J Appl Electrochem (2009) 39:185–189
DOI 10.1007/s10800-008-9652-x

ORIGINAL PAPER

# Indirect electrochemical synthesis of active oxygen in dilute sulfate solutions

**Mark M. Goldin · Mogely Sh. Khubutiya ·
Vladimir A. Kolesnikov · Michail M. Abakumov ·
Anatoly K. Evseev · Alexander George Volkov**

Received: 28 March 2008 / Accepted: 14 August 2008 / Published online: 2 September 2008

**Abstract** Anodic oxidation of dilute solutions of sodium sulfate was developed to generate oxidants into aqueous solutions with a diaphragm electrolyzer, which consisted of titanium anodes covered with mixed oxides of iridium, ruthenium and tin, a titanium cathode, and Teflon cation-exchange membrane. An electronic device was created for continuous self-purification of cathode surface from hardness salt deposits. The anodic products of electrolysis were molecular oxygen and sodium persulfate. It should be noted that sodium persulfate was the only active oxidant. The synthesized anolyte was tested for its oxidizing activity towards certain metabolites and toxicants. Disinfecting properties of anolyte were detected towards gram-positive and gram-negative bacteria. The comparison of redox potentials of commercial samples of persulfate and the synthesized anolyte showed that the redox potential value for the anolyte is much higher than for solutions with the same concentration of commercial persulfate.

**Keywords** Anodic oxidation · Bacteria · Persulfate · Oxygen · Medical electrochemistry · Exotoxicants · Blood

M. M. Goldin · M. Sh. Khubutiya · V. A. Kolesnikov ·
M. M. Abakumov · A. K. Evseev
N. V. Sklifosovsky Research Institute for Emergency Medicine,
3 B. Sukharevskaya Pl., Moscow 129010, Russia

A. G. Volkov (✉)
Department of Chemistry, Oakwood University,
7000 Adventist Blvd., Huntsville, AL 35896, USA
e-mail: gvolkov@oakwood.edu; agvolkov@yahoo.com

## 1 Introduction

Many physiological homeostasis processes are electrochemical, such as electrical signaling and nervous impulse transduction, charge transfer in electron transport chains, respiration, and ion transport across cell membranes. Hence, electrochemical medical applications are important for various areas of medicine. One example of the use of electrochemical methods in medicine is detoxification by electrochemical hemosorption [1]. Moreover, electrochemically synthesized solutions of active oxygen in the form of NaOCl [2] are used for medical treatment of certain pathological states of the organism. The main disadvantage of hypochlorite solutions is the high probability of formation of toxic chloroorganic compounds in the form of micro impurities during the electrosynthesis. However, the idea of generating active oxygen into aqueous solutions is a relevant issue because many oxidizers such as hydrogen peroxide, ozone, and molecular oxygen are widely employed in medicine for so-called oxidative therapy [3]. Therefore it is possible that electrochemically synthesized sodium persulfate could be quite reactive with reference to toxic metabolites and certain exotoxicants. Electrosynthesis of persulfate ion from sulfates should pose no danger to the organism because chlorine is not generated in the electrolyte. At the same time, sulfates are nontoxic even in high concentrations, whereas the expected medicinal concentration of persulfate is below $10^{-1}$ g/L [2]. Sodium sulfate, for example, has an $LD_{50}$ value of 5.989 g/kg [4]. The synthesized persulfate ion is stable; however, the interaction of persulfate ion with any acceptors of oxygen or a reducing agent, such as oxidizable biological substrates, bacteria, or incompletely oxidized toxic organic compounds, leads to formation of the initial sulfate ion.

The first attempt to generate the active oxygen into aqueous solution for organism detoxification with the help of anodic oxidation of dilute solution of sodium sulfate in a diaphragm electrolyzer was successful [5], and the detoxifying activity and hemocompatibility of such solutions were shown. To follow-up on the previous work [5], we should determine the composition of anodic products and investigate the influence of anodes covered with a catalyst composed of mixed oxides of ruthenium, tantalum and tin on the redox potential of synthesized solutions. It is interesting to compare this new catalyst with the iridium oxide catalyst used earlier in reference [5]. The goal of such study is to increase the oxidizing activity of the synthesized solutions by using new anodes with higher corrosion stability functioning at more positive potentials [6].

The possibility of using tap water for production of disinfectants and sterilizing agents has not been investigated. This problem is important since electrochemical treatment can sterilize solutions [7]. It is also significant for the cathodic process because tap water contains quite considerable quantities of salts causing water hardness. Alkalization of the cathode layer and cathodic chamber as a result of hydrogen formation on the cathode leads to precipitation of hardness salts. Precipitation of the slightly soluble calcium and magnesium hydroxides and bicarbonates on the cathode, in the cathodic chamber, and on the diaphragm leads to irregular operation of the electrolyzer due to increases in the total resistance of the system. At the same time, the probability of diaphragm damage increases due to precipitation of hydroxides and hydrocarbonates, which can penetrate through the pores of the diaphragm and damage it. The main goals of this work are development of a method of persulfate generation in dilute aqueous solutions of sulfate with optimization of process parameters; identification of the products of electrolysis that determine the oxidizing ability of anolyte; determination of erythrocyte stability with respect to the anolyte; determination of detoxifying activity of the anolyte towards blood, bacteria, and exotoxicants; the possibility of using the electrochemical method of generating persulfate dianion in aqueous media from sulfate anion for disinfection of water.

## 2 Experimental

A diaphragm electrolyzer with an ion-exchange polymer membrane MF-4SK, a titanium cathode, and a titanium anode covered with a mixture of oxides $IrO_2$, $RuO_2$ and $SnO_2$ (Fig. 1) was used to oxidize the sodium sulfate. The corrosion stability of anodes with coating thickness of 4 μm was 7,300 h under a current density of 3.5 A/dm$^2$. Volumes of both cathode and anode chambers were 2.5 cm$^3$. Aqueous solutions of sodium sulfate with concentration ranging from 0.07 to 0.28 M were used as electrolytes. Electrolyte were passed through the chambers of the electrolyzer by a peristaltic pump *Bellco BL 759B*, with a flow rate of 2.6–7.9 mL/min and a current density of 1–7 A/dm$^2$.

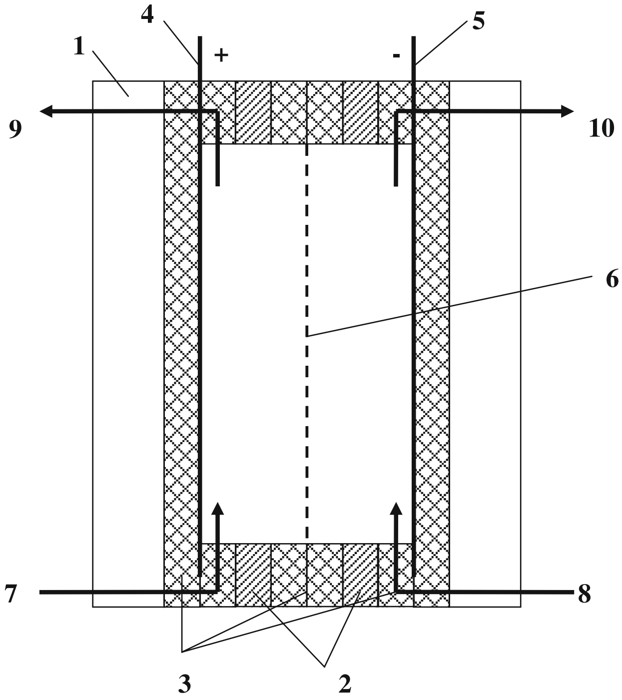

**Fig. 1** The electrolytic cell: 1, case; 2, plastic frame; 3, rubber gasket; 4, anode; 5, cathode; 6, membrane; 7, anodic inlet; 8, cathodic inlet; 9, anodic outlet; 10, cathodic outlet

The anodic products were analyzed by the iodometric method at wavelengths of 270–400 nm [8] using a UV-2401PC (*Shimadzu*) spectrophotometer. Dissolved molecular oxygen $O_2$ in anolyte was determined by an Ecotest-2000 electrochemical oxygen meter (*SPA Econics*). The chemiluminescent reaction of anolyte with luminol in the presence of chlorohemin was used to determine hydrogen peroxide. Redox potentials (RP) were measured on a platinum electrode versus a silver/silver chloride reference electrode. In order to ensure reproducibility of the measurements, the platinum electrode was treated by cyclic impulses with a rate of scanning of 500 mV/s for 50 cycles in the potential range from $-400$ to $+800$ mV and then for 10 cycles in the range from $+300$ to $+400$ mV. This treatment led to a stable value of the working electrode potential in deoxygenated solution.

Common blood analyses were done by standard biochemical methods [9]. Medinal and myoglobin were determined spectrophotometrically [10, 11]. Polarization measurements were made on an IPC-Pro potentiostat (*NTF«Volta»*).

## 3 Results and discussion

The harmful effect of precipitation of calcium and magnesium hydroxides and bicarbonates on the cathode and diaphragm was eliminated by periodically washing the cathodic chamber with a 10% hydrochloric acid solution. It was necessary to repeat this procedure every 200 h when the concentration of calcium and magnesium salts was about 80–100 mM. In order to improve the electrolyzer, we created a device for preventing adhesion of hardness deposits to the cathode by periodic anodic shifts of the cathode potential in the course of operation of the electrolyzer.

The circuit diagram of the electronic device developed is shown in Fig. 2. The anode was used as the auxiliary electrode, and the cathode received anodic impulses from the anode. This device was tested: Sustained performance occurred for at least 350 h, over against 16 h without the device, for the following electrolyte composition: 20% sodium chloride, total concentration of hardness salts ca. 400 mg/L, working current density of ca. 12 A/dm$^2$, and terminal voltage of ca. 15 V.

Solutions of 0.07–0.28 M $Na_2SO_4$ were oxidized under current densities of 1–7 A/dm$^2$. Absorption peaks consistent with the presence of sodium persulfate (Fig. 3, a–c) were found around 289 and 352 nm in the UV/visible spectrum of the electro-synthesized solutions (Fig. 3, 1–4). However, hydrogen peroxide $H_2O_2$ and ozone $O_3$ also absorb light in the same region. Besides, it was necessary to check the oxidizing activity of $O_2$, because its presence was established in anodic gases by an electrochemical oxygen meter.

Since $O_2$, $H_2O_2$, $O_3$, $Na_2S_2O_8$ or their mixtures were possible anodic products, it was necessary to ascertain their presence or absence first. Naturally, the probabilities of formation for the above products are quite different: For example, potentials of their formation are ca. 0.0 V for $H_2O_2$ [12], 1.23 V for $O_2$ [13], over 1.5 V for $S_2O_8^{2-}$ [13] or 1.77 V according to reference [14], and over 2.0 V for $O_3$ [13]. Besides, the likelihood of $H_2O_2$ being a product was negligible because $H_2O_2$ decomposes rapidly under low anodic potentials on electrode-catalysts [15].

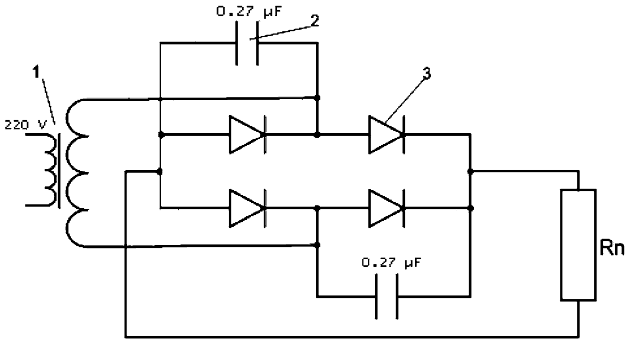

**Fig. 2** Circuit diagram of the hardness salt cleaning module. 1, transformer; 2, capacitor; 3, diode; $R_n$, load resistance

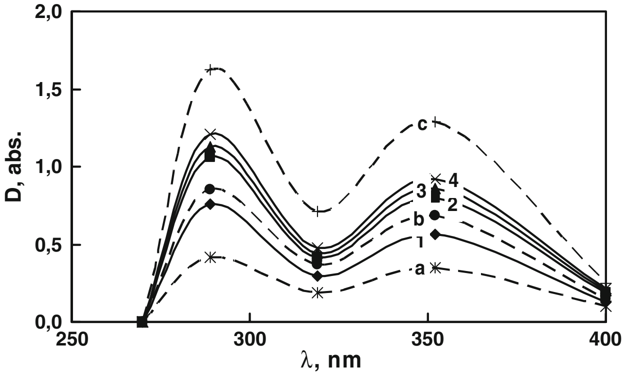

**Fig. 3** UV-spectra of sodium persulfate solutions (dashed lines: a, 1.068 mM; b, 2.135 mM; c—4.271 mM) and anolyte solutions synthesized by electrolysis of 0.14 M $Na_2SO_4$ with a flow rate of 5.3 mL/min under various current densities (solid lines: 1, 1 A/dm$^2$; 2, 3 A/dm$^2$; 3, 5 A/dm$^2$; 4, 7 A/dm$^2$)

Since iodometry is not selective for the above mentioned oxidizers, the presence of $H_2O_2$ and $O_3$ were checked first. It was decided to vacuumize a vessel with anolyte in order to remove all gases dissolved in anolyte. The hermetical vessel with 100 mL anolyte and 50 cm$^3$ air through special glass pipe was vacuumized during 30 min by oil vacuum pump to residual pressure of $10^{-2}$ Pa. Spectra of vacuumized and initial anolytes were practically identical. The experiment showed the absence of ozone in anolyte.

The absence of $H_2O_2$ in anolyte was shown by chemiluminescence analysis with luminol as a reactant. The addition of luminol to anolyte did not yield any signal, whereas the solution of 0.1 M $Na_2SO_4$ containing $10^{-4}$ M $H_2O_2$ gave a well-defined signal. When $O_2$ was bubbled through 0.1 M $Na_2SO_4$ for 20 min with subsequent addition of aqueous KI, its spectrogram was identical to the spectrogram of anolyte. Therefore, the presence of dissolved $O_2$ in anolyte does not interfere with the determination of oxidizers.

The presence of persulfate anion was determined in anolyte by qualitative analysis with silver nitrate. A black precipitate formed, probably $Ag_2O_2$ ($Ag^{I}Ag^{III}O_2$), which could be indirect evidence of the presence of persulfate in anolyte.

Polarization measurements were complicated due to $O_2$ evolution on the anode and the ohmic voltage losses (*iR*). Therefore, the polarization curve for the anodic process (Fig. 4) was obtained with automatic *iR* compensation. According to these data, the anodic process occurred at the potential of ca. 1.5 V, which is more negative than potential of 1.77 V corresponding to persulfate anion direct formation [14]. Therefore it was supposed that direct

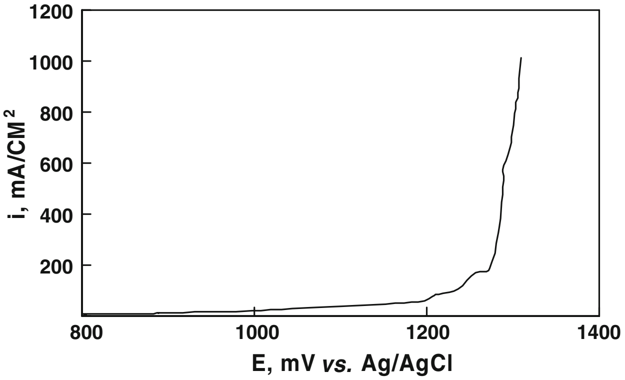

**Fig. 4** The anodic polarization curve. The potential scanning rate was 50 mV/s in 0.14 M $Na_2SO_4$ electrolyte with a flow rate of 5.3 mL/min

anodic oxidation of sulfate into persulfate could not occur. The anodic reaction may likely be described by Eqs. 1 and 2 below:

$$H_2O \rightarrow 2H^+ + [O]^* + 2e^- \quad (1)$$

$$[O]^* + 2SO_4^{2-} + H_2O \rightarrow S_2O_8^{2-} + 2OH^- \quad (2)$$

In this scheme, formation of active oxygen [O]* is the first step of the anodic reaction, with [O]* subsequently oxidizing sulfate ions to persulfate. Such a mechanism has been proposed in an earlier work [13]; however, it has not yet had any reliable experimental confirmation.

The activity of synthesized compounds toward elements of blood, bilirubin, and Medinal was investigated in vitro. Synthesized solutions were added to blood, in ratios of 1 part of solution to 5 part of blood and 1 part of solution to 10 parts of blood. Concentrations of free hemoglobin, bilirubin, and Medinal were measured before and after addition. Similar to earlier data [4], hemolysis did not take place, despite the regime of electrolysis being significantly intensified (maximum current density was 7.0 A/dm$^2$, over against 3.0 A/dm$^2$ in the reference [4]. The concentration of sodium sulfate was 1–5%. Thus, the synthesized solutions containing oxygen, sodium sulfate, and sodium persulfate were indifferent toward erythrocytes for a large range of current densities and initial concentrations of the electrolyte. Detoxifying ability of the synthesized solutions was studied with bilirubin as an example of an endotoxicant and Medinal as an example of an exotoxicant. The level of bilirubin was decreased to 50% wt. in 48 h when the solution was added in a ratio of 1:10. It should be noted that the kinetics of the decrease observed in bilirubin levels was quite physiological, whereas an abrupt decrease in the level of similar metabolites would be dangerous to the organism [14].

Experiments with Medinal were performed with the initial concentration of Medinal in blood ca. 4 mM. Medinal was added to anolyte and the ratio blood/anolyte was 1/10. This ratio corresponds to usual ratio of 500 mL volume of physiological solution for treatment of patient volume/5 L of blood in the organism. It was found that a 20% decrease in concentration occurred in the first hour, and after 24 h a decrease of over 80% occurred, as compared with the initial Medinal concentration. These results agree with the kinetics of detoxification from Medinal by indirect electrooxidation with hypochlorite [2].

The sterility of synthesized solutions was also studied. It was observed that microflora did not grow for 14 days in anolyte with a redox potential of ca. 500 mV. These experiments confirmed that electrochemically synthesized anolytes are sterile.

Finally, as noted earlier, electrochemically synthesized hypochlorite is used in medicine for detoxification of organism as an intravenous medication, whereas commercial hypochlorite is used only as a disinfectant. A probable reason for medical interest towards the makeup of the synthesized product could be the special oxidizing activity of such freshly prepared substances.

In order to check this hypothesis, RP values for solutions of industrially prepared and electrochemically freshly synthesized sodium persulfate were compared. It turned out that the RP for industrial samples was 150–530 mV, depending on concentration (Fig. 5, curves 2–6). At the same time, the redox potential for anolyte containing $1.0 \times 10^{-4}$ M of synthesized sodium persulfate was more positive than that for the industrial sample containing $4.2 \times 10^{-2}$ M persulfate: 672 and 587 mV, respectively (Fig. 5, curves 6, 8).

Since the magnitude and sign of redox potential reflect the redox properties of the tested medium, the experimental data obtained show that freshly prepared electrochemically

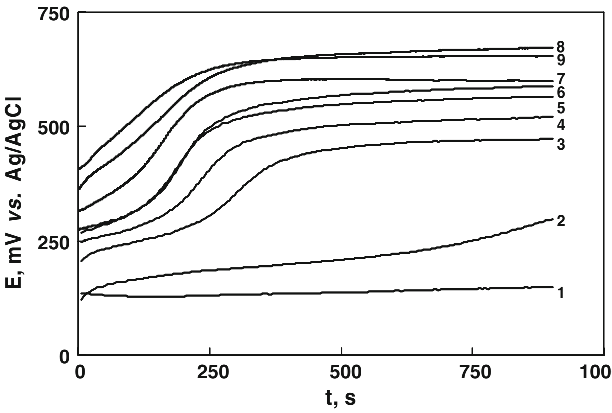

**Fig. 5** Redox potentials versus time for various electrolyte solutions. 1, $Na_2SO_4$; 2–6, commercial samples of $Na_2S_2O_8$ (2, $4.2 \times 10^{-4}$ M; 3, $2.1 \times 10^{-3}$ M; 4, $4.2 \times 10^{-3}$ M; 5, $2.1 \times 10^{-2}$ M; 6, $4.2 \times 10^{-2}$ M); 7, anolyte containing $1.5 \times 10^{-5}$ M $Na_2S_2O_8$; 8, anolyte containing $1.0 \times 10^{-4}$ M $Na_2S_2O_8$; 9, anolyte containing $6.6 \times 10^{-4}$ M $Na_2S_2O_8$

synthesized sodium persulfate has a higher oxidizing activity than the industrial samples of the same oxidant.

## 4 Conclusions

A method of synthesis of dilute solutions of sodium persulfate has been developed for medical applications by anodic oxidation of dilute solutions of sodium sulfate in a diaphragm electrolyzer on titanium anodes covered with mixed oxides of iridium, ruthenium, and tin. An electronic device has been developed and employed to realize the self-purification of the cathode surface from hardness deposits during the operation of the electrolyzer. It was found that sodium persulfate was the only product of electrolysis except for molecular oxygen, which is an inactive oxidant. Oxidizing activity of the synthesized anolyte toward certain metabolites and toxicants was confirmed. The sterility of anolyte was shown experimentally by the lack of germination of any micro flora in the tested anolyte during two weeks. A comparison of redox potentials of industrial samples of persulfate with freshly synthesized anolyte solutions containing persulfate showed a considerable difference in their oxidizing activities.

## References

1. Goldin MM, Volkov AG, Goldfarb YS, Goldin MM (2006) J Electrochem Soc 153:J91
2. Vasilyev YB, Sergienko VI (1987) Russ J Electrochem 22:151
3. Altman N (1995) Oxygen healing therapies. Healing Arts Press, Rochester
4. Okahara K (1963) Food Hyg J 4:15
5. Goldin MM, Volkov AG, Goldfarb YS, Luzhnikov EA (2004) Toxicol In Vitro 18:791
6. Franks CR, Schenker BA, O'Leary KJ, Kolb JM (1975) US Patent No. 3875043
7. Malchesky PS, Fricker CM (2003) US Patent No. 6623695
8. Harris DC (1998) Quantitative chemical analysis. Freeman, New York
9. Henry JB (2006) Clinical diagnosis and management by laboratory methods. Saunders, New York
10. Luzhnikov EA, Goldin MM, Morozov VS (1982) In: Menshikov VV (ed) Rukovodstvo po klinicheskoi laboratornoi diagnostike. Meditsina, Moscow (in Russian)
11. Rukazenkov AD (1983) Laboratornaya diagnostika ostrykh otravleni. Voenizdat, Moscow (in Russian)
12. Tarasevich MR (1984) Electrokhimiya uglerodnykh materialov. Nauka, Moscow (in Russian)
13. Michaund PA, Mahé E, Haenni W, Perret A (2000) Electrochem Solid State Lett 3:77
14. Seryshev GA (1984) Chemistry and technology of hydrogen peroxide. Leningrad, Khimiya (in Russian)
15. Lopukhin YM, Molodenkov MN (1978) Hemosorption. Meditsina, Moscow (in Russian)