CATALYSTS FOR SULFIDE AND SULFITE OXIDATION. CONSTRUCTION OF ELECTRODES FOR A FUEL CELLS BASED ON SULFIDE AND SULFITE OXIDATION

N. Dermendzhieva, E. Razkazova-Velkova, V. Beschkov, L. Ljutzkanov

Institute of Chemical Engineering, Bulgarian Academy of Sciences,
Akad. G. Bonchev, str, bld.103, 1113 Sofia, Bulgaria

Abstract

Sulfides and sulfites are toxic pollutants from different industrial, domestic and natural sources. A way for their disposal and transformation to harmless products, even with a market value is their oxidation. Different type of catalysts for sulfide and sulfite oxidation to sulfates are studied and compared. The aim is to make a screening for the most appropriate catalyst for the process that can be used separately or that can be incorporated into electrodes in a fuel cell driven by the oxidation process. The technology for manufacturing of electrodes on the base of the obtained catalyst is given.

Key words: *catalysts, oxidation, sulfides, sulfites, fuel cells, electrodes*

1. INTRODUCTION

Sulfide ions occur naturally in some geothermal springs and closed deep water basins. Their presence in geothermal springs is due to volcanic gases, whereas that in closed deep water basins is due to anaerobic sulfate reducing bacteria decomposing the sulfur-containing organic matter and reducing sulfates.

Because of the high toxicity of the sulfides they are threatening to humans' and animals' health and their high chemical reactivity is causing corrosion to metal and concrete parts.

The possibilities for their disposal and decomposition can be broadly divided as follows:

Among the most common processes are adsorption and absorption. They can be used individually or combined with oxidation processes – with air (Cotrino et al. (2007), Seredych & Bandosz (2007), Yasyerli et al. (2002), Wang (2003)), with strong oxidizing agents (Tomar & Abdullah (1994)), biological oxidation (Kodama & Watanabe (2003)) or precipitation with metals (Henze et al. (1997)). Methods for thermal and electrochemical decomposition and oxidation (Gerçe et al. (2008), Zaman & Chakma, (1995), Yourong et al. (2001)) are also developed. The most well-studied and used method is the Claus process (Capone (1997)), which is extremely energy intensive and requires expensive catalysts.

Sulfites are by-product in flue gas desulfurization systems. They also present into the content of the waste streams in the Kraft pulping process. Since they are dangerous and can not be stored outdoors, they have to be oxidized to sulfates, which are stable and more environmentally friendly compounds with some commercial application as building gypsum (calcium sulfate) and fertilizer (ammonium sulfate).

The oxidation process of sulfites is one of the essential processes in the flue gas desulfurization technologies but it is very cost ineffective. Many publications are dedicated to optimizing the process of oxidation of the calcium sulfite in the limestone flue gas desulfurization process by improving the design of the oxidation tank (Gómez et.al (2007), Zheng et al. (2002), Zheng et al. (2003), Clean. (2001), Rathi, and Benson US Patent (1990), Gohara and Feeney US Patent (1996)) and the catalysts used (Lancia et al. (1997), Pisu et. al.(2004) , Karatza et. al. (2004), Karatza et. al (2008), Lancia and Musmarra (1999)).

2. RESULTS AND DISCUSSION

2.1. Catalysts for oxidation of sulfites

2.1.1. Preparation of Fe – Mn catalysts incorporated into a matrix of activated carbon

Pyrolyzed organic material as a support for Fe – Mn is investigated. The ratio of the metals is 3:1 respectively. In literature (Lancia A. et al. (1997)) Fe and Mn have synergetic effect on the oxidation of sulfite exactly when this ratio is 3:1. The pyrolysis with simultaneous activation is carried out by a patented method (Ljutzkanov et al. (2011)). The material is powder and its quantity is 0.1g in 300 ml volume.

The X-ray powder diffraction (XRD) of the obtained material is given in Fig.1.

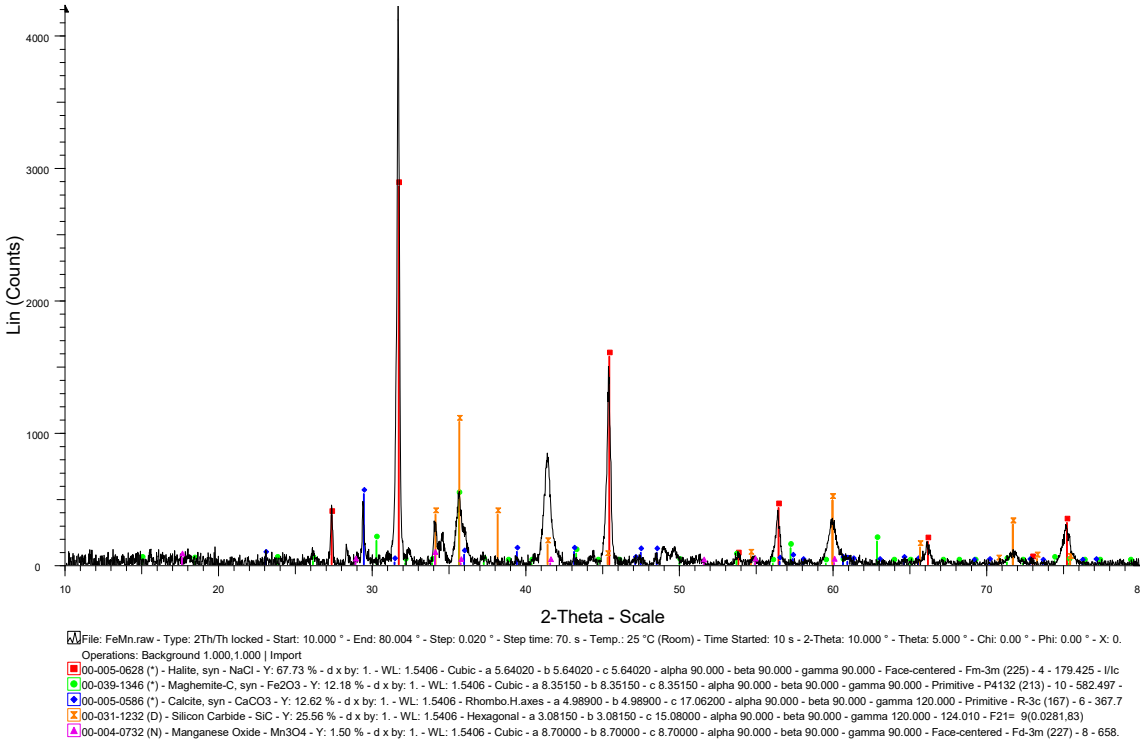

Fig.1. XRD pattern of the pyrolized organic material with the Fe and Mn additives

Since the material of the catalyst is of plant origin, the pattern has a significant background pollution. The obtained form of the Fe is Fe_2O_3 and this of the Mn is Mn_3O_4.

2.1.2. Catalysts constructed as electrodes

An electrode made by incorporating Fe_2O_3 (10 mass %) into a matrix of carbon black Vulcan 72 (55 mass %) and Teflon (35 mass %) onto a stainless steel mesh. The surface area of the electrode is 10 cm^2. The mixture is put into a matrix of appropriate shape and size and heated to 150°C while simultaneously pressed.

Another electrode is prepared by the same method but with Co-porfirin (10 mass %) instead of the Fe_2O_3.

Catalyst formed as electrodes on the base of higher fullerens and Mn and carbon black Norit. An electrode on the base of higher fullerens (C60/C70) and Mn $(C_2H_3O_2)_2$ and on the base of carbon black Norit were configured using the same technology as for the previous electrodes.

2.1.3. Plated graphite fabric

Ni -plated graphite fabric is prepared according to the method used by BG patent №110265 Sachkov. An XRD analysis is done before and after 25 hour of work of oxidation, shown on Fig.2. and Fig.3. respectively. Fig.3. shows that some of the coating is lost.

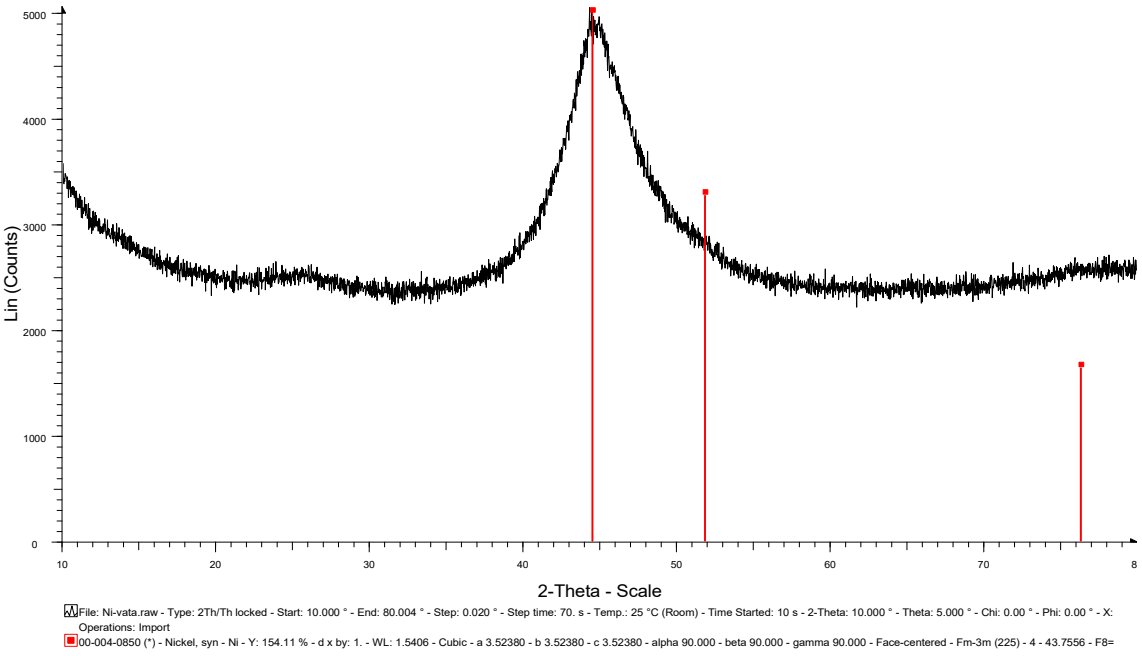

Fig.2. XRD pattern of the plated graphite fabric before work

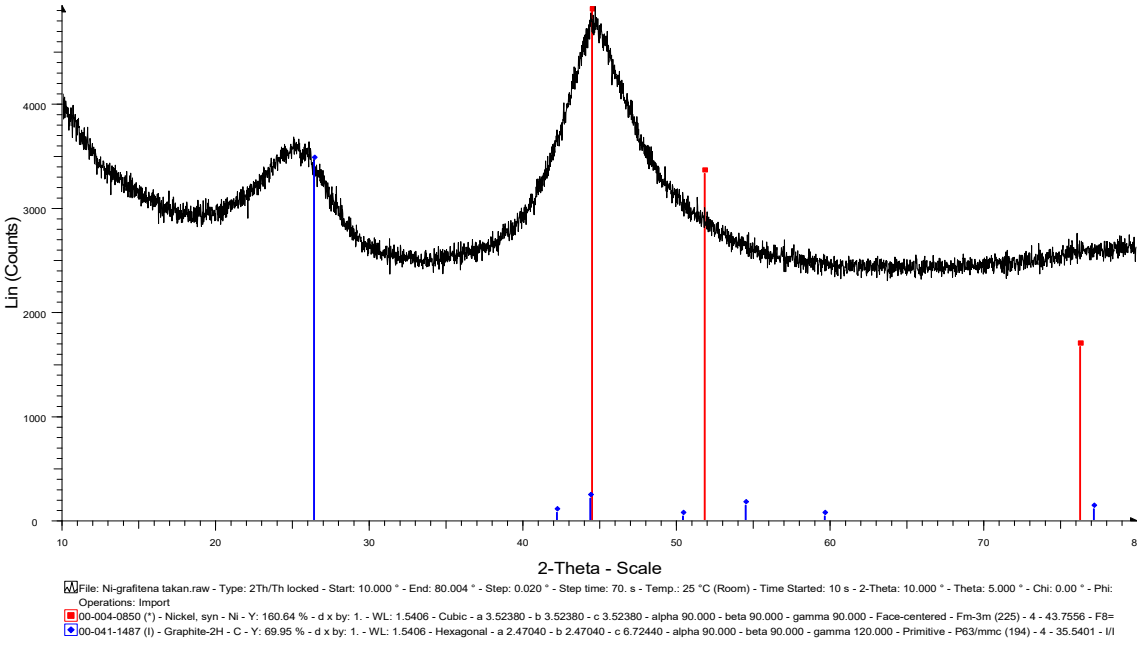

Fig.3. XRD pattern of the plated graphite fabric after work

A BET analysis is done to the Fe/Mn-incorporated pyrolyzed organic material and the Ni-plated graphite fabric. The results are shown in Table 1.

Table 1. BET analysis for Fe/Mn-incorporated pyrolyzed organic material and the Nickel-graphite fabric

Sample	S_{BET}, m^2/g	S_{mi}, m^2/g	S_{ext}, m^2/g	V_t, cm^3/g	V_{mi}, cm^3/g	D_{av}, nm
Fe/Mn	366	298	67	0.23	0.11	2.6
Nickel-graphite fabric	1	-	-	<0.01	-	-

S_{BET} – specific surface

V_t – total pore volume (at pressure 0,99 atm)

V_{MI} – total micropore volume

S_{MI} – specific surface of the micropores

S_{EXT} – specific outer surface

The analysis consists of low temperature nitrogen adsorption (77,4°K) with Quantachrome Instruments NOVA 1200E (USA). The samples are pretreated for 16 hours in vacuum at 150°C to remove any gases from the pores.

2.1.4. Oxidative properties for sulfites of the prepared catalysts

The oxidation of Na_2SO_3 as a function of time is given in Fig.4. The initial solution has a relatively low concentracion – 500 mg/l and the volume is 300 ml in all experiments.

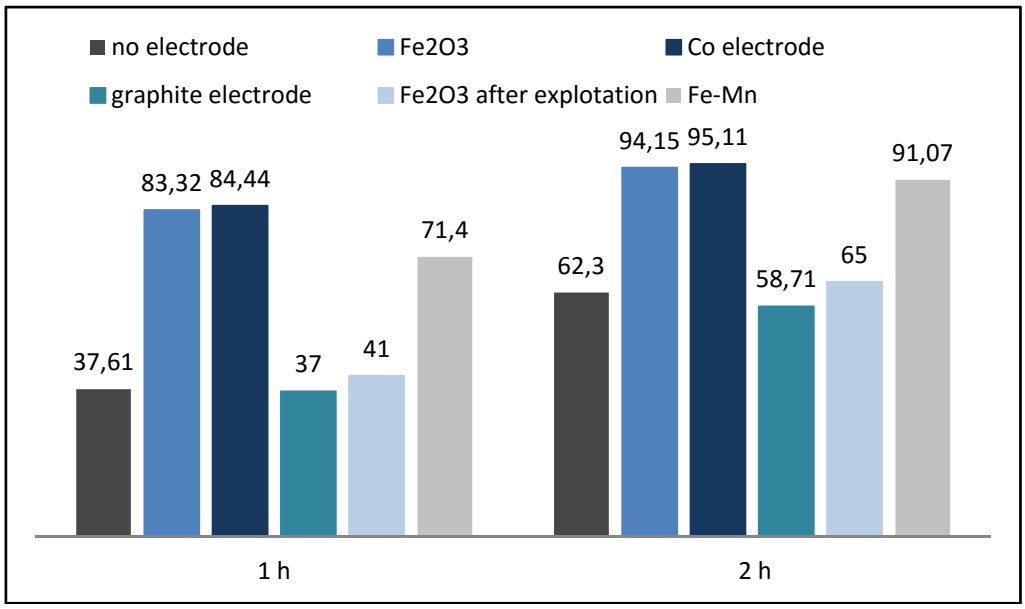

Fig.4. Percent oxidation of Na_2SO_3 for two hours using different catalysts

The results of oxidation of sulfite in the absence of a catalyst and with graphite rods are conducted as a comparison. The experiments were carried out at room temperature and with constant stirring rate of 300 rpm. Fig.4. shows that both types of electrodes have a similar catalytic activity which is two times higher than that of the natural oxidation of sulfite ions at the same conditions also presented in the figure. The results for the electrode containing Fe_2O_3 after working as an electrode in a fuel cell is shown. As seen they are comparable to these without catalyst, indicating that the catalyst was poisoned or catalytic mass was exported out from the volume on electrodes during operation.

Fig.5. shows oxidation rate of Na_2SO_3. The solutions used are much more concentrated (2.5 mass %) as this concentration was established to be optimal for sulfite fuel cell. Also this concentration is close to a real desulfurization process. A comparison between the catalytic properties for oxidation of sulfites by Ni-incorporated graphite fabric and Norit and fullerene (high order and Mn $(C_2H_3O_2)_2$) is shown in Fig.5. (the ratio of electrode surface to solution volume is the same in all experiments). As a comparison an experiment without catalyst is shown.

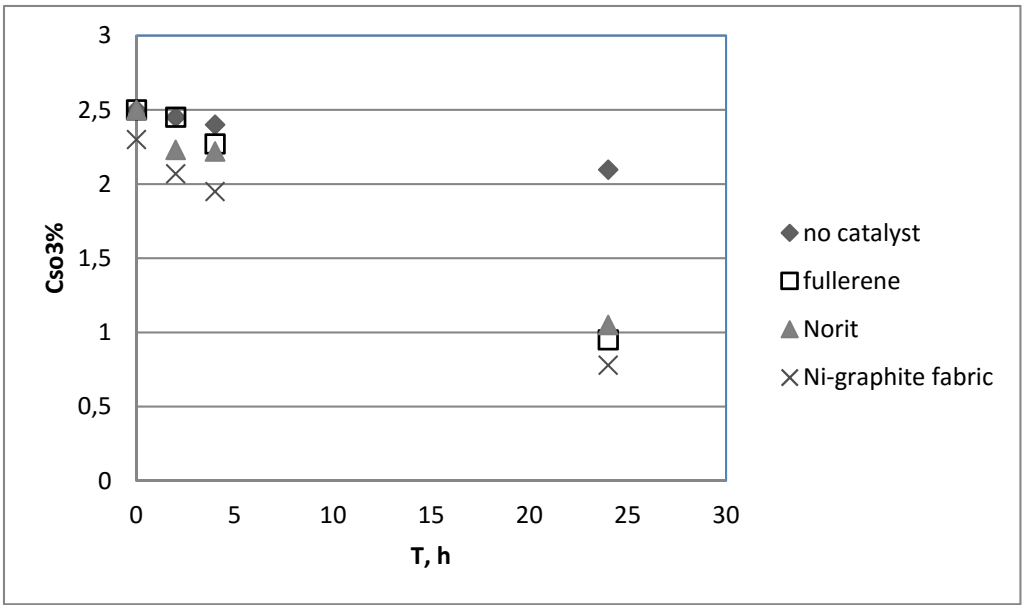

Fig.5. Oxidation rate of Na_2SO_3 with different catalysts

The Nickel-graphite fabric exhibits about 18% greater catalytic activity compared to the rest of the catalysts.

2.2. Catalysts for oxidation of sulfides

2.2.1. Catalysts incorporated on activated carbon

Catalysts for oxidation of sulfide ions are investigated. Me^{2+} (Me^{2+}= Mn, Co, Ni, Fe, Cu) ions are proven as catalysts for oxidation of sulfide ions (Demirbas (2009), Goifman et al. (2005)). It is not possible to use the pure metals as they interact with the sulfides in the form of precipitates.

As catalysts are tested four types of metal oxides incorporated into an activated carbon matrix. Two type spinel – type oxide (Co^{2+}, Mn^{2+}), ZrO_2, Pd^{2+} and activated carbon. Production of spinel-type oxides from organic compounds is done according to (Ljutzkanov L., Atanasov A., BG patent № 63594 /26.06.2002) and includes their impregnation with a solution of pre-determined salt and followed by pyrolysis and simultaneous activation. The catalytic effect is determined by adding them in the volume of the solution. As a catalyst is tested activated carbon with the same organic origin.

The results are shown in Fig.6. The oxidation rate for the non-catalyzed process at the same conditions is given for comparison. The initial concentration is chosen to be 65 $mg.l^{-1}$ because at this

concentration there is no retard of the oxidation rate due to parallel processes (Dermendzhieva et al. (2013), Razkazova-Velkova et al. (2013). The amount of the catalyst is the same (0.5 $g.l^{-1}$) for all experiments.

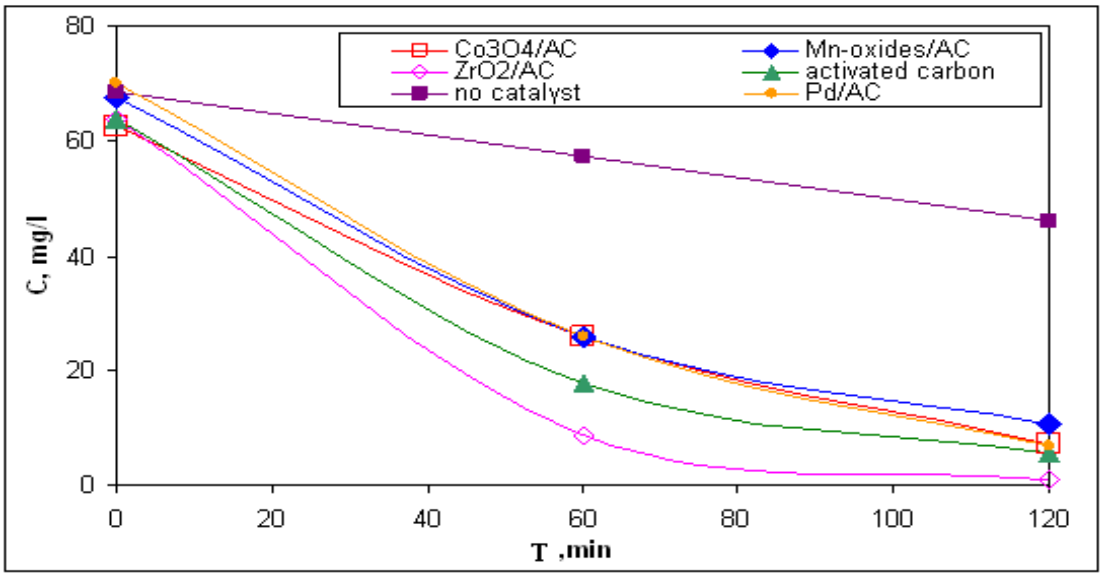

Fig.6. Influence of the type of catalyst on the oxidation rate. AC means activated carbon

Figure 6 shows that the oxidation of sulfide ions without catalyst is slow (about 10 % reduction of the sulfide ions by first sixty minutes). The addition of the catalyst into the reactor volume leads to a considerable acceleration of the process (from 50 to 90% reduction of the sulfide ions in the first sixty minutes). The effect of Co^{2+}, Mn^{2+} and Pd^{2+} catalyst is comparable and the activated carbon also has good catalytic activity. ZrO_2 – catalyst has 40% higher oxidation rate from the other metal catalysts. The catalyst is characterized through X-ray analyzes (Fig.7):

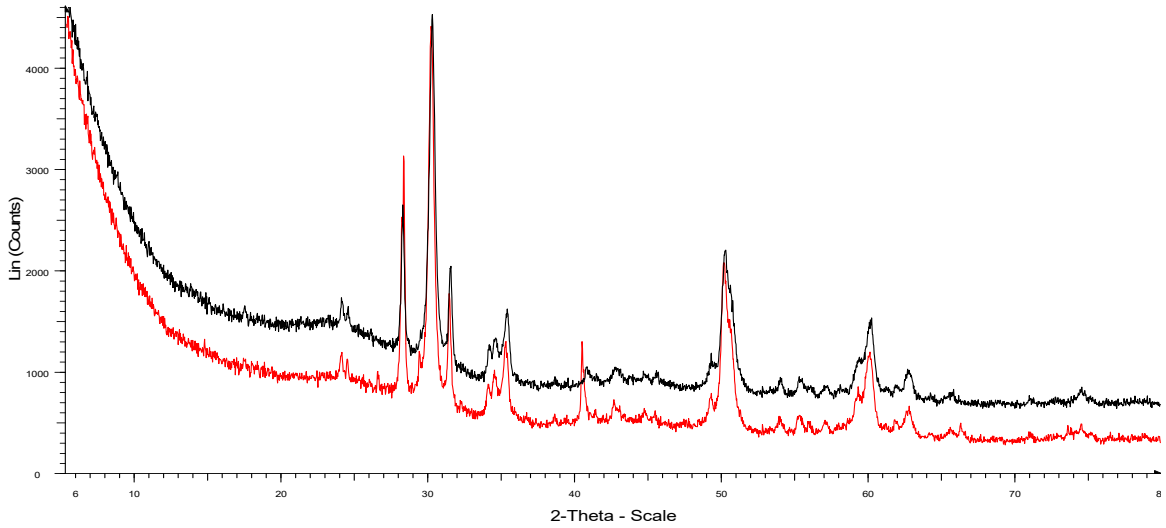

Fig.7. XRD patterns of zirconium catalyst before (upper X – ray gram, black) and after sulfide oxidation process (lower X – ray gram, red)

The ZrO_2 is in monoclinic and tetragonal form. Comparison before and after conducting the oxidation process is also shown in Fig.7. As it can be seen from it, the structure and the composition of the catalyst are the same before and after performing sulfide oxidation. This means that there is no transformation of its surface.

2.2.2. Pyrolyzed and activated carbon fabric

The source material used for the pyrolysis is commercial product – polyester (P150), Fibermax composites®. The pyrolysis is carried out at 830°C with simultaneous activation with water vapor (Ljutzkanov L. A., BG patent № 63594 / (2002)). As an additional advantage the material can be used to concentrate the sulfide ions on the electrodes via adsorption. Such an effect increases the efficiency of the cell due to reactions taking place on the surface of the electrodes. Previous studies show that adding catalyst directly into the volume of the solution drastically reduces the power generated by the fuel cell (Razkazova - Velkova E. et al., (2013)).

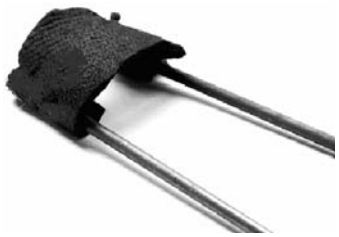

Fig.8. Pyrolyzed and activated carbon fabric

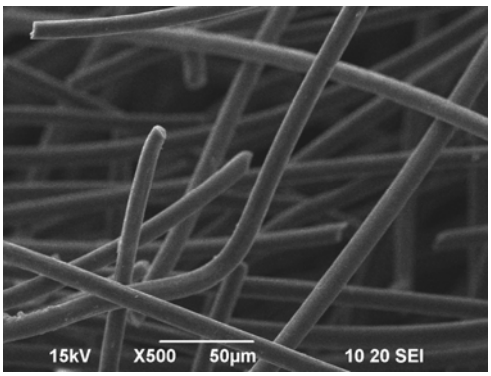

Fig.9. SEM of a pyrolyzed and activated carbon fabric

An electrode of activated structured carbon on the base of pyrolized fabric was obtained (Razkazova - Velkova E. et al., (2013)). It was successfully used electrode in a sulfide driven fuel cell. This material can be used as a carbon matrix and initial material for synthesis of structured metal containing catalysts and electrodes.

CONCLUSION

The results of oxidation of sulfite in the absence of a catalyst and with graphite rods are shown. Two types of electrodes have a similar catalytic activity which is two times higher than that of the natural oxidation of sulfite ions at the same conditions. Unfortunately, after some time of exploitation in a fuel cell, the Fe_2O_3 containing electrode was poisoned or the catalytic mass was exported out of the volume of the electrodes.

The Nickel-graphite fabric exhibits about 18% greater catalytic activity compared to the rest of the catalysts.

The oxidation of sulfide ions without catalyst is slow (about 10 % reduction of the sulfide ions by first sixty minutes). The addition of the catalyst into the reactor volume leads to a considerable acceleration of the process (from 50 to 90% reduction of the sulfide ions in the first sixty minutes). The effect of Co^{2+}, Mn^{2+} and Pd^{2+} catalyst is comparable and the activated carbon also has good catalytic activity. ZrO_2 – catalyst has 40% higher oxidation rate from the other metal catalysts.

The structure and the composition of the catalyst are the same before and after performing sulfide oxidation. This means that there is no transformation of its surface.

An electrode of activated structured carbon on the base of pyrolized fabric was obtained. It was successfully used electrode in a sulfide driven fuel cell. This material can be used as a carbon matrix and initial material for synthesis of structured, metal containing catalysts and electrodes.

ACKNOWLEDGEMENT

This work was accomplished within the project E02-15/12.12.2014 of National Science Fund, Ministry of Education, and Science, Republic of Bulgaria.

REFERENCES

BG patent №110265 Sachkov.

BG patent № 63594 / (2002) Ljutzkanov L. A., Method for Treatment of Carbon – Containing Materials.

Capone M., in: J.K. Kroschwitz, M. Howe-Grant (Eds.), Encyclopedia of Chemical Technology, vol. 23, Wiley, New,York, 1997, p. 432.

Clean M., (2001), Coal Demonstration Project: A DOE Assessment, DOE/NETL-2001/1156, U.S. Department of Energy National Energy Technology Laboratory, August.

Cotrino R., A.D. Levine, P. Amitzoglou, J. S. Perone, (2007), Removal of Hydrogen Sulfide from Groundwater Using Packed-Bed Anion Exchange Technology,C., Florida Water Resourses Journal, pp. 22-25.

Demirbas A., (2009), Utilization, and Environmental Effects, Energy Sources, Part A: Recovery, Volume31, Issue 20, 1866-1872.

Dermendzhieva N., Razkazova-Velkova E., Martinov M., Ljutzkanov L., Beschkov V., (2013), Journal of Chemical Technology and Metallurgy 48,5, 465-468.

Gerçe Özgül, A. Savas Koparal, Ülker Bakır Öğütveren, (2008), Removal of hydrogen sulfide by electrochemical method with a batchwise operation, Separation and Purification Technology 62, 656–660.

Goifman A., Gun J., Gelman F., Ekeltchik I., Leva O., Donner J., Bőrnick H., Worch E., (2006), Applied Catalysis B: Environmental 63, 296–304.

Gómez A., N. Fueyo, A. Tomás, (2007) Detailed modelling of a flue-gas desulfurisation plant, Computers and Chemical Engineering 31 1419–1431.

Henze M., Harremoë s P., la Cour Jansen J., Arvin E., (1997), Wastewater Treatment: Biological and Chemical Processes,second ed. Springer, Berlin.

Karatza D., M. Prisciandaro, A. Lancia, D. Musmarra,(2004), Calcium Bisulfite Oxidation in the Flue Gas Desulfurization Process Catalyzed by Iron and Manganese Ions, Ind. Eng. Chem. Res., *43,* 4876-4882.

Karatza D., M. Prisciandaro, A. Lancia, D. Musmarra, (2008) Reaction rate of sulfite oxidation catalyzed by cuprous ions, Chemical Engineering Journal 145 285–289.

Kodama, Y., Watanabe, Y., (2003), Isolation and characterization of a sulfur oxidizing chemolithotroph growing on crude oil under anaerobic conditions. Appl. Environ. Microbiol. 69, 107–112.

Lancia A., D. Musmarra, F. Pepe, M. Prisciandaro, (1997), Model of oxygen absorption into calcium sulfite solutions, Chemical Engineering Journal 66 123-129.

Lancia A., D. Musmarra. (1999), Calcium Bisulfite Oxidation Rate in the Wet Limestone-Gypsum Flue Gas Desulfurization Process, Environ. Sci. Technol., 33, 1931-1935.

Ljutzkanov Ljutzkan A., Razkazova-Velkova Elena N., Kolev Nikolai N., Dzhonova-Atanasova Daniela B., Kolev Dimitar N., Oxidation of $CaSO_3$ by air in the technology for purification of flue gases from SO_2, 13 International Symposium "Materials, Methods and Technologies", Journal of International Scientific Publications, Materials, Methods and Technologies, Volume 5, Part 1, (2011), pp. 304-325.

Pisu M., A. Cincotti, G. Cao, F. Pepe, (2004) Prediction of Uncatalysed Calcium Bisulphite Oxidation Under Operating Conditions Relevant To Wet Flue Gas Desulphurization Plants, Chemical Engineering Research and Design, 82(A7): 927–932.

Razkazova-Velkova E. N., Martinov M. S., Ljutzkanov L. A., Dermendzhieva N. Dr., Beschkov V. N., (2013), Journal of International Scientific Publications: Materials, Methods & Technologies, Volume 7, Part 1, ISSN 1313-2539.

Razkazova-Velkova E., Martinov M., Ljutzkanov L., Dermendzhieva N., Beschkov V., "Energy Efficiency of an Electrochemical Fuel Cell for Oxidation of Sulfide Ions from Deep Black Sea Water: Part II: Selection of electrodes", Scientific works of University of Food Technologies- Plovdiv**,** **V**olume LX (2013), 1092-1096.

Seredych M., T.J. Bandosz, (2007), Sewage sludge as a single precursor for development of composite adsorbents/catalysts, Chem. Eng. J. 12859-67.

Tomar M., Abdullah, T.H.A., (1994), Evaluation of chemicals to control the generation of malodorous hydrogen-sulfide in wastewater. Water Res. 28, 2545–2552.

Wang R., (2003), Investigation on a new liquid redox method for H2S removal and sulfur recovery with heteropoly compound, Sep. Purif. Technol. 31 111–121.

Yasyerli S., I. Ar, G. Dogu, T. Dogu, (2002), Removal of hydrogen sulfide by clinoptilolite in a fixed bed adsorber, Chem. Eng. Process. 41 (9) 785–792.

Yourong Wang, Yan Heqing, Wang Efeng, (2001), The electrochemical oxidation and the quantitative determination of hydrogen sulfide on a solid polymer electrolyte-based system, Journal of Electroanalytical Chemistry 497, 163–167.

Zaman J., A. Chakma, (1995), Production of hydrogen and sulfur from hydrogen sulfide, Fuel Processing Technology 41, 159-198.

Zheng Y., S. Kiil, J. E. Johnsson, (2002) Qin Zhong, Use of spray dry absorption product in wet flue gas desulphurization plants: pilot-scale experiments, Fuel 81 1899–1905.

Zheng Yuanjing, Søren Kiil, Jan E. Johnsson, (2003), Experimental investigation of a pilot-scale jet bubbling reactor for wet Flue gas desulphurization, Chemical Engineering Science, 58, 4695 – 4703.