

Membraneless fuel cells for remediation of sulfide- and nitrate-contaminated fluxes

S. Stefanov*, Ts. Parvanova-Mancheva, L. Ljutzkanov, E. Razkazova-Velkova

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

Received: December 07, 2021; Revised: June 13, 2022

Sulfides and nitrates are dangerous environmental pollutants with sources both natural and anthropogenic. The search for cheaper wastewater treatment techniques and alternative energy sources has led to a new branch of scientific interest – fuel cells for wastewater treatment. The present research is dedicated to remediation of sulfide- and nitrate-polluted fluxes in the anodic and cathodic compartments, respectively, of a membraneless fuel cell of our own design. The core of the fuel cell is a cylindrical tube of activated carbon, playing the role of both an electrode and a non-selective membrane. Both abiotic and microbial fuel cells (FCs and MFCs, respectively) are being investigated for their efficiency at neutralization of contaminated fluxes with different initial concentrations of sulfide and nitrate ions, as well as their electrical power output. *Pseudomonas putida* 1046 is used in the MFC for sulfide oxidation.

Keywords: Membraneless fuel cell, remediation of contaminated fluxes, sulfides, nitrates, *Pseudomonas putida*.

INTRODUCTION

The constant reduction of fossil fuel sources and quantities makes the search for new renewable energy sources a priority. Another major problem facing humanity is the generation of increasing amounts of wastes – in liquid, solid, or gaseous form. Fuel cells, although still not widely implemented in this context, represent a good prospect for redox waste disposal, combined with electricity generation.

Generally, a fuel cell (FC) consists of anode and cathode with catalysts incorporated into them and separated by a membrane [1]. A lot of the scientific efforts in the field are focused on increasing the FC power output, directly proportional to the rate of the oxidation / reduction of the fuel, and in the case of FCs for waste decontamination of the polluted fluxes. To this end, research is dedicated to increasing the efficiency of the catalysts for different redox reactions [2], their incorporation on the electrode surface [3], the configuration of the electrodes within the FC and the characteristics of the membranes used. The latter are an essential component for both high electricity yields and waste disposal. The main difficulties lie in their reliable installation and especially the preservation of their properties during operation. Of scientific interest is the degradation of the membrane's electrochemical characteristics during operation and under varying conditions [4, 5, 6, 7, 8]. Another limitation of the polymer membranes are their operating temperatures – polymer electrolyte membrane (PEM) fuel cells typically operate at temperatures no

higher than 60-80 °C due to structural limitations of the membranes, though attempts are made for elevation of the operation temperature of the PEM fuel cells [9]. Factors such as durability and cost still remain as major barriers to fuel cell commercialization [7].

An interesting and innovative approach in the development of FCs is the construction, design and investigation of membraneless fuel cells [10, 11, 12].

The aim of the present study is the preliminary investigation of a membraneless FC constructed from a tube of activated carbon that serves both as a semi-permeable non-selective membrane and an electrode.

Sulfide- and nitrate-contaminated fluxes are chosen as pollutants to be remediated into the anodic and the cathodic compartments of the FC, respectively. As there are a lot of sources of these severe pollutants (both anthropogenic and natural) and the classical methods used for their neutralization and disposal are expensive and energy intensive, they are appropriate candidates to be processed in FCs.

The most effective and widely applied method for efficiency increase for classical FCs is the incorporation of catalysts. Another way to increase the efficiency is the use of microorganisms instead of conventional catalysts in the so called microbial fuel cells (MFCs). *Pseudomonas* sp. are known to oxidize sulfides [13, 14] so *Pseudomonas putida* is chosen for comparison between abiotic membraneless FC without catalyst and membraneless MFC.

* To whom all correspondence should be sent:
E-mail: s.stefanov@iche.bas.bg

MATERIALS AND METHODS

Experimental set-up

A scheme of the laboratory-scale fuel cell is presented on Fig. 1A. The core of the fuel cell is a pyrolyzed cylindrical carbon tube (Fig. 1B), used as both electrode and semi-permeable non-selective membrane. The initial material for pyrolysis of the tubes are cellulose rolls. The once pyrolyzed tube is plugged at one end, thus forming two separate spaces (internal (30 mL) and external (130 mL)) that can be used as the cathodic and anodic compartments of the fuel cell. Additionally, the inner compartment is fitted with a standard graphite rod (SGR, Fig. 2A) attached firmly to the wall of the tube to be used as a current collector for the compartment. The tube is pyrolyzed by a patented technology with simultaneous activation [15]. The process allows easy incorporation of different catalysts, making the design very flexible.

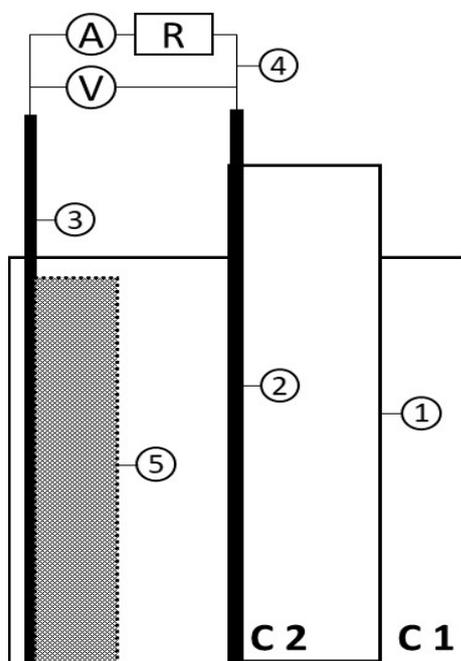


Fig. 1A. Scheme of the membraneless fuel cell: C 1 – Compartment 1 (external); C 2 – Compartment 2 (internal); 1 – pyrolyzed carbon tube; 2 – graphite electrode (of Comp. 2), 3 – graphite electrode (of Comp. 1); 4 – external electrical wiring; 5 – (optional) pyrolyzed carbon felt.

Different electrode configurations for the anodic compartment are investigated: i) three standard graphite rods; and ii) two pyrolyzed and activated carbon felts (ACFs, Fig. 2B) and three SGRs (used as a current collectors). The source material of the felts is commercially available as PAN carbon felt SCF510001000 and is pyrolyzed and activated by the same technology as the tubes [15]. The ACFs are situated in the external compartment next to the

pyrolyzed carbon tube and the SGRs pierce the felt, ensuring good electrical connection. To evaluate the influence of an increased surface area of the cathodic electrode some of the experiments (Experiments № [12-18], Table 1) were performed with 15 g (30 mL) of activated carbon (AC, Fujikasau®, Japan, 680 m²·g⁻¹) added in the cathodic compartment.



Fig. 1B. Pyrolyzed cylindrical carbon tube.



Fig. 2A. Standard graphite rods (SGR).

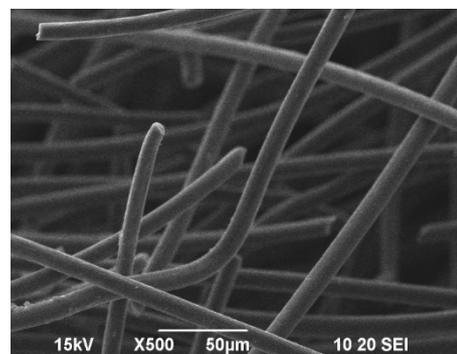
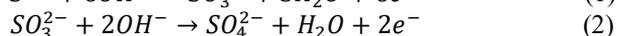


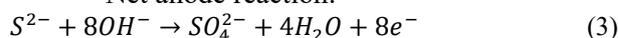
Fig. 2B. Activated carbon felt (ACF, SEM image).

The main reactions taking place in the anodic and in the cathodic compartment are as follows:

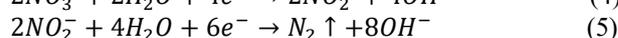
Anode:



Net anode reaction:



Cathode:



Net cathode reaction:

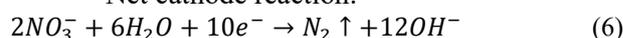


Table 1. Experimental parameters.

№	Cell Resistance, Ω		Anodic					Cathodic				
	0 hour	1 hour	Electrode	Concentration				Electrode	Concentration			
				Initial, $\text{mg}\cdot\text{L}^{-1}$	FFD level	Final, $\text{mg}\cdot\text{L}^{-1}$	Depletion, %		Initial, $\text{mg}\cdot\text{L}^{-1}$	FFD level	Final, $\text{mg}\cdot\text{L}^{-1}$	Depletion, %
1	250	163	3 SGR	60	(-1)	2	96.67	1 SGR	500	(+1)	497	0.60
2	327	254	3 SGR	60	(-1)	28	53.33	1 SGR	100	(-1)	99	1.00
3	334	244	3 SGR	150	(0)	95	36.67	1 SGR	100	(-1)	99	1.00
4	333	190	3 SGR	240	(+1)	136	43.33	1 SGR	100	(-1)	99	1.00
5	357	215	3 SGR	60	(-1)	29	51.67	1 SGR	300	(0)	284	5.33
6	347	194	3 SGR	150	(0)	70	53.33	1 SGR	300	(0)	299	0.33
7	204	169	3 SGR	240	(+1)	137	42.92	1 SGR	300	(0)	299	0.33
8	238	171	3 SGR	60	(-1)	28	53.33	1 SGR	500	(+1)	499	0.20
9	296	168	3 SGR	150	(0)	86	42.67	1 SGR	500	(+1)	498	0.40
10	238	168	3 SGR	240	(+1)	155	35.42	1 SGR	500	(+1)	493	1.40
11	322	191	3 SGR	150	(0)	85	43.33	1 SGR	1000 ⁴		960	4.00
12 ¹	96	94	Wet ACF	74 ²		4	94.59	AC+1 SGR	504		-	-
13	74	65	Dry ACF	56 ²		Traces	100.00	AC+1 SGR	504		67 ³	86.71
14	103	98	Wet ACF	65 ²		3	95.38	AC+1 SGR	504		-	-
15	107	95	Dry ACF	68		-	-	AC+1 SGR	500		132 ³	73.60
16	128	119	Wet ACF	63		-	-	AC+1 SGR	500		71 ³	85.80
17	59	55	Dry ACF	61 ²		3	95.08	AC+1 SGR	502		341	32.07
18 ¹	70	60	Wet ACF	62 ²		3	95.16	AC+1 SGR	505		390	22.77

¹ Microbial fuel cell (MFC); ² Sulfide solution with phosphate buffer; ³ Concentration at 24th hour mark; ⁴ Nitrate concentration twice higher than the highest examined in the full factorial design.

Analytical procedures

The anodic and cathodic solutions were prepared by dissolving the appropriate amounts of analytical grade $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$ and KNO_3 (Sigma Aldrich), respectively. For improving the conductivity of both solutions, NaCl (analytical grade) with concentration of $16.5 \text{ g}\cdot\text{L}^{-1}$ was used for all experiments. For the experiments with constant pH of the anodic (sulfide) solution phosphate buffer was used (Experiments № [12-14] and [17-18], Table 1).

The concentration of the sulfide ions was determined photometrically by converting them to methylene blue by addition of N,N -p-phenylenediamine [16], and the concentration of nitrates was determined by UV photometry following the method of Goldman & Jacobs [17]. All analyses of the concentration of the sulfide and nitrate ions were performed for the initial solutions and at the 2nd hour mark, except in the cases explicitly stated otherwise.

Electrical measurements

Current and voltage output of the FC at a fixed load (100Ω) were measured simultaneously during operation. Prior to the initiation of the experiment and after one hour of work, by varying the external resistance in the range $[\infty - 1 \Omega]$ the resistance of the fuel cell was calculated as the slope of the curve $U = f(I)$ and is presented in Table 1.

Pseudomonas putida 1046 cultivation and immobilization

Pseudomonas putida 1046 was chosen as an electrogenic strain capable of oxidizing sulfide ions [13, 14]. The medium used for its cultivation was: $10 \text{ g}\cdot\text{L}^{-1}$ meat extract, $10 \text{ g}\cdot\text{L}^{-1}$ peptone and $5 \text{ g}\cdot\text{L}^{-1}$ NaCl and the cultivation was performed for 24 hours at 30°C on a shaker (50 rpm).

The pyrolyzed carbon felt was immersed into the pre-cultured bacterial suspension. It was then transferred to shaking flasks and incubated at 30°C for 48 hours. Following this methodology the immobilized cells of the *Pseudomonas putida* strain are able to produce exo-polysaccharides, which serve as binding agents between the microbial cells and the carbon felt [18].

RESULTS AND DISCUSSION

Electrical power output and depletion of sulfides and nitrates with graphite rods used as electrodes in membraneless FC

In order to evaluate the influence of the initial concentration of both contaminants a full factorial design (3^2) (FFD) was performed (Experiments № [2-10]), varying the concentration of sulfide (60, 150 and $240 \text{ mg}\cdot\text{L}^{-1}$ as levels -1, 0 and +1, respectively) and nitrate (100, 300 and $500 \text{ mg}\cdot\text{L}^{-1}$ as levels -1, 0 and +1, respectively) ions. The concentration ranges were chosen based on previous experience of the research group [19, 20]. A preliminary run (Experiment № 1) was performed to assess the

influence of the volume of each solution (with the anodic compartment being the internal one (30 mL) and the cathodic being the external one (130 mL)). When comparing Experiments № 1 and № 8 (same concentrations, but the anodic compartment being 130 mL and the cathodic – 30 mL) the latter vastly exceeds the former in terms of electrical characteristics. Following this evaluation a decision was made that all the experiments from the factorial design, as well as the additional ones presented in

Table 1 will be performed with the anodic compartment being the larger (external) one.

The electrical power output per unit volume of the catholyte of selected experiments is presented in Fig. 3. The experimental conditions are described in Table 1. Although the concentration ranges being investigated are relatively wide, the electrical performance of the FC does not differ significantly except for the initial output at higher concentrations.

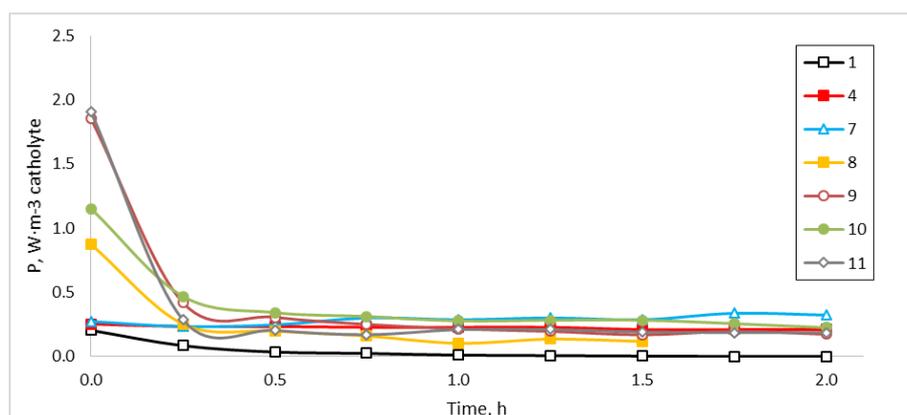


Fig. 3. Power output of the FC per unit volume of catholyte – selected experiments.

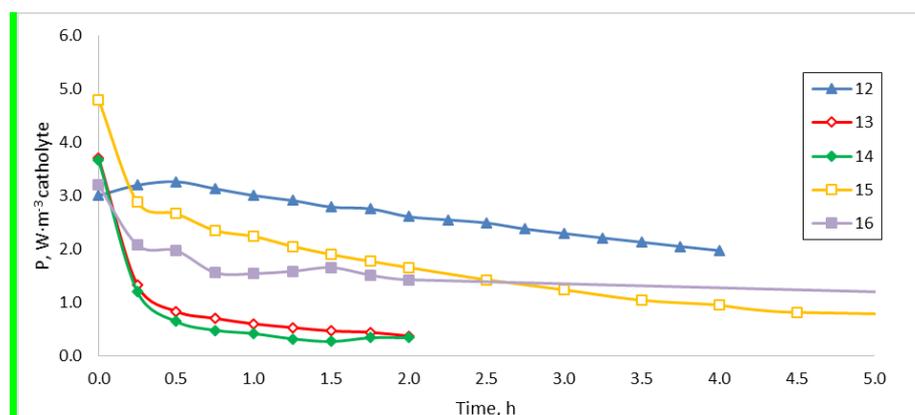


Fig. 4. Power output per unit volume of catholyte for membraneless FC with activated carbon felt electrode: dry ACF (empty symbols), wet ACF (filled symbols).

The depletion of the ions of the investigated configurations in Fig. 3. is presented in Table 1. The oxidation of sulfide ions corresponds closely to the electrical output obtained and is in the range of [35-55] % at the 2nd hour mark. The outlying fast oxidation of the sulfides of Experiment № 1 is due to the fact that the volume of the sulfide solution used in this experiment is only 30 mL (as opposed to all others experiments – 130 mL), making the amount of sulfide ions about 4 times less. The reduction of nitrates does not exceed 6 % in all cases for 2 hours of work as a FC, in accordance with the chemical characteristics of nitrate ions – a very

stable and hard to reduce pollutant, in contrast to the very active and easily oxidized sulfide ions.

Electrical power output and depletion of sulfides and nitrates with pyrolyzed carbon felts used as electrodes in the anodic compartment of membraneless FC.

In order to increase the electrical power output of the FC a different type of electrodes were used – pyrolyzed activated carbon felt. Two square-shaped felts (100 cm² each) were used as anode. Additionally, to increase the surface area of the cathode 15 g (30 mL) of activated carbon was added in the cathodic compartment. The power output of

the cell per unit volume of catholyte vs time is given on Fig. 4. The experimental conditions are summarized in Table 1, Experiments № [12-16]. Previous work of the research team [19] has shown that *Pseudomonas putida* is a viable microorganism for use in sulfide-driven microbial fuel cells. The research also showed that substantial substrate inhibition occurs at sulfide concentrations over 70 mg·L⁻¹, so for this part of the study sulfide concentrations were limited to about 70 mg·L⁻¹. In order to further compare the results for the FC and MFC two sets of experiments were conducted – with dry (Experiment № 15) and wet (Experiment № 16) ACFs. The felts with immobilized *P. putida* for the MFC were stored in saline solution (0.9 % NaCl), meaning they are always wet, while those for the FC can be either dry or wetted (with sterile saline solution) prior to being put into the fuel cell. The higher initial power output of the experiments with dry AFCs is due to fact that the dry AFCs adsorb immediately a large quantity of the sulfide ions, substantially increasing the local concentration of the sulfides in the pores of the felt.

On the other hand, the experiments with wet felts show lower resistance drops between the initial cell resistance and the 1 hour one. We attribute this to the fact that the felts are already soaked with conducting saline solution and the resistance drop is a consequence of the substitution of the saline solution with the more conducting anolyte (9 g·L⁻¹ vs 16.5 g·L⁻¹ NaCl, respectively, plus the additional conductivity provided by the sulfide ions present). This effect is even more prominent for the experiments with dry carbon tube and graphite rods, where the tube is the only adsorbing material – it takes a lot longer to soak than the felts, hence the difference in the internal resistance reaches up to 40 % (Experiments № [1-11]). Additional experiments with buffered sulfide solutions were performed (Experiments № [13-14]) in order to assess the viability of the configuration at lower (and stable) pH values and to compare it to the MFC, which operates at pH = 7.00. As can be seen on Fig. 4. the electrical output of the FC with buffered anodic solutions is lower which is partly due to the fact that at this pH value (7.00) part of the sulfide ions are in the form of hydrogen sulfide and they desorb from the anodic solution, lowering the concentration of the “fuel” [21]. Regardless of this effect the highest power output was obtained with the MFC (Experiment № 12), showing the viability of the MFC in generating energy in addition to the decontamination of polluted fluxes. The depletion of the ions follows the same tendency as the

experiments without buffered solutions (Experiments № [12-14] vs № [15, 16]), although in contrast to the experiments with only SGR used as electrodes (Experiments № [1-11]) the neutralization of sulfide ions is twice as effective, reaching up to [94 – 100] % (compared to [35-50] % for the SGR ones). The reduction of nitrates, on the other hand, reaches up to [73-87] % for 24 hours, while that of the SGR experiments is in the range of [0.2-5.3] % for 2 hours of work. Part of the depletion of nitrate ions concentration may be due to adsorption by the activated carbon used to increase the surface area of the cathode – this has the added benefit of boosting the electrical and electrochemical parameters of the FC (by increasing the local concentration of ions contacting the cathode), but at the same time impairs the direct and accurate determination of nitrate ions concentration.

Comparison between classical PEM FC and membraneless FC

In order to evaluate the viability of the membraneless FC design investigated in this work we compared its electrical and chemical parameters with those of a classical PEM FC (using Fumapem® membrane) from our previous work (Experiments № [17-19]). The initial concentrations for both experiments were identical – 65 mg·L⁻¹ sulfide ions and 500 mg·L⁻¹ nitrate ions. The reference membrane FC was designed with equal anodic and cathodic compartments of 300 mL, in contrast to the disproportional compartments of the membraneless FC evaluated in this study (130 mL for the anodic and 30 mL for the cathodic), but when the power output was normalized to a unit volume the two designs showed comparable values (Fig. 5). Additionally, in terms of oxidation of sulfide ions the depletion percent for the FC (with carbon felt used as anode) shows identical results and the FC with standard graphite rods is half as effective as the PEM FC for 2 hours of operation. In terms of nitrate ions reduction, though, the PEM FC outperforms both set-ups of membraneless FC presented, achieving [23-32] % depletion in 2 hours, while for the SGR set-up the depletion was in the range of [0.2-5.3] % for the same amount of time and for the ACF it was in the range of [74-87] % for 24 hours of operation.

These results prove that the proposed membraneless fuel cell design is competitive in terms of energy harvest and sulfide oxidation to established FC designs and at the same time eliminates one of the classical PEM FCs main disadvantages – the very expensive and delicate membranes.

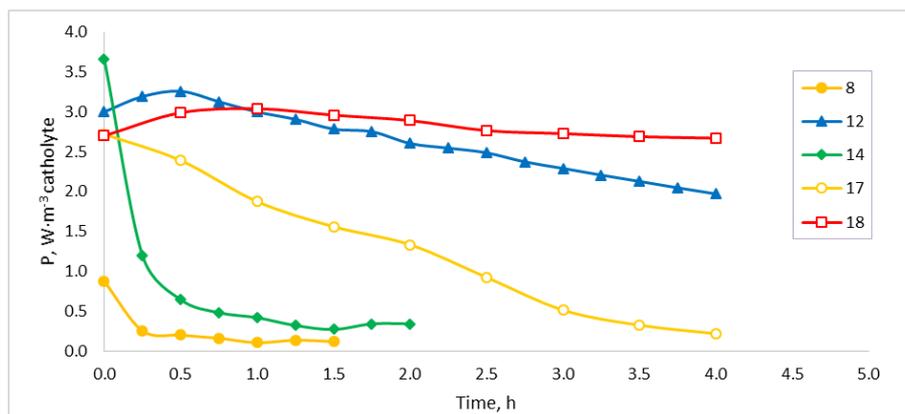


Fig. 5. Power output per unit volume of the catholyte: membraneless FC with graphite rods (Exp. 8); membraneless MFC (Exp. 12) and FC (Exp. 14) with carbon felt; PEM FC (Exp. 17) and PEM MFC (Exp. 18).

Additionally, the carbon felt electrodes improve both electricity generation and oxidation/ reduction of the investigated pollutants when compared to pure graphite electrodes.

Coulombic efficiency of the fuel cell

Based on the main reactions presented in Eq. [1-6] and the experimental results obtained the Coulombic efficiency for the anodic and cathodic reactions was calculated and is presented in Table 2.

Table 2. Coulombic efficiency of the fuel cell for anodic and cathodic reactions.

Exp. №	Anodic Reaction ¹	Cathodic Reaction ²
1	1.25	7.04
2	1.58	235.58
3	0.90	230.72
4	0.57	273.67
5	1.51	13.61
6	0.78	290.56
7	0.65	310.68
8	1.61	238.97
9	0.92	137.41
10	0.74	41.76
11	0.91	6.86
12	4.26	2.75
13	2.72	1.62
14	2.15	1.23
15	3.90	3.41
16	3.65	2.52
17	11.39	19.08
18	15.78	37.66

¹ 6 electron transfer by Eq. (1); ² 10 electron transfer by Eq. (6).

Qualitative analysis performed on the anodic solution proved that no elemental sulfur was present in the solution or deposited onto the anode during operation of the FC, while the presence of sulfite and sulfate ions in the anolyte was confirmed (with sulfite ones being more prominent than sulfate ones).

Thus, the Coulombic efficiency presented corresponds to the sulfide-to-sulfite reaction ($S^{2-} \rightarrow SO_3^{2-}$, Eq. (1)) and the transfer of 6 electrons. In terms of electrical efficiency, the results for Experiments № [1-11] were low [0.6-1.6] % but a 2 to 3 times increase was observed for the experiments with carbon felt (Experiments № [12-16]) and up to [11-16] % efficiency was achieved by the membrane FC (Experiments № [17-18]). Highest efficiencies (in their respective sets) were achieved by the MFCs compared to the same condition FCs (Experiments № 12 vs № 14 and Experiments № 18 vs № 17, with 4.26 % vs 2.15 % and 15.78 % vs 11.39 % efficiency, respectively). Still, in terms of ecological parameters for the anodic solution neutralization the novel design of the FC (with activated carbon felts used as anode) showed comparable results with traditional PEM FC.

The Coulombic efficiency for the reduction reaction is based on Eq. (6) with 10 electrons transferred. When examining the results presented in Table 2 an interesting phenomenon is observed – the first batch of experiments (Experiments № [1-11] with just graphite electrodes) show efficiencies over the maximum theoretical values, especially the lower initial nitrate concentrations (100 and 300 $mg \cdot L^{-1}$). We attribute this to two factors: i) at lower nitrate concentrations reduction of dissolved oxygen in the catholyte is also contributing to the cathodic reactions, while for the higher concentration examined (500 $mg \cdot L^{-1}$) the majority of the electron transfer is related to nitrate reduction; and ii) as nitrate ions are very stable ions it takes a lot longer to reduce them than to oxidize the sulfide ones in the anodic compartment. This is evident from the depletion percent presented in Table 1 – for 2 hours of operation of the FC only [0.2-5.3] % of the nitrates present are reduced, compared to [73-87] % for 24 hours of operation of the FC, albeit with different electrodes used (Experiments № [1-11] vs

Experiments № [12-16]). The addition of activated carbon in the cathodic compartment, while increasing the power output, drastically reduces the cathodic efficiency. Both of these effects are consequence of the adsorption of the nitrate ions onto the surface of the carbon – on one hand the adsorption increases the local concentration on the surface of the electrode, thus the power output; while on the other hand as the nitrate ions are very stable the reduction rate is low, thus part of the ions are still not converted to nitrogen, yet they are not in the solution and because the chemical analysis cannot account for this adsorbed quantity the actual amount of converted ions is most likely lower than the analyses show.

CONCLUSIONS

A membraneless fuel cell for remediation of contaminated fluxes is presented and investigated. Compared to a classical membrane fuel cell it shows comparable characteristics. Its advantage is the elimination of the expensive and difficult for exploitation polymer membrane. Additional advantages are the possibility to work at elevated temperatures and the relatively cheap manufacture and exploitation costs.

From an ecological standpoint the innovative FC design has a couple of advantages – it converts a waste (the carbon tube) into a product that further helps remediate sulfide- and nitrate-contaminated fluxes, effectively applying the principles of the circular economy. Depending on the initial concentrations [35-53] % of the sulfide ions present are remediated in the first two hours of operation when standard graphite rods are used as electrodes and [94-100] % are converted when activated carbon felt is used as an electrode in addition to the graphite one over the same time period. In terms of nitrate reduction the conversion rate is low when only SGR are used for two hours of work [0.2-5.3] %, while when activated carbon is employed in addition to the SGR as cathode and activated carbon felt is used as an anode reduction of up to 87 % can be achieved at the 24th hour mark.

All experiments show a drop in the internal cell resistance of the FC after 1 hour of operation due to the fact that conducting solution enters the pores of the electrodes. This effect is more prominent when the only adsorbent material is the pyrolyzed tube itself (up to 40 % resistance drop), though the use of pyrolyzed felt as anode lowers the internal resistance of the FC two to three times, making it comparable to a membrane FC.

Coulombic efficiency for the anodic reaction is low when SGR are used as anode [0.6-1.6] % but the

use of carbon felts as anode increases the efficiency to [2.1-4.3] %. These results are still far from the ones obtained by a traditional PEM FC [11.4-15.8] %. MFCs show better efficiencies than FCs of the same design and at the same conditions (4.3 % vs 2.1 % and 15.8 % vs 11.4 % efficiency for the membraneless and PEM MFC vs FC, respectively).

The Coulombic efficiency for the cathodic reaction with SGR shows that additional reaction takes place, most likely reduction of dissolved oxygen. This can be avoided by using higher initial concentrations of nitrate ions. The electrical efficiency drops to [1.2-3.4] % for 24 hours of operation, yet the depletion percent increases from [0.2-5.3] % to [74-87] %. Similar to the anodic efficiency, MFCs show better cathodic efficiency than the corresponding FCs.

Microbial fuel cells (both membraneless and classical membrane ones) show better electrochemical characteristics than regular FCs of the same design. The use of immobilized electrogenic cells in the anodic compartment allows their repeated use, on one hand, and on the other hand, it lessens the effect of substrate inhibition at higher concentrations of sulfide ions, thus expanding the range of application of the MFC.

Based on all the results obtained a process can be designed to tap into the advantages of the rapid and not so electrochemically effective oxidation of sulfide ions and the steady, efficient reduction of nitrate ones – fresh anolyte can be fed to the anodic compartment while a static, nitrate-rich catholyte can be used to realize an effective fuel cell for remediation of sulfide- and nitrate-contaminated fluxes.

Acknowledgements: *This work has received funding from the National Research Program “Low Carbon Energy for the Transport and Household (E+)” and by the National Research Programme “Young Scientists and Postdoctoral students” approved by DCM # 577 / 17.08.2018 both granted by the Bulgarian Ministry of Education and Science.*

REFERENCES

1. K. Scott, H. Y. Eileen, Amsterdam, Elsevier WP Woodhead Publishing 2016, 2015.
2. T. Napporn, Y. Holade, Electrolyzers, and Metal-Air Batteries, 1st edn., G. Korotcenkov (ed.), Elsevier, 2021.
3. S. Bapat, C. Giehl, S. Kohsakowski, V. Peinecke, M. Schäffler, D. Segets, *Adv. Powder. Technol.*, **32**, 3845 (2021).
4. H. M. A. Sharif, M. Farooq, I. Hussain, M. Ali, M. A. Mujtaba, M. Sultan, B. Yang, *J. Taiwan Inst. Chem. Eng.*, **129**, 207 (2021).

5. J. Zhao, X. Li, C. Shum, J. McPhee, *Energy and AI*, **6**, 100114 (2021).
6. Y. Liu, B. Xiao, J. Zhao, L. Fan, X. Luo, Z. Tu, S. H. Chan, *Energy Convers. Manag.: X*, **12**, 100114 (2021).
7. Y. Wang, K. S. Chen, J. Mishler, S. C. Cho, X. C. Adroher, *Appl. Energy*, **88**, 981 (2011).
8. P. C. Okonkwo, I. B. Belgacem, W. Emori, P. C. Uzoma, *Int. J. Hydrog. Energy*, **46**, 27956 (2011).
9. C. Zhang, W. Zhou, M. M. Ehteshami, Y. Wang, S. H. Chan, *Energy Convers. Manag.*, **105**, 433 (2015).
10. Q. Wang, F. Chen, Y. Liu, T. T. Gebremariam, J. Wang, L. An, R. L. Johnson, *J. Power Sources*, **404**, 106 (2018).
11. H. An, H. Jeon, J. Ji, Y. Kwon, Y. Chung, *J. Energy Chem.*, **58**, 463 (2021).
12. Y. Yang, P. Xu, S. Dong, Y. Yu, H. Chen, J. Xiao, *J. Clean. Prod.*, **307**, 127306 (2021).
13. H. Guo, C. Chen, D.-J. Lee, A. Wang, N. Ren, *Enzyme Microb. Technol.*, **53**, 6 (2013).
14. Y.-C. Chung, C. Huang, C.-P. Tseng, *Biotechnol. Prog.*, **12**, 773 (1996).
15. L. Ljutzkanov, A. Anastasov, Method of processing carbon containing materials, Bulg. Pat. 63594, 2002.
16. T. D. Rees, A. B. Gyllenspetz, A. C. Docherty, *Analyst*, **96**, 201 (1971).
17. E. Goldman, R. Jacobs, *J. Am. Water Work*, **53**, 187 (1961).
18. F. H. Romano, V. Beschkov, in: Biocatalysis Research Progress, Nova Science Publishers Inc., 2008, p. 281.
19. E. Razkazova-Velkova, S. Stefanov, T. Parvanova-Mancheva, M. Martinov, *Bulg. Chem. Commun.*, **52** (A), 87 (2020).
20. E. Razkazova-Velkova, M. Martinov S. Stefanov, *Sci. Works Univ. Food Technol.*, (2017).
21. H. Marianne H. Hasler-Sheetal, *Front. Mar. Sci.*, **1**, 11 (2014).