

Electrolytic cell for hydrogen and sulfuric acid production

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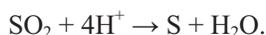
The anodic depolarization of sulfur dioxide reduces the thermodynamic potential of water splitting from 1.23 V to 0.29 V at 50 % H₂SO₄ wt. and temperature of 25°C. This process leads to hydrogen and sulfuric acid production. The major problem of the electrolytic cell is the permeation of SO₂ into the cathode compartment where the 'parasitic' reaction of SO₂ + 4H⁺ → S + H₂O takes place, thus decreasing the hydrogen efficiency and poisoning the cathode catalyst. The original idea, supporting this study, is to use gas diffusion electrodes (GDEs) as anodes, designed to electrochemically oxidize SO₂. Carbon GDEs have been developed and modified with cobalt phthalocyanine (CoPc). The GDEs serve as a membrane attenuating SO₂ permeation. An electrolytic cell with GDE has been designed and tested with: (i) different types of GDE; (ii) with and without membranes; and (iii) utilizing J/J₂ as a mediator. It has been found that when operating with gas mixtures which contain up to 20% vol. SO₂, the main issue, namely its permeation into the electrolyte, can be solved. This beneficial approach can be used to treat waste gases with low SO₂ concentration which would have a favorable impact on the environment.

Keywords: hydrogen, sulfuric acid, electrolytic cell.

INTRODUCTION

The water electrolysis is a pollution free technique for hydrogen production substituting the hydrocarbon use. In the conventional electrolyzers, the high operational voltage, caused by the kinetic hindrances of oxygen evolution, increases the production costs of the electrolyzed hydrogen multifold in comparison with the hydrogen, produced by the liquid fuel treatment. The anodic depolarization of sulfur dioxide reduces the water splitting thermodynamic potential from 1.23 V down to 0.29 V at 50 % H₂SO₄ wt. and a temperature of 25°C [2]. This process results in both, hydrogen and sulfuric acid production.

The process has deserved the research efforts of many countries, and up to date number electrolyzer designs of this type have been developed [2–8]. Their construction employs immersed electrodes where the SO₂ enters the anodic space jointly with the electrolyte. However, this immediately creates one of the major problems, inherent to this type of electrolyzers, namely the permeation of SO₂ through the cation exchange membrane separating the anodic and the cathodic spaces and the SO₂ cathodic reduction according to the reaction:



Another disadvantage, even for the well working electrolyzers ($E = 0,7 \text{ V}$ at $i = 200 \text{ mA}\cdot\text{cm}^{-2}$), is that the electrodes are platinum catalyzed, which makes them quite sensitive to catalytic poisoning, particularly to the sulfur dioxide content (SO₂), due to its penetration into the cathodic space. All efforts to solve these problems are directed to the electrolyzer design. An example of such design is to using two cation exchange membranes with an individual electrolyte circulation loop between the cathodic and the anodic space. [1]. In such cases, however, the problem with the intermediate electrolyte clean-up of the surfaces arises [9].

Our original idea is to use gas diffusion electrodes for electrolyzing cells which will operate with waste gases, produced by many industrial sources (thermoelectric power plants, enriching factories in the mining industry, etc.). Thus, the sulfur-acid electrolyzing method would be employed in its full capacity for the hydrogen production and SO₂ purification, and which is very important this would be beneficial economically and environmentally.

THE CELL DESIGN

An novel electrolyzing cell was designed based on already developed immersed electrodes for sulfur dioxide oxidation, catalyzed with tungsten carbide.

Figure 1 illustrates the cell outline. The cell is designated to produce hydrogen from sulfur-acidic

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solutions with SO₂ as anodic depolarizer. Other electrolyzing cell modifications have also been constructed with anodes, targeting at 95 – 100% SO₂ utilization. The cell allows for utilization of ion-exchange membranes which serve to separate the anolyte from the catholyte and enables the addition of KJ or HJ in the anolyte, aiming to support the homogeneous catalytic reaction between the SO₂ and the J⁻.

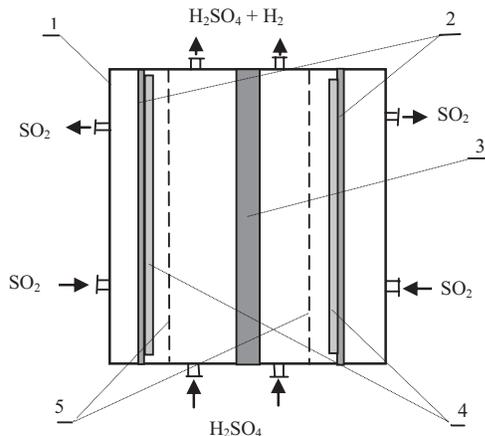


Fig.1. 1 - Cell housing, 2 - Gas diffusion anodes catalyzed with active carbon; 3 - Tungsten carbide cathode; 4 - Graphitized waddings soaked in potassium iodide; 5 - Cation exchange membranes.

This particular design has its fundamental advantages: 1) The GDEs serve as membranes, hence the SO₂ concentration in the electrolyte is considerably lower than the SO₂ concentrations when immersed types of anodes are employed. The membranes protect the cathodic space against sulfur dioxide penetration; 2) The activity of the cathode, manufactured with non-noble catalyst, is not influenced by the low SO₂ concentrations that may possibly penetrate into the cathodic space. The components of this electrolyzing cell are made of circularly shaped plexiglass. They are assembled as a filter-press-type stack. This facilitates the assembly of diverse modifications of the electrolyzing cell featuring various electrode positions, i.e. the distances between anode and cathode, as well as including cation-exchange membranes.

EXPERIMENTAL CONDITIONS

The experiments employed a three-electrode cell with double layered working GD-electrodes [3], a tungsten carbide catalyst, and a (Hg/HgO) in 4.5 N H₂SO₄ reference electrode. The controlling electronic potentiostat was of the Radelkis type. All measurements were taken at the range from 20 to

70°C. The active electrode surfaces varied between 10 cm² and 200 cm². The electrolyte circulation was sustained by a peristaltic pump throughout the experiment. The studies, related to the experimental set-up operation with Air-SO₂ gas mixtures, were controlled by Brooks 5850 gas-mixing equipment which was used to mix precisely and maintain the desired proportion of the gas mixture components.

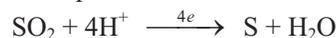
EXPERIMENTAL RESULTS

The volt-amp characteristics have been taken at different temperatures and long term studies were also conducted. Throughout the measurements the SO₂ quantity, penetrated into the electrolyte, was controlled by iodometric analysis, and the produced hydrogen quantity was determined by volume exercising proper adjustments for the SO₂

The oxidation efficiency for the SO₂ quantity, oxidized onto the GDE to the total SO₂ quantity within the anodic space, was calculated by the following basic equation:

$$X = (1 - C_{\text{out}} / C_{\text{in}}) \times 100 \%, \quad (1)$$

where C_{out} is the SO₂ concentration at the outlet of the gas chamber, and C_{in} at the inlet. The optimal electrolyte flow rate was selected in a way to prevent the penetration of sulfur dioxide from the anodic compartment into the cathodic space, and its reduction to sulfur. Figure 2 depicts the level of reduction of the SO₂ concentration. SO₂ penetrates into the catholyte and increases the hydrogen output as a function of the electrolyte flow rate. Figure 2 illustrates also the fact that at the selected flow rate of 5 – 6 L/h the "parasitic" reaction of



does not take place practically. Taking this into consideration, all measurements were conducted at this electrolyte flow rate.

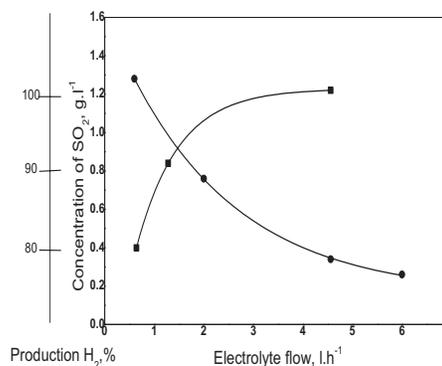


Fig.2. Influence of electrolyte flow rate on the yield of hydrogen (■) and oxidation of SO₂ (●). $S_{\text{cl-d}} = 10 \text{ cm}^2$; 20 % H₂SO₄, $t = 20 \text{ }^\circ\text{C}$.

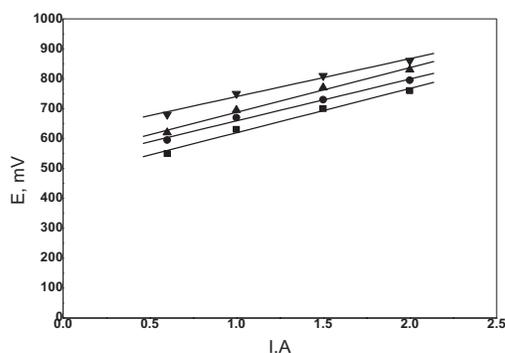


Fig. 3. Volt-ampere characteristics of electrolytic cell taken at different temperatures. For producing of Hydrogen from sulfuric-acid solution as anodic depolarized with sulfur dioxide. $S_{el-d} = 10 \text{ cm}^2$; 20 % H_2SO_4 ; $d_{el-d} = 6 \text{ l/h}$; (∇) - 20 °C; (\blacktriangle) - 40 °C; (\blacklozenge) - 60 °C; (\blacksquare) - 70 °C.

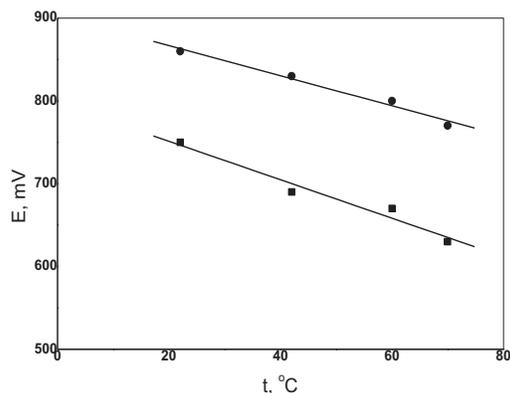


Fig. 3a Temperature dependence for the same cell; (\blacksquare) - $I = 1 \text{ A}$; (\bullet) - $I = 2 \text{ A}$.

Figure 3 shows the electrolyzer cell volt-amp characteristics, taken at different temperatures. Shown in the subsequent Figure 3a, a single temperature rise of 10°C results to some 20 mV of voltage reduction. It was calculated, based on the individual electrode volt-amp characteristics, that the ohmic losses are 30 mV at $I=1\text{A}$ and close to 60 mV at $I = 2\text{A}$, respectively.

The long term studies have demonstrated that at the designed cell is functionally stable for 100 hours. The voltage necessary to support the operation of such type of electrolyzing cell is with some 0.5 Volts lower compared to the conventional water electrolyzers, even for the most unfavorable working conditions at 20°C [9]. The sulfur dioxide penetration through the GDEs, resulting in its reduction to sulfur on the cathode and in collector corrosion in sustainable operational mode, could be considered as disadvantage of this system,

particularly for electrolyzing cells with electrode surface area of $S_{el} = 200 \text{ cm}^2$. In this case, the sulfur dioxide practical utilization does not surpass 40%.

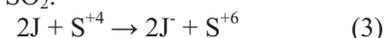
The experimental results have confirmed that semi-permeable cation-exchange membranes utilization does not lead to radical solution of the problem, in spite of some SO_2 reduction within the cathodic space (1.24 g/L in the anolyte and 0.280 g/L in the catholyte), but is still sufficient to back up the SO_2 reduction to sulfur at a perceptible rate.

In order to solve the issue for the proposed electrolyzing cell design, improved gas diffusion electrodes were developed to attain practically a 75% sulfur dioxide utilization [3]. This aim was achieved by means of variation of the active layer composition. These GDEs of enhanced sulfur dioxide utilization facilitate the cathodic space protection against SO_2 penetration. Unfortunately the 75% utilization, achieved up to date, is not sufficient enough to solve the problem of SO_2 permeation into the cathodic space.

Another approach was looked after, namely employing the addition of a redox couple iodine-iodine ion to the anolyte. It is well known [10] that in this cases the following anodic reaction takes place:



while the produced iodine oxidizes the penetrated into the solution SO_2 :



which is a homogeneous catalytic reaction.

It is easily observed that the J_2/J^+ couple serves as a mediator for the SO_2 oxidation. These reactions lower the anodic reaction potential, acquiring the electrochemical potential of the redox couple.

To back-up the above reactions a new family of GDEs were developed as well as a novel cell design, where graphitized wadding, impregnated with potassium iodide, were inserted behind the anode. The iodide amount was experimentally optimized, taking into account the penetration of non-reacted sulfur dioxide through the GDE. The final optimal value is $C_{KI} = 1.2 \cdot 10^{-1} \text{ moles/L}$. Behind the anode, a cation exchange membrane has been positioned to separate the anodic and the cathodic spaces. Figure 4 is an illustration of the relationship, describing the sulfur dioxide utilization as a function of the current density. It is observed that at a current density of $I > 70 \text{ mA/cm}^2$, the SO_2 utilization reaches the desired 100%. A cell of such design with electrode surface area of 10 cm^2 was operational for 40 hours ($I = 100 \text{ mA/cm}^2$)

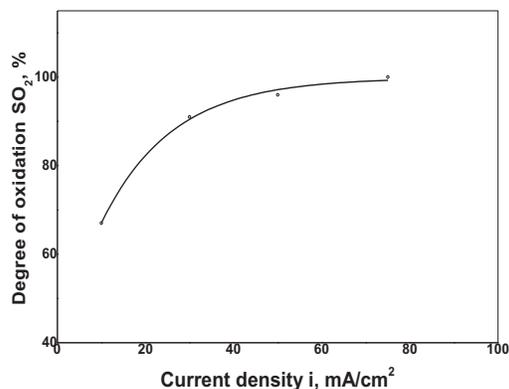


Fig. 4. Relationship between degree of oxidation of sulfur dioxide and current density. $C_{KJ} = 1.2 \cdot 10^{-1} M \cdot l^{-1}$; $S_{el-d} = 10 \text{ cm}^2$; $t = 25^\circ C$; $4.5 \text{ N H}_2\text{SO}_4$.

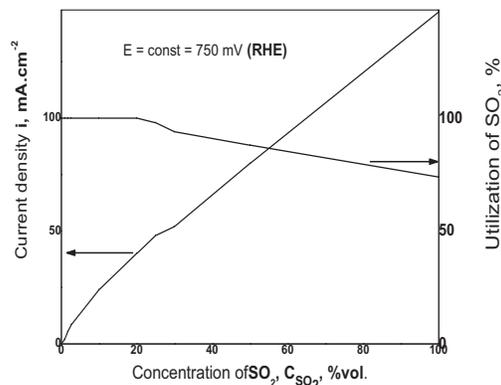


Fig. 6 Relationship between current density and degree of oxidation on the SO_2 concentration in the gas mixture (air + SO_2) at constant potential; $E = 750 \text{ mV vs RHE}$; $t = 25^\circ C$; $4.5 \text{ N H}_2\text{SO}_4$; catalyst: Norit – NK/CoPc.

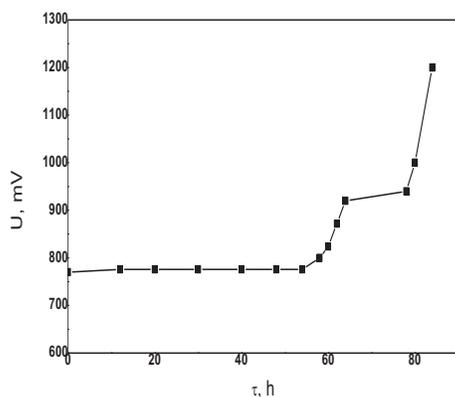


Fig. 5. Long- term test of electrolytic cell operating with homogenous catalyst potassium iodide. $20\% \text{ H}_2\text{SO}_4$; $20^\circ C$; $C_{KJ \text{ anolit}} = 2.5 \cdot 10^{-2} M$; $S_{el-d} = 10 \text{ cm}^2$ usability $\text{SO}_2 = 95 - 100\%$; $i_a = 100 \text{ mA/cm}^2$.

without any registered presence of SO_2 in the catholyte, circulating with a flow rate of some 0.3 L/h . The cell voltage throughout this study varied from 750 to 810 mV , as seen on Figure 5. Unfortunately, other problems occur either related to the iodide separation from the produced sulfur dioxide or to the metallic iodine blockage of the gas diffusion anodes.

We searched an innovative solution to solve finally the problems, associated with the sulfur dioxide electrolysis, based on utilizing gas mixtures of sulfur dioxide and air. As mentioned above our original idea was to feed the GDE anode, employed as electrolyzer, with waste gases, containing SO_2 . The waste gases utilization implies reduced SO_2 partial pressure in the gas and the resultant decline. Figure 6 shows the correlation, describing the current density and the SO_2 oxidation level on the

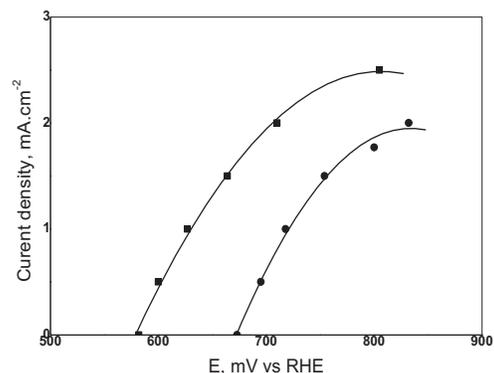


Fig. 7. Polarization curves of gas diffusion electrodes operating with $\text{SO}_2 + \text{air}$ mixture; $t = 25^\circ C$; $4.5 \text{ N H}_2\text{SO}_4$; (●) Norit + CoPc, $0.24\% \text{ vol. SO}_2$; (■) Norit NK, $1\% \text{ vol. SO}_2$.

SO_2 concentration in the gas mixture at constant potential of $E = 750 \text{ mV (RHE)}$, at which as shown in Figure 4, the electrodes maintain their stability. It is again easily observed that the electrodes attain current densities of $I = 50 \text{ mA} \cdot \text{cm}^{-2}$ at SO_2 concentration of $C_{\text{SO}_2} = 25\% \text{ vol.}$ and $I = 80 \text{ mA} \cdot \text{cm}^{-2}$ at $C_{\text{SO}_2} = 50\% \text{ vol.}$ The other correlation shown in Figure 6 and displays the $100\% \text{ SO}_2$ oxidation level at $C_{\text{SO}_2} = 20\% \text{ vol.}$ This result is extremely important since it provides for solving the major problem for sulfur-acidic electrolysis, namely the SO_2 permeation into the cathodic space. The plot shows also that this is accompanied by reduction of the operational current density, too.

As mentioned above, the capability of the GDEs to operate at low partial SO_2 pressures is of practical significance from the environmental point of view. Since the SO_2 concentration in the waste gases of many chemical processes is below 1% by

volume, comprehensive measurements were carried out at these low concentrations. Figure 7 presents the polarization curves for the SO₂ oxidation at C_{SO₂} = 0.24 vol. % on the catalyst with Norit + CoPc and with Norit only. The current densities at 750 mV vs. RHE are from 1.5 to 2.0 mA.cm⁻² for both catalysts. The Norit + CoPc exhibits high catalytic activity and the above cited current density had been attained at a fourfold lower SO₂ concentration than in the case of pure Norit catalyst. These polarization curves demonstrate the GDE capability to operate at low SO₂ concentrations, whereby the penetration of SO₂ into the electrolyte is avoided, cf. Figure 6.

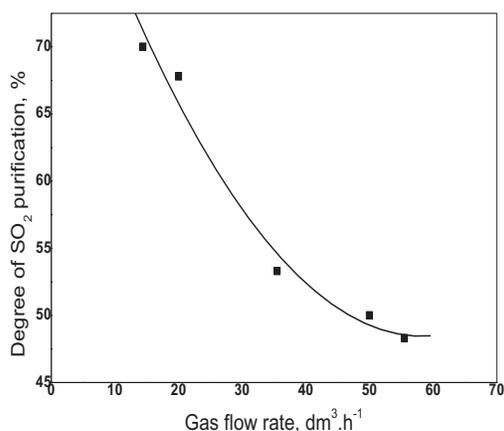


Fig. 8. Relationship between degree of SO₂ purification on the low rate of the gas mixture at constant potential: E = 750 mV vs. RHE; t = 25 °C; 4.5 N H₂SO₄; GDE: S = 200 cm²; 1 vol % SO₂ in air; i ≈ 2 mA.cm⁻².

In this manner specific amounts of waste gases (at selected low gas flow rates in the gas chamber) can be purified. Figure 8 illustrates the correlation between the level of SO₂ removal by a GDE of 200 cm² surface area and the flow rate of the gas mixture (SO₂ + air), supplied to the electrode. The electrode potential was maintained at constant 750 mV vs. RHE. The attained current density of about 2 mA.cm⁻² varied insignificantly with the gas mixture flow rate. It is evident that under these conditions the electrode removes some 50 to 70 % of the SO₂ from the waste gas which initially contained a concentration of C_{SO₂}=1.0 % vol. This

implies a considerable environmental effect, even with the less active Norit –NK catalyst.

CONCLUSION

The major problem, inherent to the sulfur-acidic method for hydrogen production, namely SO₂ permeation into the cathodic space, was successfully resolved.

An innovative electrolyzing cell design was proposed. This design involves an advantageous GDE exploitation, providing for utilization of the SO₂ containing waste gases. The feasibility of the GDEs' operation at low SO₂ partial pressures was demonstrated.

This inventive technique provides for both, hydrogen production and harmful sulfur dioxide pollutant purification.

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ЕЛЕКТРОЛИЗНА КЛЕТКА ЗА ПОЛУЧАВАНЕ НА ВОДОРОД И СЯРНА КИСЕЛИНА

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(Резюме)

Анодната деполяризация на серния диоксид понижава термодинамичния потенциал за разлагането на водата от 1.23 V до 0.29 V в сярно-кисела среда от 50 % (тегл.) H₂SO₄ при 25°C. Този процес води до получаването на водород и сярна киселина. Основният проблем на електролизната клетка в този случай е проникването на SO₂ в катодното пространство, където протича “паразитната” реакция $\text{SO}_2 + 4\text{H}^+ \rightarrow \text{S} + \text{H}_2\text{O}$, като при това се понижава ефективността по водород и се отравя катодния катализатор. Оригиналната идея, породила това изследване е в използването на газови дифузионни електроди (GDEs) като аноди, предназначени за окислението на SO₂. Разработени са въглеродни GDE-електроди, като са модифицирани с кобалтовфталоцианин (CoPc). Газово-дифузионният електрод служи като мембрана, забавяща проникването на SO₂. Разработена е електролизна клетка и е изпитана при: (а) различни типове GDE; (б) с и без мембрани и (в) използващи редокс-системата J/J₂ като медиатор. Намерено е, че при работа с газова смес, съдържаща до 20% (об.) SO₂, се решава основния въпрос, т.е. проникването на серния диоксид в електролита. Този подход може да се използва за третирането на отпадъчни газове с благоприятен ефект върху околната среда.