transfer from the chemical species $SO_2/HSO_3^-/SO_3^{2-}$ directly to the pure metal is unlikely since upon anodic polarization, in aqueous electrolyte solutions, the surface of metals is generally covered with a layer of oxide or adsorbed oxygen. For this reason, initial studies of the anodic oxidation of $SO_2/HSO_3^-/SO_3^{2-}$ chemical species were carried out on platinum, on which the oxide layer formed upon anodic polarization is very thin, assimilated to a monomolecular layer of adsorbed atomic oxygen [18].

The experimental part of the thesis presents the study of the sulfite oxidation process on five different anodes.

Electrochemical measurements were performed in 1 mol L^{-1} Na_2SO_4 and NaOH, respectively, in the absence and presence of different sulfite concentrations (10^{-3}, 10^{-2}, 10^{-1}, $5\cdot10^{-1}$ and 1 mol L^{-1}).

By applying a set of electrochemical analysis techniques, it was possible to highlight the processes that take place at the electrode/electrolyte interface, identify the characteristic potential range for sulfite oxidation, the influence of the sulfite concentration added to the electrolyte solution, the influence of the polarization rate and determine the degree of sulfite ion transformation.

In this regard, cyclic voltammograms were recorded at different scan rates, between 5 - 500 mV s^{-1}, while linear polarization curves were recorded at low scan rate (1 mV s^{-1}) to ensure a quasi-steady state. Also, the kinetic parameters (anodic transfer coefficient - α and exchange current density - i_0) were determined for the sulfite oxidation process on each electrode. Electrochemical impedance spectroscopy (EIS) studies were performed using the SP-150 impedance module, in the frequency range from 0.1 Hz to 100 kHz and alternating voltage amplitude of 10 mV. For each spectrum, 60 points were collected, with a logarithmic distribution of 10 points/decade. The EIS experimental data were modeled on an equivalent electrical circuit (EEC) by the Levenberg–Marquardt CNLS method, using the ZView software – Scribner Associates Inc. Chronoamperometry, chronocoulometry and chronopotentiometry were applied to determine the efficiency of sulfite oxidation at different potential values.

The electrode materials tested in both neutral and alkaline environments are stainless steels, while lead and graphite anodes were tested only in neutral environments, and bright nickel anodes only in alkaline environments. The starting point was the graphite anode, given its high catalytic properties, repeatedly proven in various studies.

The experimental data presented confirmed the possibility of oxidizing SO_3^{2-} to SO_4^{2-} on a graphite electrode. The electrocatalytic effect of this type of electrode was studied for the oxidation of sulfite in neutral solution applying cyclic and linear voltammetry, DPV, SWV.

Cyclic voltammetry studies revealed that at low current densities and low sulfite concentrations in neutral solution, sulfite oxidation is mediated by atomic oxygen adsorbed on the surface of the graphite electrodeAt high sulfite concentrations (>10^{-1} mol L^{-1}), due to good access of sulfite ions to the electrode surface, direct oxidation of sulfite occurs together with mediated oxidation.

The electrocatalytic effect of the lead metal anode for the sulfite oxidation process in neutral electrolytes by various electrochemical methods: cyclic and linear voltammetry, chronoamperometry and chronopotentiometry, the results being encouraging. The lead electrode proposes a considerable decrease in the production costs of fuel cells, given the electrocatalytic effects of lead for oxidation processes in neutral environments.

Regarding the Incoloy 800 electrode, cyclic voltammetry analyses indicated that, at low current densities and sulfite levels, sulfite oxidation is facilitated by atomic oxygen adsorbed on the surface of the stainless steel electrode. At high sulfite concentrations (>101 mol L^{-1}), the effective access of sulfite ions to the electrode surface leads to direct oxidation of sulfite, which occurs simultaneously with mediated oxidation. Conversely, at much higher current densities, in addition to the aforementioned processes, OER occurs.

The kinetic parameters determined by the Tafel slope method indicate a single-electron transfer process. It is important to note that the exchange current density has a relatively high value, characteristic of fast electron transfer reactions. Chromoamperometric plots confirmed that, at advanced anodic polarization, the oxidation of sulfite to sulfate is accompanied by OER.

Distinct patterns of electrochemical impedance spectra were observed for the oxidation of low and high concentrations of sulfites, based on the two proposed oxidation mechanisms: mediated oxidation and direct oxidation of sulfite.

Cyclic voltammograms, recorded on AISI 420, in 1M NaOH alkaline solution without and with different concentrations of Na_2SO_3 (10^{-3}, 10^{-2}, 10^{-1}, 0.5 and 1 mol L^{-1}, respectively) showed that the process is controlled by the charge transfer step.

To highlight the processes occurring at the anode, chronoamperometric studies were performed on an AISI 420 electrode, at potential values of 0.40, 0.50, 0.60, 0.70, and 0.80 V in 1M Na_2SO_4 solutions with the addition of Na_2SO_3.

The mechanism of sulfite oxidation is very complicated, being carried out in several steps. In the studied potential range, the overall process is controlled by the charge transfer step, as confirmed by the EIS data. It is observed that the values obtained for α and i_o are significant, while the direct oxidation of sulfite to sulfate can occur concomitantly with the formation of adsorbed atomic oxygen.

Based on the electrochemical methods applied in the study on bright nickel electrode, the characteristic range of the optimal potential for each concentration of sulfite added to the alkaline electrolyte solution was identified. The specific current densities for sulfite oxidation and the degree of transformation as a function of electrolysis time were also determined. The kinetic parameters (α and i_o) were calculated, showing that the overall process is controlled by the charge transfer step.

It was found that the efficiency of the oxidation process is influenced by the potential value at which this process is carried out and by the concentration of sulfite ions in the electrolyte. The optimal potential is 0.60 V for sulfite concentrations higher than 10^{-2} mol L^{-1} added in alkaline media. We conclude that anodic sulfite oxidation occurs at a faster rate, as R_{ct} values decrease with increasing sulfite content. With increasing polarization, double layer capacitance (C_{dl}) values increase.

The electrochemical behavior of SO_3^{2-} suggests that this chemical species can be used as a fuel in an 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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