SULFITE DRIVEN FUEL CELL FOR ENVIRONMENTAL PURPOSES: OPTIMIZATION OF THE OPERATING CONDITION

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Abstract

Sulfite ions are by-products in different industrial processes. As they are highly toxic the way for their disposal is to oxidize them to harmless sulfates that can be commercially useful product such as building gypsum or fertilizers. The oxidation process used up to now is an expensive and energy consuming one. The present study is an attempt for their removal with energy generation at the same time in a fuel cell of our design. In our previous papers, we have shown the process of optimization of the design of the cell and the electrodes. This paper shows the process of optimization of the operating conditions by the choice of membranes, initial concentrations, electrolyte content and pH.

Kew words: *sulfite driven fuel cell, operating condition, optimization*

1. INTRODUCTION

In our age the demand for energy, electric or other, is ever increasing. According to the International Energy Agency, [IEA, http://www.iea.org/] for 2015 over 80% of all energy gained has come from fossil fuels. Fossil fuels contain varying quantities of sulfur that becomes a real environmental problem after the burning of the fuel when the sulfur is transformed to sulfur dioxide. Methods are developed to neutralize this hazardous product, but most of them are either too expensive for massive industrial applications or as in the cases of the lime and limestone methods require additional treatment that further complicates and increases the cost. Nevertheless all the ecological directives of the EU dictate that it is absolutely prohibited to release SO_2 in the atmosphere in high concentrations, which forces all factories and power plants to neutralize their flue gases despite the high costs.

The most economical way of scrubbing SO_2 from flue gases is via hydrated lime ($Ca(OH)_2$) or limestone ($CaCO_3$) to $CaSO_3$ and via caustic soda (NaOH) to Na_2SO_3.

Other industries whose wastewaters are contaminated with sodium sulfate are the pulp and paper industries (Kraft process), photographic industry (fixer), mineral processing (froth flotation), oil industry (oil recovery), food industry (preservatives) and textile industries (dyes).

But sulfates in wastewaters are substances that need to be oxidized to sulfites before their disposal in the environment. The oxidation process is a high energy consuming one and is accompanied with a lot of exploitation difficulties. Many studies are dedicated to the kinetics of oxidation [Karatza D et al., (2004), Karatza D et al.,(2008), Lancia A. et al.(1997), Lancia A. et al.(1999), Pisu M et al. , (2004)] as well as the improvement of apparatuses equipment [Gohara Wadie F.and Steve Feeney, Zheng Y et al.(2003), Zheng Y et al.(2004),]. The high expenses make them inefficient for small-scale desulfurization installations.

In recent years there is accelerating scientific interest for oxidation of different pollutants (including organic) in fuel cells (FC) [Kwiyong Kim and Jong-In Han, (2014), Razkazova-Velkova, E Razkazova-Velkova, E et al (2014), Zhai Lin-Feng, et al,]. This increasing interest is due to the possibility of eliminating pollutants with minimum exploitation costs while harvesting electrical energy at the same time.

Particularly relevant way to be intensifying the process of oxidation of the pollutions is the use of micro-organisms in a so-called microbial fuel cells (MFC). But the possibilities for use of modern microbial fuel cells in our case are very limited because the sulfites are preservatives and are toxic for most bacterial species.

Lately there are some studies [Enache A., et al.2015, Dan M.L. et al.2016 Dermendzhieva N.et al. 2016,] that try to improve the oxidation of sulfites in a fuel cell by using different catalysts, electrodes and changes in the design. The purpose of this study is to further investigate the optimal operating conditions for a particular design of a fuel cell made by our team with the goal of reducing the internal resistance of the cell by selecting a suitable membrane, concentration of the working agent, pH and accumulation of products of the process.

2. MATERIAL AND METHODS

The preparation of the sulfite solution is done by dissolving Na_2SO_3 (analytical grade) in distilled water. The $CaSO_3$ suspension is prepared after precipitating of $CaCl_2$ and Na_2SO_3. The obtained suspension is then washed up of all the chloride ions. The presence of chloride ions is verified qualitatively with $AgNO_3$. The latter is done in order to be certain that the chloride ions won't influence the results of the obtained electrical power of the fuel cell. The concentration of the sulfites is determined by iodometric titration.

The pH is corrected using sodium hydroxide.

Analytical grade of sodium sulfate is used to increase the conductivity as sulfates are the desired end products.

The studied membranes are listed in Table 1. Their main characteristics are also given.

Table 1. Characteristics of the studied membranes

Membrane	Type	Material	Thickness	El. res. ($\Omega.cm^2$)	Usage
CelGard® 3501	Anion	Polypropylene	25 µm	2.55	Alkaline battery separator
Fumapem® FFA-3-PK-75 (OH^- form)	Anion	fumion® F Polymer	55 µm	1.26	Alkaline battery separator
Neosepta® AFN	Anion	Polypropylene	160 µm	0.50	Acid recovery; Desalination of organic acids
Nafion® N117	Cation	perfluorosulfonic acid/PTFE	180 µm	2.50	Electrolysis

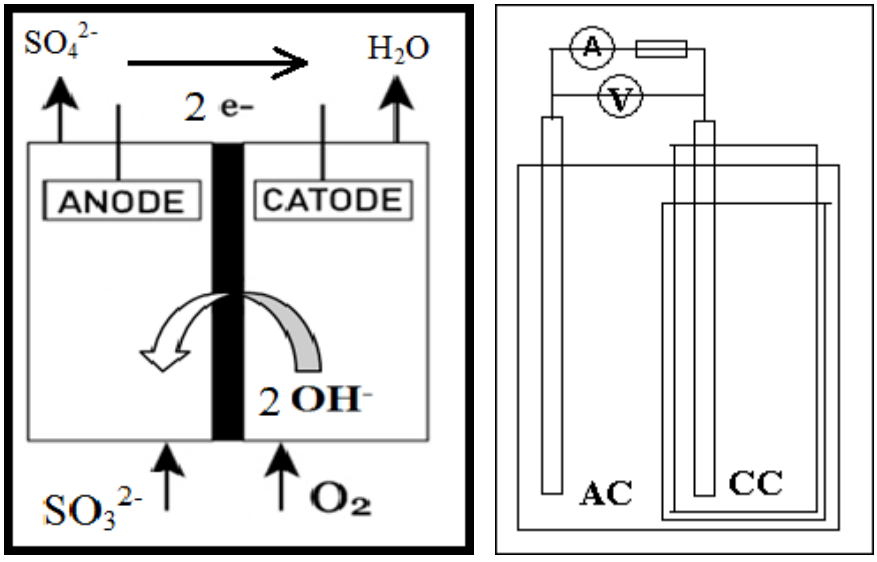


Fig. 1. Principal and practical scheme of the experimental fuel cell.

The principal and practical scheme of the experimental installation are shown in Fig. 1. It consists of two concentrically situated compartments with a 50 ml operating volume each. The membrane (S = 700 mm^2) is placed on the bottom of the inner one. The outer space is the anode compartment

(AC) and the inner one is the cathode compartment (CC).One graphite rod (d = 6 mm, L = 200mm, S = 20000 mm^2) is used in the AC. In order to increase the effective surface area of the cathode 20 g active carbon (Fujikasau, Japan, 680 m^2/g.) is placed in it. Air with flow rate of 30 l/h is blown into the compartment. A solution of NaCl (16,5 g/l) is added in order to improve the electrical contact and the conductivity into the cathode compartment.

The reactions that are intended to be conducted in the anode and cathode space are as follows:

Anode: $SO_3^{2-} + 2OH^- = SO_4^{2-} + OH^- + H^+ + 2e^-$

Cathode: $1/2\ O_2 + 2H^+ + 2e^- = OH^- + H^+$

From current-voltage characteristic via linearization of the data the internal electrical resistances of the fuel cell in different cases are determined. These curves were made by varying the external resistance in the range 1-1000 ohms (1000, 500, 250, 100, 50, 10, 5, 1 **Ω**).

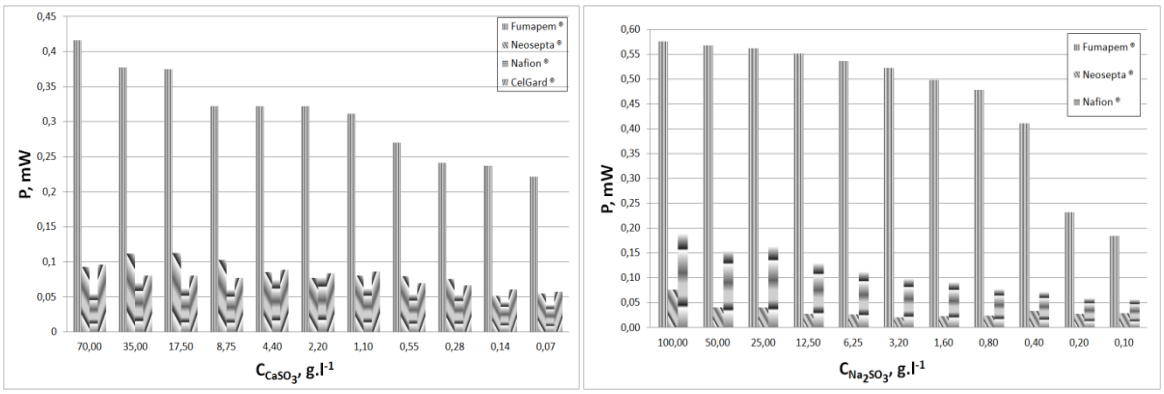
3. RESULT AND DISCUSSION

3.1. Influence of initial concentration and type of membrane.

The experiments are divided into two series, conducted in parallel, respectively for the two used starting materials (calcium and sodium sulfite). It should be noted that we expect a big difference in the obtained results, due to the substantial difference in the solubility of the substances as sodium sulfite is a solution while calcium sulfite is a suspension.

From preliminary experiments we have determined that membrane CelGard® practically showed incompatibility with Na_2SO_3 (electrical parameters were too low) therefore the experiments with sodium sulfide using this membrane were not conducted.

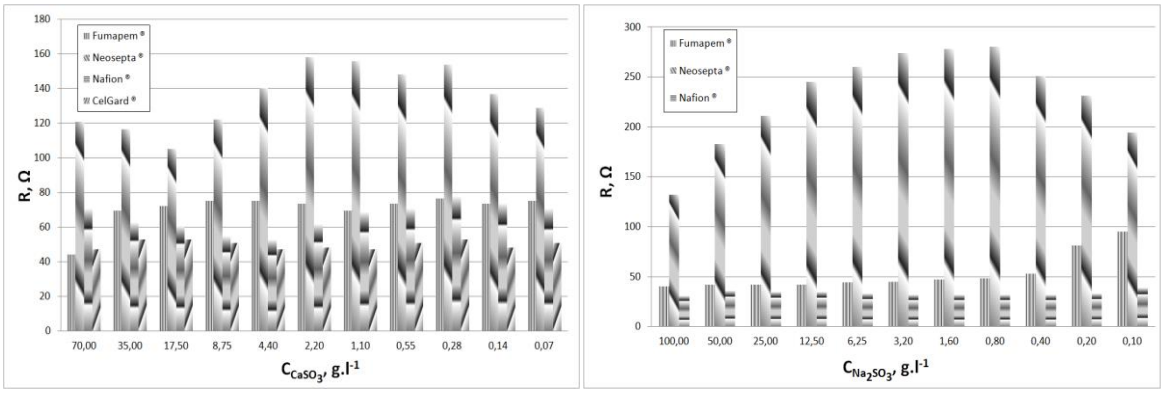
The first set of experiments is carried out with all types of membranes (except the CelGard® for sodium sulfite (see above)) and different initial concentrations in the range 0.07 to 70 g/l for calcium sulfite and in the range 0.1 to 100 g/l for sodium sulfite. The maximum obtained value from the electrical power (Fig. 2) and the internal electrical resistance (Fig 3) as a function of the initial concentration for the different membranes for calcium sulfite (a) and for sodium sulfite (b) are plotted.



a **b**

Fig. 2. Electrical power for different initial concentrations and the investigated membranes with calcium sulfite suspension (a) and sodium sulfite solution (b).

As to be expected, increasing the concentration of the initial agents, power output increases for both starting materials. This effect is explained by the increased amount of substance (fuel) involved in the process. With regard to the internal resistance, influence of the initial concentration is not linear, but tends to decrease with an increase in concentration (conductivity in the solution increases with the increasing the quantity of ions).



a **b**

Fig. 3. Internal electrical resistance for different initial concentrations and the investigated membranes with calcium sulfite suspension (a) and sodium sulfite solution (b).

With regard to the various types of membranes for both starting materials best results are obtained with Fumapem®. This can be explained by the combination of low thickness and low electrical resistance. Membrane CelGard® has lower thickness but higher electrical resistance while membrane Neosepta® has lower resistance but higher thickness and both membranes perform poorly (about 3 times lower power-wise).

The conclusion that can be made from the Figures shown is that the connection between initial concentration and generated power is not linear. Increasing the concentration 1000 times increases the power only 2 times for calcium sulfite and 3 times for sodium sulfite.

Based on the results shown above the following experiments are carried out with Fumapem® membrane and initial concentration of 25 g/l for both types of starting substances.

3.2. Influence of the pH.

The data from the study for the influence of the pH for the both substances are shown in Fig 5. The results uniquely demonstrate that the higher pH leads to higher electrical power. Best results are obtained at pH = 10, about 3 times higher than the results for pH = 7 and more than 10 times higher than pH = 3. This is a very favorable result because the real solutions from industrial desulfurization process are with a pH ≈10 and in the industrial process pH correction is not suitable.

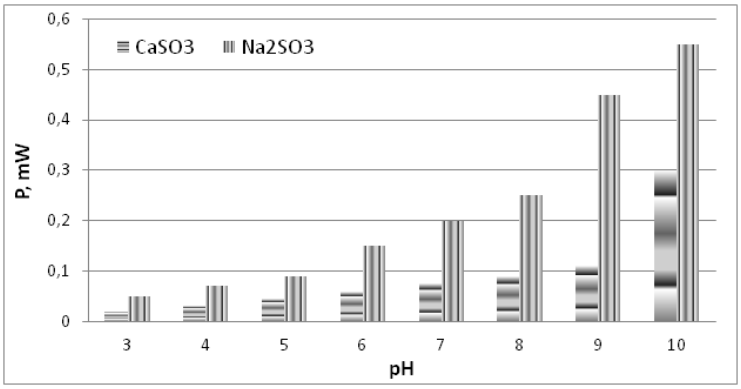


Fig. 4. Influence of the pH.

3.3. Influence of the accumulation of products of the process

To determine the rate of oxidation, respectively the accumulation of products of the process, we conducted experiments with sodium sulfite with two concentrations (25 and 100 g/l) in a fuel cell equipped with the membrane Fumapem®. The data for the depletion of sodium sulfite are given in Fig. 5.

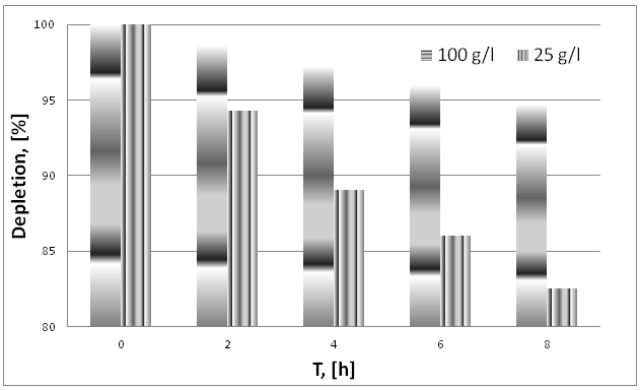
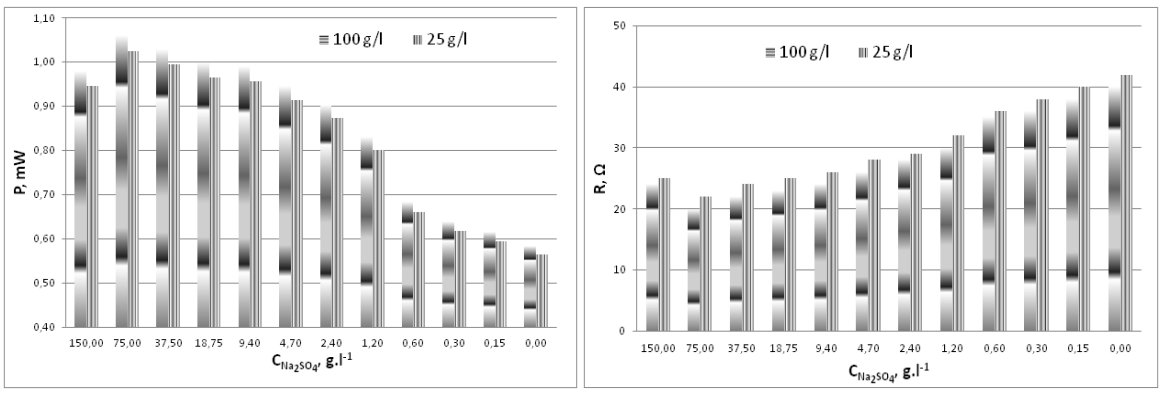


Fig. 5. Influence of initial concentration on depletion of sodium sulfite in function of time

As can be seen from the figure by increasing the concentration of the starting solution the oxidation rate decreases. This confirms our previous studies [Razkazova-Velkova E. et al. 2013, Razkazova-Velkova E. et al. 2014.] that the capability of the fuel cell to oxidize sulfides have design limitations related to the working volume, the surface of the membrane and the electrodes. For this fuel cell design the maximum achieved rate of oxidation is about 30 mg/h, yielding about 36 mg sulfates. This requires a study of the impact of the accumulation of end products of the process (sulfates) on the electrical performance of the fuel cell. For this purpose, we conducted an experiment with two concentrations of sodium sulfite (25 and 100 g/l) and different concentrations of sodium sulfate. The data for the obtained power (a) and the internal resistance (b) are shown in Fig. 6.



a **b**

Fig. 6. Electrical power (a) and internal resistance (b) for two concentrations of sodium sulfite (25 and 100 g/l) and different concentrations of sodium sulfate.

As expected, increasing the concentration of sodium sulfate decreases the internal resistance and accordingly increases the obtained power. The reason for this is that the sodium sulfate is electrolyte and enhances the conductivity within the fuel cell. This fact supports the work of the fuel cell because the increase in conductivity offset to some extent the depletion of sulfite and helps the cell to maintain good operating characteristics for longer periods of time.

4. CONCLUSIONS

Using fuel cell for oxidation of sulfite is a cheap way to solve the environmental problems associated with the deposition and use of wastewaters from industrial production for urban and agricultural purposes. Various factors (membranes, initial concentrations, electrolyte content and pH) for oxidation of sulfites are studied that affect the operating characteristics of the fuel cell of our own design. The data obtained show that the use of anion exchange membrane Fumapem® improves 2 to 3 times the energy performance of the fuel cell in a wide range of initial concentrations of sulfites. The use of the cell is appropriate in terms of the energy performance of the cell at high pH, because the most industrial wastewaters polluted with sulfates are with high pH (≈ 10).

The final products (sulfates) of the process are electrolytes and their accumulation improves the conductivity of the cell and to some extent offset the depletion of 'fuel' (sulfites), allowing the cell to maintain the good energy performance over longer periods of time.

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