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Sulfite driven fuel cell for environmental purposes: optimization of the oxidation conditions

S. Stefanov*, M. Martinov, E. Razkazova-Velkova

Institute of Chemical Engineering – Bulgarian Academy of Sciences

Acad. G. Bonchev str., Bld. 103, 1113 Sofia, Bulgaria

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The growing world population puts ever-increasing environmental requirements on all industries, be it construction, pharmacology or energy generation. One of the more potent and hard-to-neutralize industrial waste products are sulfites (typically sodium or calcium) generated by flue-gas desulfurization processes. Our project aims at neutralizing these dangerous compounds by oxidizing them in a fuel cell (FC) of our own design while simultaneously gaining electrical power. The present study's goal is to find suitable catalysts for the oxidation process. The experiments show that a nickel coated graphite fiber is an appropriate candidate to be used as electrode for the anode compartment of the fuel cell. A comparison of the electrochemical characteristics of the chosen fuel cell with different oxidizing agents (aerated seawater, hydrogen peroxide and ammonium chloride) is presented as well.

Key words: fuel cell, catalyst, sulfite ions, oxidation

INTRODUCTION

In our age the demand for energy, electricor other, is ever increasing. According to the International Energy Agency, [1] for 2015 over 80% of all energy gained is derived from fossil fuels. All 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 SO2 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 SO2 from flue gases is via hydrated lime (Ca(OH)2) or limestone (CaCO3) to calcium sulfite (CaSO3) and via caustic soda (NaOH) to sodium sulfite (Na2SO3).

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

Sulfites in wastewaters are substances that need to be oxidized to the more stable sulfates 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 [2-6] as well as the improvement of apparatuses equipment [7-9]. The high expenses make them inefficient for small-scale desulfurization installations.

In recent years there is increasing scientific interest for oxidation of different pollutants (including organic) in fuel cells (FC) [10-13]. This interest is due to the possibility of eliminating pollutants with minimum exploitation costs while simultaneously harvesting electrical energy.

Particularly relevant way to intensify the process of oxidation of the pollutions is the use of microorganisms in so-called microbial fuel cells (MFC). The possibilities for use of modern microbial fuel cells in our case are very limited because of the fact that sulfites are preservatives and are toxic to most bacterial strains.

Lately there are some studies [14-16] that try to improve the oxidation of sulfites by using different catalysts and electrodes.

Our project aims at improving the secondary oxidation step for both the limestone and the lime methods, as well as the caustic soda one by electrochemical oxidation in a membrane fuel cell of our own design. This way we can both reduce the cost of the neutralization steps as well as harvest the otherwise unused energy of the oxidation process. Our previous work [17] show that commercially available ion-exchange membrane Fumapem$^{®}$ FFA-

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* To whom all correspondence should be sent.
E-mail: stefanmartinov@yahoo.com

3-PK-75 is best suited for the fuel cell.The influence of the initial concentration, concentration of end products from the process and pH has also been investigated in the paper.

The aim of the current work is to find suitable catalysts for the oxidation process, as well as investigate alternative oxidizing agents.

EXPERIMENTAL

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 precipitation of $CaCl_2$ and Na_2SO_3. The resulting suspension is then washed up of chloride ions. The presence of said ions is verified qualitatively with $AgNO_3$. The latter is done in order ascertain that the chloride ions won't influence the results. The concentration of the sulfites is determined by iodometric titration.

Analytical grade of sodium sulfate is dissolved in the initial solution to both increase the conductivity of the solution and to simulate accumulation of the end product.

The principal and practical scheme of the experimental installation of the fuel cell are shown in Fig. 1. It consists of two concentrically situated compartments with 200 ml volume for the anodic compartment and 75 for the cathodic one. The membrane ($S = 700\ mm^2$) is placed on the bottom of the inner one. The outer volume is the anode compartment (AC) and the inner one is the cathode compartment (CC). Five standard cylindrical graphite rods (($d = 6$ mm, $L = 200$ mm, $S = 3000\ mm^2$ each) are used as electrodes in the anode compartment and 30 g. (75 ml) activated carbon (Fujikasau®, Japan, 680 $m^2.g^{-1}$.) and one graphite rod into the cathode one. The addition of activated carbon is done in order to increase the surface area of the electrode in the cathode compartment. This approach is not done for the anode compartment due to the sorption effect of the activated carbon of the desired end products.

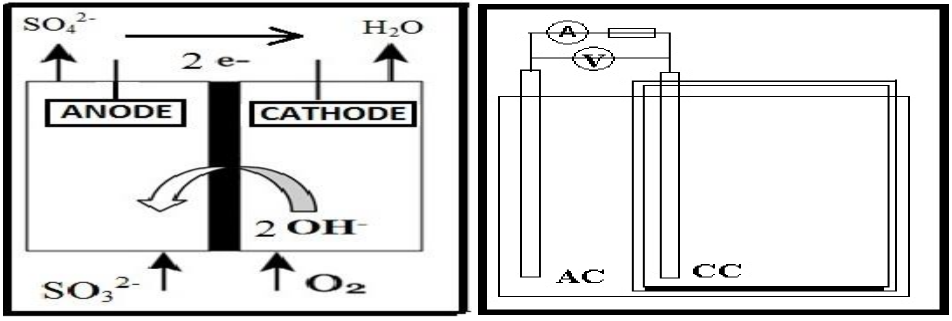

Fig. 1. Principal and practical scheme of the experimental fuel cell

The intended reactions are as follows:

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

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

A screening is done for determining an appropriate catalyst for the process. All catalysts are molded along with binding agents into electrodes with identical surface area of 2000 mm2. The molded electrodes are as follows:

1. 3 mg Fullerenes C60/C70 (Sigma Aldrich), 40 mg manganese acetate, 60 mg Vulcan XC72 and 35 % Polytetrafluoroethylene (Teflon®) as a binder pressed over stainless steel mesh at 150°C and 150 atm. for 5 minutes;
2. 8 mg Norit®, 40 mg manganese acetate, 60 mg Vulcan XC72 and 35 % Polytetrafluoroethylene (Teflon®) as a binder pressed over stainless steel mesh at 150°C and 150 atm. for 5 minutes;
3. Ni-coated graphite fiber [18], rolled over the graphite rods with the same geometrical surface.

Roentgenography of nickel-plated graphite fiber is presented in Fig. 2. The only distinct peak is corresponding to Ni and indicates that the coating is dense and evenly distributed.

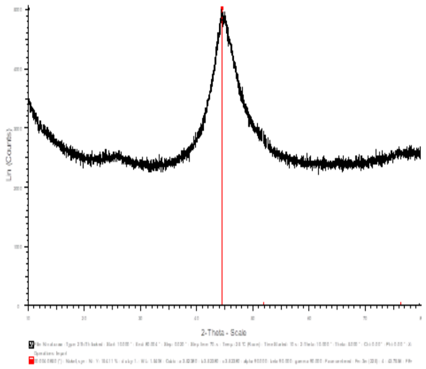

Fig. 2. Roentgenography of nickel-plated graphite fiber

RESULTS AND DISCUSSIONS

Influence of the type of pollutions

Fig. 3 shows a comparison of the electrical power output of the cell as a function of the concentration for both sodium and calcium sulfite.

It is to be expected for the calcium sulfite to have lower power output due to the fact that it is a suspension rather than a solution as is the case of the sodium sulfite. Due to the difference of one order of magnitude for further experiments we focused on the sodium sulfite and chose a concentration of 25 g.l^{-1} as it is relatively close to the real conditions [17].

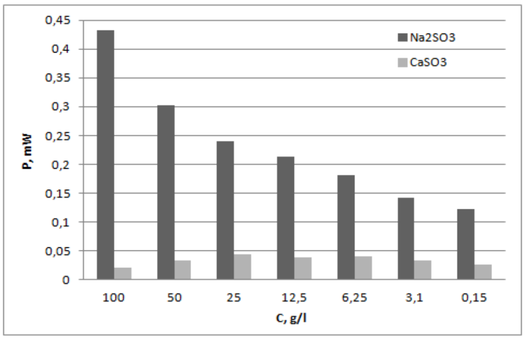

Fig. 3. Influence of the concentration of Na$_2$SO$_3$ and CaSO$_3$ on obtained electrical power

Screening for a catalyst for the process

The most common way for intensifying the oxidation process is the use of catalysts. The previously mentioned electrodes with molded catalysts are synthesized for this exact reason. Their catalytic effect is first tested in a vessel with similar volume to the fuel cell with results shown in Fig. 4. As can be seen all of them have a distinct catalytic effect (30 – 40%) compared to the experiment without catalyst. Even though the differences are within 5% by comparing the catalysts individually a distinction can be made that the Ni-coated fiber performs slightly better than the rest. For this reason this particular electrode is chosen to be used in the fuel cell as anode. In order to enhance the conductivity of the solution in the cathode compartment (saltwater with 16 g.l^{-1} NaCl) an experiment is conducted with the addition of 3% ammonium chloride with the results shown in Fig. 5. By comparing the results of both experiments as well as polarization curves we get the following:

Internal resistance of the fuel cell: when using saltwater – 40 Ω; when using saltwater with ammonium chloride – 4 Ω (an order of magnitude lower).

The power output of the fuel cell remains relatively constant between the 2^{-nd} until the 8^{-th} hour mark: when using saltwater – 0.7 mW; when using saltwater with ammonium chloride – 0.8 mW (about 15% increase).

The power output of the fuel cell at the 24^{-th} hour mark shows much greater difference: when using saltwater it is 0.45 mW while when using ammonium chloride it is 0.65 mW (about 40% increase).

A note should be made of the low wear resistance of the Ni-coating during work. After several experiments a roentgenography of the fiber (Fig. 6.) is done that shows a distinct carbon peak that is not present in the unused fiber (Fig. 2.). This indicates that portions of the Ni-coating is washed away and the underlying carbon is exposed.

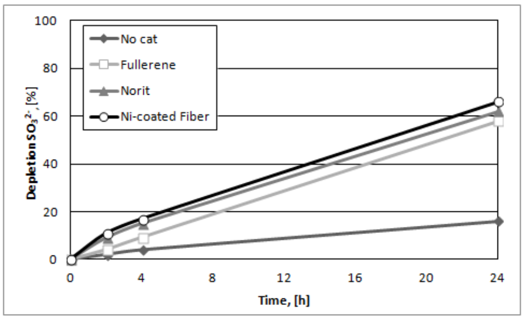

Fig. 4. Depletion of SO$_3^{2-}$ using three different catalyst

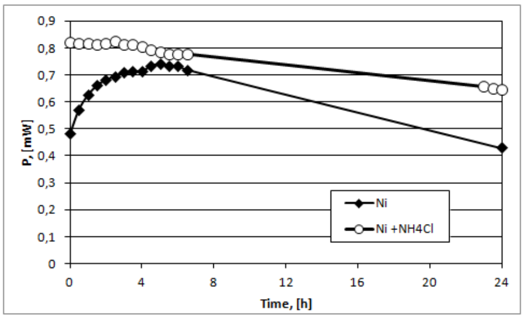

Fig. 5. Power in time using nickel-plated graphite fiber

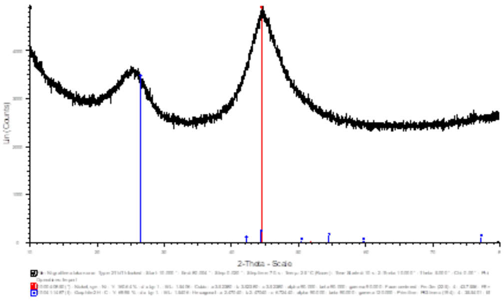

Fig. 6. Roentgenography of nickel-plated graphite fiber after 96 h

Influence of the oxidation agent

Another way for intensification of the oxidation process by using oxidizing agents. As such nitrates (with concentration of 0.5 g.l^{-1}), hydrogen peroxide (with concentration of 30 g.l^{-1}) and aerated saltwater (with atmospheric air 15 l.h^{-1}) are tested. Comparison between the power output of the cell as a function of time is shown on Fig. 7. The external resistance used is 100 Ω.

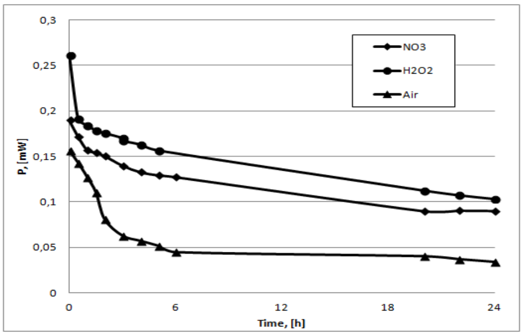

Fig. 7. Power in time using three different oxidizers

The internal resistance of the fuel cell when using nitrates, hydrogen peroxide and aerated saltwater is 50 Ω, 150 Ω and 100 Ω respectively.

The power output at the 2$^{\text{-nd}}$ hour mark for the nitrates is 0.15 mW, for the hydrogen peroxide – 0.17 mW and for the aerated saltwater – 0.01 mW.

The power output at the 6$^{\text{-th}}$ hour mark for the nitrates is 0.13 mW, for the hydrogen peroxide – 0.15 mW and for the aerated saltwater – 0.04 mW.

The power output at the 24$^{\text{-th}}$ hour mark for the nitrates is 0.09 mW, for the hydrogen peroxide – 0.10 mW and for the aerated saltwater – 0.04 mW.

It should be noted that even though the aerated saltwater shows lowest power output it remains constant for the time interval 6$^{\text{-th}}$ – 24$^{\text{-th}}$ hour unlike the nitrates and the hydrogen peroxide. An explanation of this phenomenon can be derived from the rate of the depletion of the sulfite ions in Fig. 8 which shows that the concentration of sulfite ions remains higher for longer periods of time compared to the other oxidizing agents.

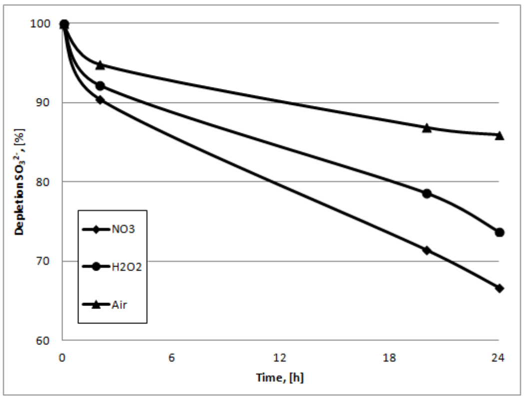

Fig. 8. Depletion of SO_3^{2-} using three different oxidizers

As shown in Fig. 8. the sulfite depletion rate is highest when using nitrates as an oxidant (about 10% higher than the peroxide and about 20% more than the aerated saltwater). Comparing with the power graph (Fig. 7.) the peroxide fuel cell that has the highest power output does not have the highest oxidation rate. Perhaps the use of hydrogen peroxide initiates other secondary reactions besides the desired, respectively produce more power. This may be the reason for the higher electrical resistance in that case.

CONCLUSIONS

- The use of a fuel cell for sulfite ion neutralization is more effective in the case of sodium sulfite compared to calcium sulfite;
- The use of catalysts intensifies the oxidation rate of the sulfite ions in the fuel cell;
- All the investigated catalysts show definite catalytic effects on the oxidation of Na_2SO_3. Nickel-plated graphite fiber shows both best oxidation rate as well as lowest production cost but it also has very low wear resistance;
- Using more potent oxidizing agent enhances the oxidation rate of the sulfite ions and correspondingly the power gained;
- Of the studied oxidizing agents the nitrates show best results at increasing the oxidation rate of sulfite ions.

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СУЛФИДНА ГОРИВНА КЛЕТКА С ЕКОЛОГИЧНА НАСОЧЕНОСТ: ОПТИМИЗАЦИЯ НА ОКИСЛИТЕЛНИТЕ УСЛОВИЯ

С. Стефанов, М. Мартинов, Е. Разказова-Велкова

Институт по инженерна химия – Българска академия на науките, ул. „Акад. Георги Бончев”, бл. 103, 1113, София, България

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(Резюме)

Увеличаващото се световно население поставя все по-големи екологични изисквания върху всички индустрии, били те строителната, фармацевтичната или производството на електроенергия. Един от по-опасните и трудни за неутрализиране индустриални отпадъци са сулфитите (обикновено под формата на натриев и калциев сулфит), генерирани от пречистването на сяросъдържащите димни газове, получени при изгаряне на фосилни горива. Целта на нашия проект е неутрализирането на тези опасни съединения чрез окислението им в горивна клетка, разработена от екипа ни, като едновременно с това се генерира и електроенергия. Текущото изследване се фокусира върху намиране на подходящ катализатор за окислителния процес. Резултатите от експериментите показват, че графитна тъкан, покрита с никел, е подходяща за използване като аноден електрод в горивната клетка. Показани са и сравнения на електрохимичните показатели на избрана конфигурация на горивната клетка при използване на различни окислители (аерирана морска вода, водороден пероксид и амониев хлорид).

Ключови думи: горивна клетка, катализатор, сулфидни йони, окисление