Research Article **Open Access**

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Electrochemical synthesis of hydrogen with depolarization of the anodic process

DOI 10.1515/eetech-2016-0003
Received Feb 06, 2016; accepted Apr 22, 2016

Abstract: A new active composite coating for graphite gas diffusion electrode for hybrid sulfur cycle was proposed. The kinetics of oxidation of SO_2 were studied on porous graphite anodes with different catalytic coatings. It was shown that the most efficient composite coating is based on activated carbon and platinum supported on graphite gas diffusion substrate. The voltage drop in the laboratory electrochemical cell was 1.3 V at a current density of 1000 $A{\cdot}m^{-2}$. This corresponds to a specific consumption of 3.1 kWh electric energy per 1 m^3 of hydrogen.

Keywords: Active composite coatings; hydrogen; depolarization

1 Introduction

The world experience defines hydrogen as the most promising energy carrier. Producing hydrogen by electrolysis helps effectively solve the problem of peak loads and failures arising from the different structure of energy consumption during the day [1, 2].

Thermoelectrochemical cycles for hydrogen production are intensively studied in Kharkov Polytechnic Institute, Kharkov, Ukraine. Further development of hydrogen production by electrolysis of water is associated with implementation of hybrid sulfur cycle (“Westinghouse cycle”) [1]. It is a two–step process, first a low-temperature electrochemical step (1):

$$2\,H_2O + SO_2 \xrightarrow{298K,2F} H_2 + H_2SO_4 \qquad (1)$$

and second a high temperature step (2):

$$H_2SO_4 \xrightarrow{900K} H_2O + SO_2 + 0,5\,O_2 \qquad (2)$$

The clear advantage of the hybrid sulfur cycle process is that the standard reversible voltage E_0 of the net cell reaction (2) is only 0.17 V. For comparison, conventional water electrolysis requires $E_0 = 1.23$ V. In laboratory-scale tests, the realized cell voltage of SO_2 depolarization electrolysis has been 0.5. . . 1.3 V, depending on the current density and other operational parameters compared with 1.8. . . 2.0 V of commercial alkaline water electrolysis. Thus, SO_2 depolarization electrolysis would require 25. . . 60% of the electrical energy required for direct water splitting by conventional electrolysis. The electrochemical process is far from technical implementation and intensively studied in recent years.

Hybrid sulfur cycle was intensively studied for practical implementation using platinum, gold and palladium anodes [2, 3]. Further investigation is connected with using more affordable anode materials. According to the E-pH diagram, ruthenium, molybdenum, tungsten and their oxides are the most promising catalyst materials.

2 Materials and methods.

Active porous anodes were obtained by covering the porous graphite basis by active carbon, Pt, MoO_3, RuO_2, WO_3. Coverage with active carbon was prepared by impregnating the graphite basis in sugar solution, followed by drying and thermal decomposition. The other composite coatings were prepared by impregnating with a sugar solution and solutions of $H_2[PtCl_6]$, $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$, $(NH_4)_4W_5O_{17}$, followed by drying and thermal decomposition at 600. . . 650 K. The cylindrical anodes had 20 mm diameter and 5 mm thickness.

They were inserted into a special holder made of titanium-coated PTFE consisting of a current–conducting tube with welded sample holder (Fig. 1). Samples were fixed with a holder nut. Current-voltage measurements were carried out in a plastic cell with anode and cathode separated by s cation exchange membrane. Electrode potentials were measured relative to a mercurous sulfate reference electrode and converted to the standard hydrogen electrode scale.

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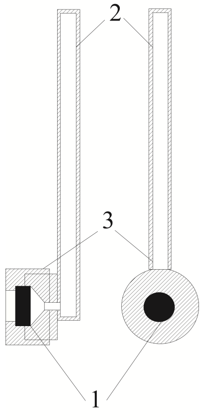

Figure 1: Cross-section and frontal view of the anode holder: 1 – porous cylindric anode; 2 – holder with current and gas lead; 3 – union nut.

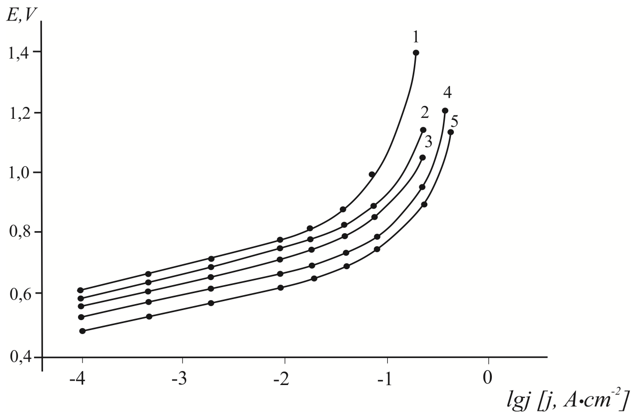

Figure 2: Dependence of the anode performance on material: 1 – activated carbon; 2 – activated carbon + WO_3; 3 – activated carbon + MoO_3; 4 – activated carbon + RuO_2; 5 – activated carbon + Pt.

Investigation of catalytic activity was carried galvanostatically. Sulfur(IV)dioxide was brought through the lead up to the back of the samples with a pressure of 20 kPa. The anode current density was calculated based on the exposed front side of the geometric surface of graphite anode.

3 Results and discussion

Polarization curves were obtained in sulfuric acid solution with concentration 1 mol·dm^3 at 293 K. It was found that all catalysts catalyze the SO_2 oxidation. The catalytic activity can be arranged in the following sequence: Pt > RuO_2 > MoO_3 > WO_3 > activated carbon (Fig. 2).

Activation of the graphite anodes with platinum increases the rate of SO_2 oxidation at the anode in 0.6 to 4 times, with and oxides of ruthenium, molybdenum and tungsten – in 3.3...3.5 times. Polarization curves obtained with the activated samples show Tafel behavior up to a current density of 1500 A·m^{-2}. The coefficient *b* of Tafel equation in this region is 65...70 mV.

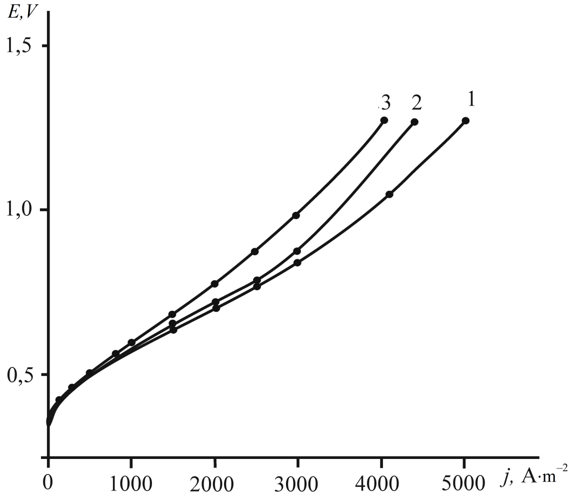

Figure 3: The influence of amount of platinum in active anode coating (mg•cm^{-2}): 1–1,8...2,0; 2–3,0...3,2; 3–5,6...5,9.

Accounting for the resistive components the reduced polarization dependence in the entire range of current densities (up to 4300 A·m^{-2}) shows that the electrochemical stage is the rate-limiting. Confirmation of the nature of the resistive component of the anode potential is the linear dependence of the current – voltage drop measured between the anode and the reference electrode. The ohmic resistance increases in the series – Pt, RuO_2, MoO_3, WO_3, in accordance with the data of the electrical conductivity of these materials.

The influence of catalyst addition in the activated anodes is presented for a graphite electrode coated with active carbon and platinum (Fig. 3). Anode potential decreases with the increase of added amount at all current densities (50...1600 A·m^{-2} for active coal and 100...6000 A·m^{-2} for platinum). Optimum amounts of catalytic additives were defined experimentally and have been established corresponding to the maximum value of the catalytic activity (mg·cm^{-2}) activated carbon: 35...39; WO_3 – 3,8...4,0; Pt – 2,0...2,1; MoO_3 – 13...15; RuO_2 – 3,0...3,2.

Laboratory experiments have shown that the most promising alternative for expensive platinum coating is the composition of RuO_2 with active carbon. Combinations of MoO_3 and WO_3 with active carbon are inferior in catalytic activity, but their advantage is the possibility of regenerating these oxides in the coating of the active compounds by introducing soluble Mo and W componds in the anolyte.

The obtained results indicate the significant influence of sulfuric acid concentration on the activity of the anodes. Anode potential increases with increasing H_2SO_4 concentration. Simultaneously, the limiting current density of the anode activated with platinum decreases from 4000 A·m^{-2} in the 1 M sulfate electrolyte to 1000 A·m^{-2} in 10 M electrolyte. These results can be explained by assuming an increase of adsorption of HSO_4^-ions on the surface of the anodes.

The range of H_2SO_4 concentrations of 1.0. . . 2.5 M corresponds to the Tafel coefficient *b* in the range 65. . . 75 mV, and for 5,0. . . 10 M the coefficient *b* was 120 mV. This allows suggesting a change of the mechanism of the anodic process as a result of changes of the adsorbed species on the anode. In the range of concentration from 5.0 M to 10.0 M H_2SO_4 are these species at the anode.

The obtained results allow us to offer the following guidelines for choosing the H_2SO_4 concentration in the anolyte using SO_2 to depolarize the anode process. When conducting electrolysis to produce hydrogen, anolyte should be used at a concentration of sulfuric acid 1.0. . . 2.5 mol·dm^{-3}. Increasing the concentration of sulfuric acid in the anolyte results in a substantial increase of the voltage and specific energy consumption. This mode is not appropriate for the production of hydrogen with SO_2 depolarization. However, when the aim of electrolysis is utilization of SO_2, it is possible to increase the H_2SO_4 concentration in anolyte to 10 M.

Extended laboratory tests were hold in a laboratory setting (Fig. 4) which consists of one bipolar electrolytic cell, the collector 2 for bringing SO_2 to the anode surface, and anode spray separator 3 and 4 for the anode and cathode cells, electrolyte level controller 5. The cell is composed of three cells of the membrane type. Electrode 7 is bipolar, 8 – monopolar anode, 9 – monopolar cathode. The anode and cathode cells are separated by the membrane MF–4SK 13. The reference electrodes 14 are mercurous sulphate ones.

Anode included active carbon and catalytic coatings as a disc with diameter of 170 mm and a thickness of 15 mm. Cathode was made from steel 904 L. In a bipolar electrode, an anode and a cathode were attached to the main sheet with special anchors.

The anode and cathode cells were filled with electrolyte based on sulphuric acid. SO_2 was brought to the back side of the anode. Quantity of delivered SO_2 was determined so as to provide a gas diffusion mode across the surface of graphite anode.

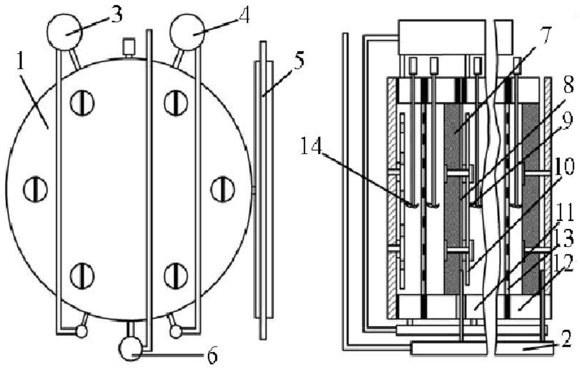

Figure 4: Laboratory electrolyser scheme: 1 – the bipolar electrolyser, 2, 6 – collector for SO_2 feed, 3 – separator of SO_2-spray, 4 – separator of H_2-spray, 5 – controller of electrolyte level, 7 – gas-diffusion anode of bipolar electrode, 8 – cap of gas-diffusion anode, 9 – perforated cathode, 10 – monopolar gas-diffusion anode, 11 –cathode shell, 12 – anode shell, 13 – membrane , 14 – reference electrodes.

The electrolysis unit is operated at a current density of 1250 A·m^{-2}, in which the ohmic component of the anode potential does not exceed 50 mV. Parameters of electrolysis using activated carbon anode composition of active carbon and platinum are shown in Table 1. The amount of generated hydrogen was determined with a gas meter. Average output of hydrogen was 99.0 0.2% of the expected amount. The loss of 1% is related to leakage currents through the lead collectors.

Test results of the laboratory facility with gas diffusion anodes have confirmed the possibility of technical implementation of the hybrid sulfur cycle with activated carbon anodes. Difficulties in the laboratory setting were associated with the establishment of the hydrodynamic regime of the gas diffusion electrode, which provides a uniform part in the work of the entire front surface of the activated graphite.

Alternatively, for the gas diffusion electrode a mode of operation can be considered with the possibility to feed SO_2 at the bottom of the anode chamber from the front side of the graphite anode. Such mode of operation will significantly facilitate hydrodynamical stable cell behavior, however, will led to an increase in electrolysis voltage approximately by 8. . . 9% at a current density of 500 A·m^{-2} and 12. . . 14% at a current density of 1000 A·m^{-2} by increasing the voltage drop in the anolyte and the anode potential.

The utilization of SO_2 was approximately 50 and 75%, respectively, for the supply of gas through the pores of the graphite and the anolyte.

Table 1: Parameters of electrolysis using graphite anodes activated charcoal and platinum.

No	**Parameter**	**Current density, A·m^{-2}**	
		500	**1000**
1	Current, A	7,5	15
2	Consumption of SO_2, cm^3 · h^{-1}	3150	6300
3	Pressure of SO_2, kPa	5,0	5,0
4	Concentration of H_2SO_4 in catholyte, g·dm^{-3}	490	490
5	Concentration of H_2SO_4 in the beginning of anodic process, g·dm^{-3}	20	20
6	Concentration of H_2SO_4 in the end of anodic process, g·dm^{-3}	300...450	300...450
7	Flow of anolyte, cm^{-3} · h^{-1}	17...21	35...42
8	Average voltage, V	1,09	1,30
9	Cathode potential, V	-0,25	-0,30
10	Anode potential, V	0,52	0,61
11	Voltage drop:		
	– across electrolyte	0,12	0,14
	– across diaphragm	0,10	0,12
	– across contacts and electrodes	0,03	0,03
12	Consumption of electric energy, kWh	2,63	3,14

Table 2: Influence of the anode materials to anode potential.

Consistence of active material	**Amount, mg·cm^{-2}**	**Anode potential (V) and current density (A·m^{-2})**	
		500	**1000**
Pt	2.0	0.5	0.610
RuO_2	3.0	0.618	0.743
MoO_3	13.0	0.641	0.786
WO_3	3.8	0.679	0.837

Replacing the combination of platinum and activated carbon with a metal oxide activated carbon resulted in an increase in the anode potential and did not affect the other components of the overall voltage drop. Results of influence of the anode material on anode potential are shown in Table 2. Duration test were held for 600 hours. Throughout the time of testing the value of the anodic potential for all studied catalytically active materials shall not deviate by more than 5% from the nominal values given in Table 2.

These results demonstrate the high efficiency of activated carbon anodes with coatings of platinum or metal oxides and allow for economic calculation to justify the selection of the catalytically active material of the anode.

4 Conclusions

A composite coating of activated carbon and platinum supported on a graphite–based gas diffusion electrode is the most effective of the tested coatings in electrochemical oxidation of SO_2 in hybrid sulfur cycle. The quantities of substances deposited on the surface of the porous electrode corresponding to the maximum value of the catalytic activity (mg·cm^{--2}) active carbon are – 35...39; WO_3 – 3.8...4.0; Pt – 2,0...2.1; MoO_3 – 13...15; RuO_2 – 3,0 ... 3,2.

Laboratory tests have confirmed the efficiency of Hybrid Sulfur cycle compared to aqueous alkaline electrolysis. For hydrogen-producing electrolysis the anolyte should be 1.0...2.5 M of H_2SO_4. In 1.0 M H_2SO_4, at a current density of 1000 A·m^{-2} and 303 K a cell voltage of the cell laboratory was 1.30 V, which corresponds to the specific consumption of electric energy 3.1 kWh per 1 m^3 hydrogen.

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