



Cathode depassivation using ultrasound for the production of colloidal sulphur by reduction of sulphur dioxide



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ABSTRACT

The effect of ultrasound is analysed in order to avoid the passivation of the cathode as a result of blocking the electrode surface area by the sulphur produced from sulphur dioxide reduction. The experiments were carried out with a rotating cylinder electrode using either a single phase electrolyte which contained 5 g dm^{-3} sulphur dioxide, or in a biphasic system processing a gas phase with 5% of sulphur dioxide in nitrogen. In both cases the supporting electrolyte was a $0.5 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$ solution. It was found that the application of ultrasound is very effective to detach the sulphur from the cathode surface and also to improve the reactor performance in comparison with a silent system. The best working conditions were achieved at cathodic potentials in the range of -0.6 to -0.7 V. vs. SCE . Representative values for the figures of merit of the process are as follows: the space time yield was $1.4 \text{ kg m}^{-3} \text{ h}^{-1}$ and $0.7 \text{ kg m}^{-3} \text{ h}^{-1}$ for the biphasic and single phase systems, respectively. The current efficiency was 70%, 23 kWh kg^{-1} the specific energy consumption and 91% the molar yield towards the sulphur production in the biphasic system at -0.7 V . The volumetric mass-transfer coefficient was calculated from experimental data and compared with the theoretical prediction for a rotating cylinder electrode under silent condition, corroborating the beneficial effect of ultrasound for the production of colloidal sulphur. The particles have high purity and a spheroidal shape with an average diameter of $1.84 \mu\text{m}$, similar to those obtained without the application of ultrasound.

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1. Introduction

The electrochemical reduction of sulphur dioxide was analysed by Oloman [1] and Oloman and co-workers [2] for the electro-synthesis of dithionite. Stimulated by the increasing importance of sulphur dioxide pollution control, Scott et al. [3,4] reported on its reduction to elemental sulphur. Streeter et al. [5] carried out fundamental studies related to the cathodic reduction of aqueous solutions of sulphite under acidic conditions on copper electrodes. Moreover, Uzun et al. [6] recently studied the production of sulphur by the reduction of sulphur dioxide using hydrogen sulphide as a reducing agent.

Elemental sulphur powder has wide applications in various fields like pharmaceuticals, polymers, agrochemicals and explosive formulations. A large number of alternative technologies have emerged and developed for the production of colloidal sulphur [7], among them the reduction of sulphur dioxide can be recognised.

This proposal allows for the removal of a dangerous gaseous contaminant and, at the same time its transformation into a commercial product [8]. However, an important issue is represented by the cathode passivation due to the layer of sulphur deposited on the electrode surface. To overcome this problem, hydrogen evolution can be used as a cathodic secondary reaction to detach the sulphur. A second strategy was the employment of a higher temperature [9].

The use of power ultrasound is the basis for many engineering applications, and has received much attention in electrochemistry studies [10,11]. In this case, the beneficial effect of ultrasonication is attributed to the fact that it results in a strong microjet of liquid and a violent shock wave towards the solid surface when cavitation bubbles undergo asymmetrical implosion near a solid surface. Consequently, the solid–liquid mass-transfer between the electrodes and the solution is strongly enhanced and the electrode fouling is decreased. The reduction of sulphur dioxide to yield colloidal sulphur is a heterogeneous reaction generating a solid product which covers the electrode surface area. Therefore, the study of ultrasonic effect on this process comes to be a challenging task.

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The rotating cylinder electrode shows widespread acceptance in a number of interdisciplinary fields and its versatility has been fully demonstrated [12,13]. This reactor shows good mass-transfer characteristics which achieves turbulent flow conditions at low rotation rates, being the current and potential distributions substantially uniform and being it also possible to operate the system with a superimposed axial flow, which does not usually modify mass-transfer behaviour.

The purpose of this paper is to analyse an affordable reactor, based on a rotating cylinder electrode, by coupling electrochemistry with ultrasound in order to produce colloidal sulphur without passivation of the cathode.

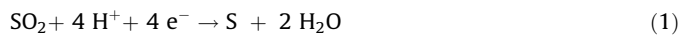
2. Experimental

The experiments were performed in an undivided batch reactor, made of acrylic material, with a 102 mm internal diameter and 138 mm total height using a rotating cylinder as a working electrode. The complete experimental arrangement is schematically depicted in Fig. 1. The working electrode was a 316L stainless steel cylinder, with a 22 mm diameter and 38 mm long, and with a surface area of 26.26 cm². The cylinder was bounded with Teflon sleeves, being them 30 mm in diameter in the lower part and 37.5 mm in diameter in the upper part. The sleeves protrude from the cathode and form a right angle with it; thus, preventing a sharp increase in the current near the edges, which homogenises the current distribution along the electrode length. Likewise, additional experiments were performed using a Teflon sleeve of a smaller diameter in the lower part of the rotating cylinder, without having observed changes in the results under sonication. The surface of the stainless steel cathode was polished with emery paper 2500 and copiously washed with distilled water. Three platinum wires, 1.0 mm diameter and 100 mm long, were used as anode and were symmetrically placed around the working electrode. The interelectrode gap was 24 mm. A saturated calomel electrode connected to a Luggin capillary, located in the mid-region at the surface of the working electrode, was used as reference. Special attention was paid to the location of the Luggin tip, which was placed at about 0.2 mm from the electrode surface to ensure an ohmic drop in solution below 5 mV. The upper end of the cylindrical rotating electrode was attached to the motor shaft. Temperature was regulated by a glass cooling coil placed inside the electrochemical cell and linked to a thermostat operating at a preset temperature, 30 °C. The reactor bottom was a planar stainless steel disc to which the source of ultrasound was firmly attached using a threaded screw and fastened with plumbing paste, in the middle of its external face to obtain a symmetric distribution of the ultrasonic field inside the reactor. The top of the acoustic horn was vertically positioned at 10 mm from the bottom of the rotating cylinder cathode. In some experiments the surface area of the disc, in contact with the electrolyte, was lacquered with epoxy resin, but no change was observed in the results. The electric power output of the ultrasonic generator was 50 W at 40 kHz while the power dissipated in the medium was about 20.9 W, as measured by calorimetry. The diameter of the acoustic horn was 45 mm, 15.9 cm² area, providing an ultrasonic intensity of 1.3 W cm⁻².

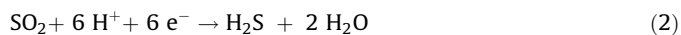
Two types of electrolyte were employed. In the single-phase experiments, a solution of 5 g dm⁻³ SO₂ was used in 0.5 mol dm⁻³ H₂SO₄ as supporting electrolyte, which was prepared by dissolving sodium sulphite into an aqueous solution of sulphuric acid to obtain the above concentrations. In the biphasic experiments, gas/liquid, a mix of 5% SO₂ and 95% N₂ was bubbled at 0.1 MPa into a 0.5 mol dm⁻³ H₂SO₄ solution via a gas distributor placed at the lower end of the rotating electrode. The gas volumetric flow rate was 1.41 × 10⁻⁵ m³ s⁻¹ under ambient conditions, and it was also bubbled through the solution for 30 min before the experiment. The concentration of sulphur dioxide in the solution under the

working conditions was 2.7 g dm⁻³, determined by iodometric analysis. Thus, sulphur dioxide is reacted with an excess of iodine in acid solution, and the remaining iodine is then determined by titration with sodium thiosulphate, using starch as an indicator [14].

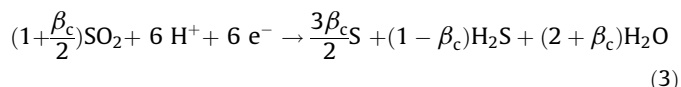
The reduction of sulphur dioxide to sulphur and hydrogen sulphide is expected to occur at the cathode, according to:



and



Combining Eqs. (1) and (2) results in



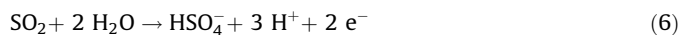
where β_c is the current efficiency for the sulphur production. Eq. (3) is valid for potentials higher than -0.5 V, against SCE, where only the sulphur dioxide reduction takes place without any secondary reactions. At potentials more negative than -0.5 V, it is also likely to get hydrogen evolution as a side cathodic reaction [8]



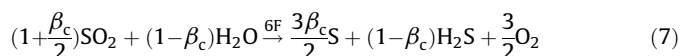
diminishing the current efficiency for the production of colloidal sulphur. However, hydrogen evolution also evinces some beneficial aspects due to the fact that it increases the mass-transfer of sulphur dioxide to the cathode and contributes to the removal of the layer of sulphur. Likewise, oxygen evolution occurs at the anode



Also, the oxidation of sulphur dioxide to sulphuric acid can take place at the anode, in accordance with



However, the presence of colloidal sulphur inhibits the oxidation of sulphur dioxide [8]. Thus, oxygen evolution can be expected as the main anodic reaction. Adding Eqs. (3) and (5) yields



which represents the overall reaction for the electrochemical reactor, being F the Faraday constant. Eq. (7) also shows that the supporting electrolyte remains unchanged during the process.

The experiments were performed potentiostatically with a solution volume of 0.5 dm³. Both cell voltage, U , and current, I , were measured. At the end of the experiment, the pH of the solution was adjusted to a value higher than 7 and the sulphur was precipitated. The solution was taken out and the amount of elemental sulphur, m , in the precipitate was determined with the method described by Morris et al. [15]. Thus, sulphur was oxidised to thiosulphate by boiling in a sodium sulphite solution, the excess of sulphite was bound with formaldehyde and the thiosulphate was determined by iodometric titration.

From the above measurements, the mean values of the current efficiency, β_c , the specific energy consumption, E_s , and the space time yield, ρ_{mean} , were calculated with the following equations:

$$\beta_c = \frac{4Fm}{M \int_0^t I(t) dt} \quad (8)$$

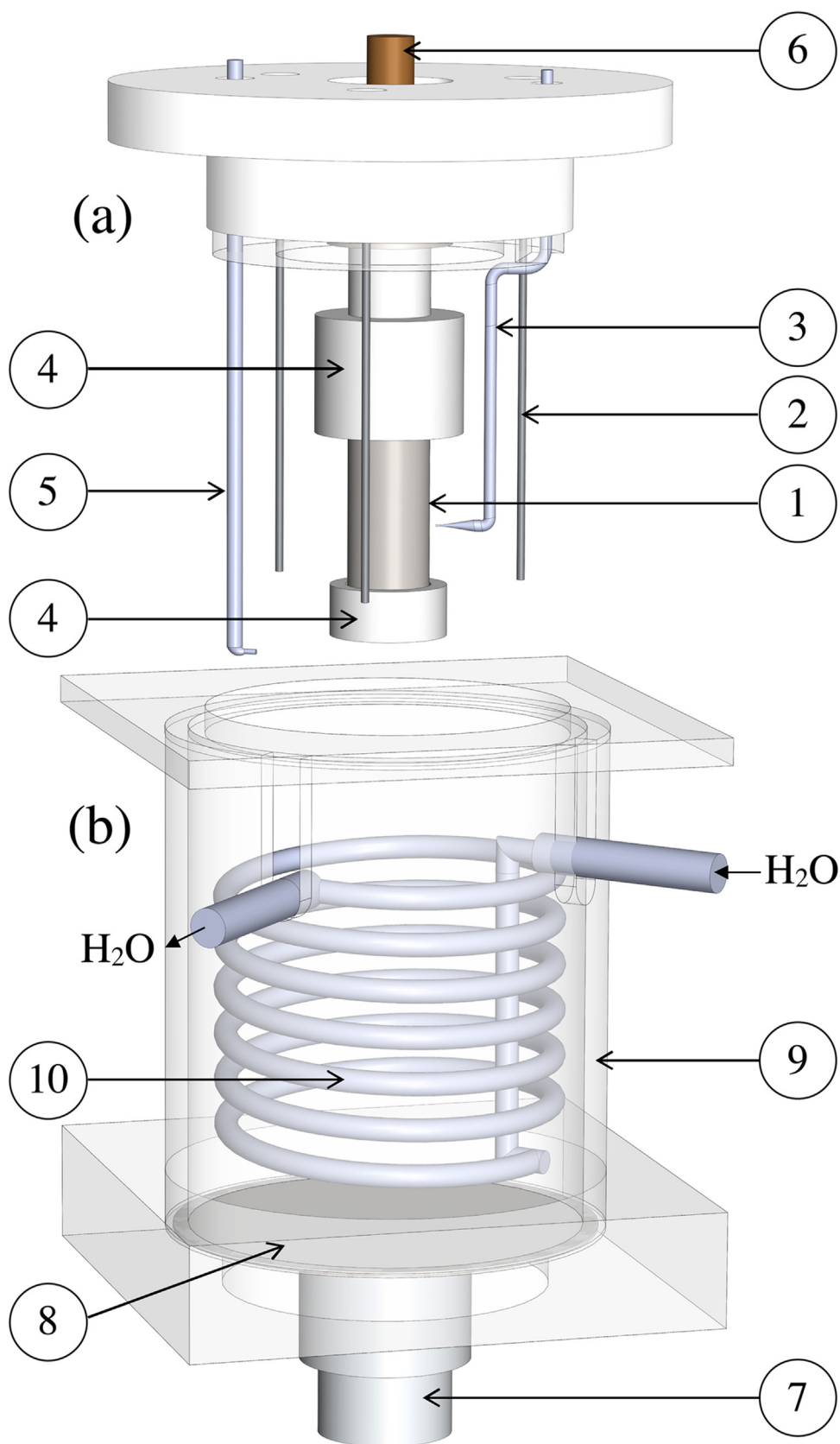


Fig. 1. Schematic representation of the electrochemical reactor with a cylindrical rotating electrode. (a) Arrangement of the electrodes. (b) Electrochemical reactor. (1) Working electrode; (2) counter electrode; (3) Luggin capillary; (4) Teflon sleeve; (5) gas feeder; (6) electrode shaft; (7) ultrasonic probe; (8) stainless steel plate; (9) electrolyte container; (10) glass cooling coil.

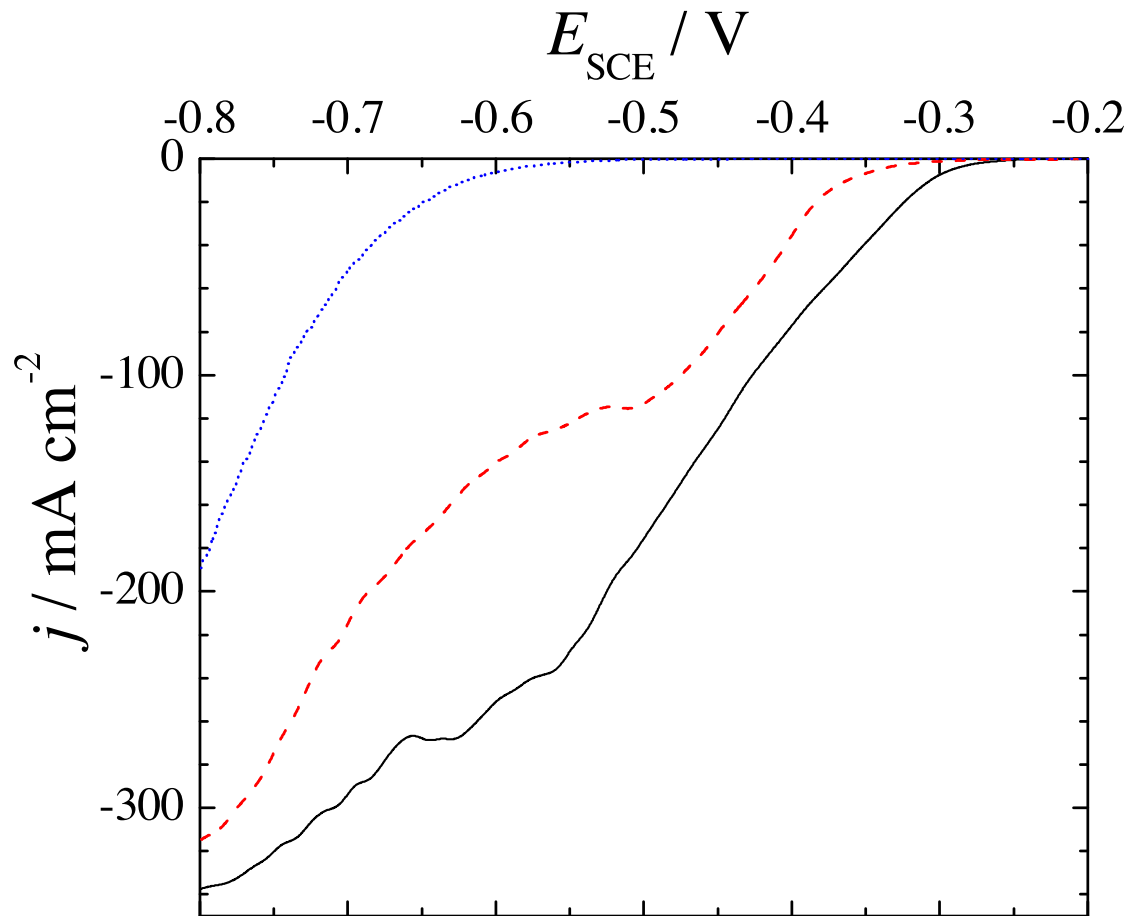


Fig. 2. Current density as a function of the electrode potential for the sulphur dioxide reduction using a rotating cylinder electrode. $5 \text{ g dm}^{-3} \text{ SO}_2$ in $0.5 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$ as supporting electrolyte. Full line: with application of ultrasound. Dashed line: without application of ultrasound. Dotted line: supporting electrolyte. $\omega = 500 \text{ rpm}$. $T = 30^\circ \text{C}$. Potential sweep rate: 2 mV s^{-1} .

$$E_s = \frac{\int_0^t I(t)U(t)dt}{m} \quad (9)$$

and

$$\rho_{\text{mean}} = \frac{m}{Vt} \quad (10)$$

where M is the molar mass of sulphur, t is the time, and V is the reactor volume.

3. Results and discussion

Fig. 2 displays cathodic polarization curves obtained using the rotating cylinder electrode with application of ultrasound, full line, and for the silent system, dashed line, for a single phase electrolyte. The dotted line corresponds to the supporting electrolyte under silent condition. The dashed line shows that sulphur dioxide reduction presents a combined diffusion and charge-transfer kinetic control and, in a narrow range of potentials near -0.5 V , vs. SCE, the reaction occurs at limiting current conditions. At potentials more negative than -0.5 V hydrogen evolution takes place as a secondary reaction. Thus, the comparison of the dashed and dotted lines corroborates previous results obtained with a rotating disc electrode [8]. Likewise, the comparison of the full and dashed lines demonstrates that ultrasound increases the rate of reduction of sulphur dioxide which improves the kinetics of the

reaction, probably due to the cleaning action of ultrasound on the electrode surface. It also enhances the mass-transfer coefficient because sonication improves stirring. A similar finding was reported by Lorimer et al. [16] for silver deposition at a rotating cylinder electrode, where the limiting current was improved by insonation for rotation rates below 1000 rpm . These authors discussed the possible contributions of sonication to kinetics and

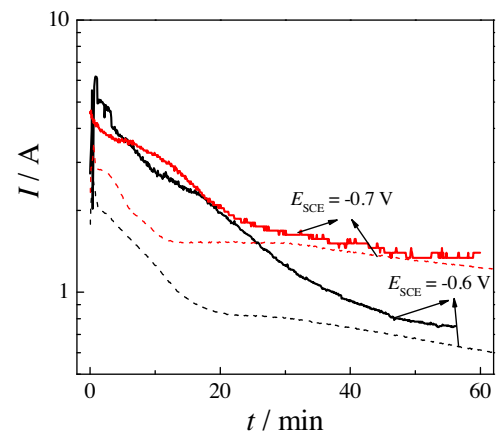


Fig. 3. Current as a function of electrolysis time for the production of colloidal sulphur in a single phase system. Full lines: with application of ultrasound. Dashed lines: without application of ultrasound. Electrolyte: $5 \text{ g dm}^{-3} \text{ SO}_2$ in $0.5 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$ as supporting electrolyte. $\omega = 500 \text{ rpm}$. $T = 30^\circ \text{C}$.

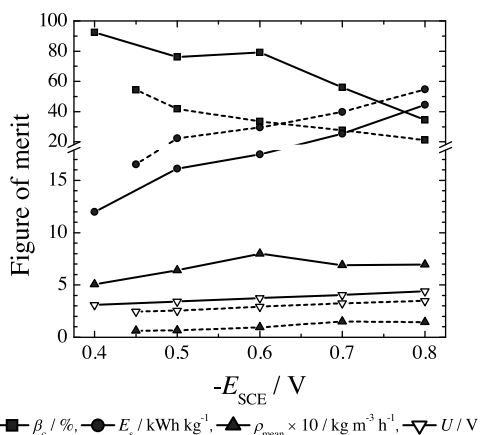


Fig. 4. Figures of merit for colloidal sulphur production at a rotating cylinder cathode as a function of the cathodic potential in a single phase system. Full lines: with application of ultrasound. Dashed lines: without application of ultrasound. Solution: $5 \text{ g dm}^{-3} \text{ SO}_2$ in $0.5 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$ as supporting electrolyte. $\omega = 500 \text{ rpm}$. $T = 30^\circ \text{C}$.

they suggested that the main factor is the disruption of the electrical double layer by cavitation effect.

Fig. 3 shows typical curves of the total current as a function of time for experiments in the absence and presence of ultrasound for a single phase electrolyte. When the current is connected, the surface of the cathode is covered with a thin and adherent layer of a dark grey colour. The analysis by EDAX of a sample scraped from this layer revealed the presence of sulphur, nickel and iron as the main elements, plus oxygen. Therefore, the formation of sulphidised nickel and iron compounds can be assumed, which come from the reaction of hydrogen sulphide generated by Reaction (2) with nickel and iron ions from the corrosion of the cathode. Among these sulphidised compounds, FeS_2 is claimed to be a good catalyst for the hydrogenation of sulphur dioxide to hydrogen sulphide [17,18] but it can be poisoned by sulphur, whereas iron group metal oxides are recognised as catalysts for the hydrogenation of sulphur dioxide to sulphur [19]. Hence, at the start of the experiment, the formation of hydrogen sulphide is expected to occur. It requires a large amount of current due to the six electrons needed for its production from the reduction of sulphur dioxide. Likewise, the evolution of hydrogen sulphide at the cathode improves the mass-transfer of sulphur dioxide to the electrode surface, by bubble-induced convection, increasing the current even further. However, after a short time, the sulphidised iron layer at the cathode is poisoned, the hydrogen sulphide evolution is restricted and the sulphur formation becomes relevant and covering the electrode, under silent condition, with a thick yellow layer of sulphur. Nevertheless, this layer was detached from the cathode surface when ultrasound was used, corroborating the efficiency of sonication for the cleaning of the electrode surface, and in this case the cathode surface showed a dark grey colour at the end of the experiment. Under silent or ultrasonic conditions, the reproducibility of the current was difficult to achieve at the start of the experiment. This is attributable to the unpredictable change of selectivity in the reduction of sulphur dioxide, according to the above discussion. From Fig. 3, it can be observed that the use of ultrasound increases the current in the intermediate times of the experiments, but at longer times the current approaches a constant value slightly higher than that obtained under silent condition.

Fig. 4 compares the figures of merit with and without the application of ultrasound, full and dashed lines respectively, in the single phase system as a function of the cathodic potential. The data for the silent system correspond to those reported in our previous contribution [8]. As expected, an increase in cell voltage

and in specific energy consumption as well as a decrease in current efficiency are observed in both cases when the cathodic potential becomes more negative. This behaviour is a consequence of hydrogen evolution as a side cathodic reaction. The current efficiency for sulphur production under insonation conditions is approximately twice the value of the silent system in the potential range of -0.5 V to -0.7 V . However, at a more negative value of the cathodic potential, hydrogen evolution becomes relevant as a secondary reaction attaining similar values for current efficiency in both systems. The use of ultrasound produces an important improvement in current efficiency and similar values in cell voltage. The combination of both parameters generates a strong diminution in specific energy consumption. The mean value of space time yield approaches a maximum at cathodic potentials more negative than -0.6 V . Likewise, a significant increase in space time yield, higher than 5 times, is observed with the application of ultrasound. The improvement of the reactor performance can be attributed to the fact that ultrasound simultaneously produces several effects that contribute to the formation of colloidal sulphur. Among them it can be mentioned the increase in mass-transfer of sulphur dioxide to the cathode surface, the detachment from the electrode surface of the sulphur that has been formed and the release of gases generated at the cathode by secondary reactions.

A relevant parameter that characterises the process is also the molar yield towards the sulphur production, defined as [20]

$$Y_s = \frac{\text{moles of sulphur formed}}{\text{moles of sulphur dioxide reacted}} \quad (11)$$

Taking into account Eq. (3) and the Faraday law, the number of moles of sulphur formed, n_s , is given by

$$n_s = \frac{\beta_c \int_0^t I dt}{4F} \quad (12)$$

Analogously, the number of moles of sulphur dioxide reacted, n_r , is

$$n_r = \frac{(2 + \beta_c) \int_0^t I dt}{12F} \quad (13)$$

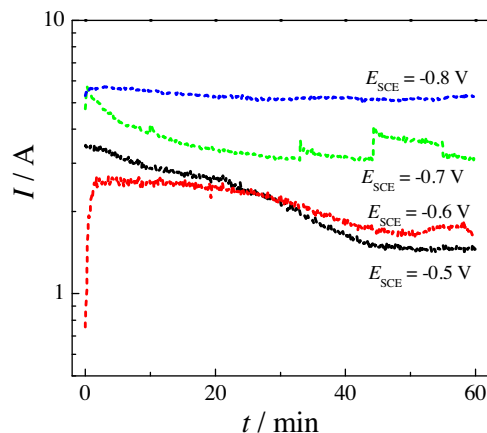


Fig. 5. Current as a function of the electrolysis time for the production of colloidal sulphur in a biphasic system with application of ultrasound. Electrolyte: dispersion of $5\% \text{ SO}_2$ and $95\% \text{ N}_2$ into a $0.5 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$ solution. Volumetric flow rate: $1.41 \times 10^{-5} \text{ m}^3 \text{ s}^{-1}$. $\omega = 500 \text{ rpm}$. $T = 30^\circ \text{C}$.

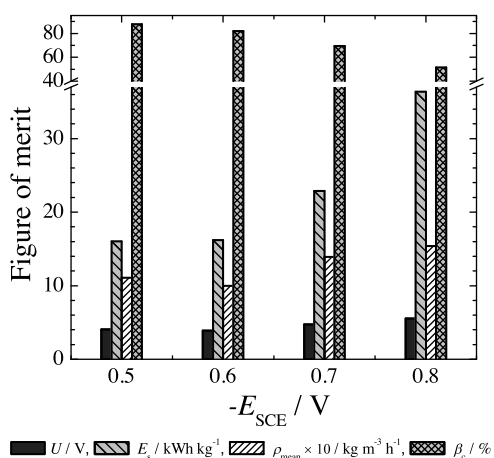
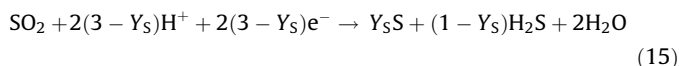


Fig. 6. Figures of merit for colloidal sulphur production at a rotating cylinder cathode as a function of the cathodic potential with application of ultrasound in the biphasic system. Electrolyte: dispersion of 5% SO_2 and 95% N_2 into a $0.5\ mol\ dm^{-3}$ H_2SO_4 solution. Volumetric flow rate: $1.41 \times 10^{-5}\ m^3\ s^{-1}$. $\omega = 500\ rpm$. $T = 30^\circ C$.

Introducing Eqs. (12) and (13) into Eq. (11) and rearranging yields

$$Y_S = \frac{3\beta_c}{2 + \beta_c} \quad (14)$$

Eq. (14) is valid for potentials higher than $-0.5\ V$, where the reduction of sulphur dioxide takes place alone. Combining Eq. (14) with Eq. (3) results in



representing the sulphur dioxide reduction in terms of the molar yield. When the molar yield is unity, Eq. (15) results in the production of sulphur, and for $Y_S = 0$ it yields the reduction to hydrogen sulphide as the only reaction. Considering the current efficiencies reported in Fig. 4, the molar yield for sulphur production is 58% for the silent system and 89% under insonation, revealing that ultrasound increases the selectivity towards the generation of sulphur in Eq. (15). The improvement in the molar yield can be explained by taking into account that insonation removes the sulphur deposited on the electrode surface allowing for the continuation of its production. This finding provides

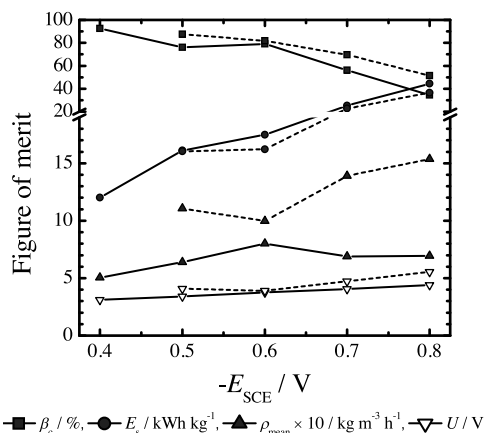


Fig. 7. Comparison of the figures of merit for colloidal sulphur production at a rotating cylinder cathode as a function of the cathodic potential with application of ultrasound. Full lines: single phase system, electrolyte: $5\ g\ dm^{-3}$ SO_2 in $0.5\ mol\ dm^{-3}$ H_2SO_4 as supporting electrolyte. Dashed lines: biphasic system, electrolyte: dispersion of 5% SO_2 and 95% N_2 into a $0.5\ mol\ dm^{-3}$ H_2SO_4 solution. $\omega = 500\ rpm$. $T = 30^\circ C$.

complementary evidence to the research on organic electrosynthesis by Cagnet et al. [21], who recognised as the most remarkable result that selectivity is deeply affected by ultrasonication. Thus, Fig. 4 shows that the application of ultrasound is completely beneficial for the production of colloidal sulphur in a single phase system.

Fig. 5 shows typical curves of the total current as a function of time for experiments with application of ultrasound in the biphasic case. Comparing Figs. 3 and 5, a current increase is observed in the biphasic system and the current presents a smaller decrease in time, remaining almost constant throughout the experiment for the more negative values of the cathodic potential.

Fig. 6 presents the figures of merit for the production of colloidal sulphur in the biphasic system as a function of the cathodic potential, in which a similar behaviour to that reported on Fig. 4 in a single phase system is observed. Fig. 6 also reveals that at cathodic potentials near $-0.7\ V$ the maximal value of the space time yield is obtained in accordance with previous results [7]. It must be remarked that the experiment at $-0.8\ V$ shows a slight improvement of the space time yield, but with a strong increase in the specific energy consumption. The molar yield towards sulphur production in the biphasic system was 91% similar to the value in the single phase case, both under ultrasonic conditions.

Fig. 7 contrasts the figures of merit in the biphasic case with those of a single phase system with application of ultrasound. It is observed that current efficiency, specific energy consumption and cell voltage are very similar in both cases, with a slight improvement in β_c and E_s in the biphasic system. However, the space time yield obtained in the biphasic system duplicates the value given in the single phase case being this the consequence of the higher current measured when a gas phase is introduced in the reactor, as it is displayed comparing Figs. 3 and 5. From Fig. 7, the conclusion is that the combined action of the effect of ultrasound together with an additional gas phase improves the reactor performance resulting in 70% for current efficiency, $1.4\ kg\ m^{-3}\ h^{-1}$ for mean space time yield with a specific energy consumption of $23\ kWh\ kg^{-1}$ when the cathodic potential is $-0.7\ V$.

4. Comparison with theoretical predictions

For a rotating cylinder electrode, the electrolyte is considered to be well-mixed at all times. Assuming that the reduction of sulphur dioxide takes place under limiting current conditions, the temporal behaviour of the concentration of sulphur dioxide, c , is given by [22]

$$c(t) = c(0) \exp(-k_m a_e t) \quad (16)$$

where a_e is the specific surface area and k_m is the mass-transfer coefficient. In the present case, the interfacial area for mass-transfer cannot be accurately determined. For this reason the mass-transfer rate will be analysed here in terms of transfer coefficients based on a unit volume of reactor, $k_m a_e$, rather than on a unit of interfacial area, k_m . The product $k_m a_e$ is also called volumetric mass-transfer coefficient.

Table 1
Physicochemical properties of the electrolyte.

Composition	$[SO_2] \cong 5\ g\ dm^{-3}$ in $0.5\ mol\ dm^{-3}$ H_2SO_4
$\nu / m^2\ s^{-1}$	1.07×10^{-6}
$D / m^2\ s^{-1}$	1.53×10^{-9}
Sc	699

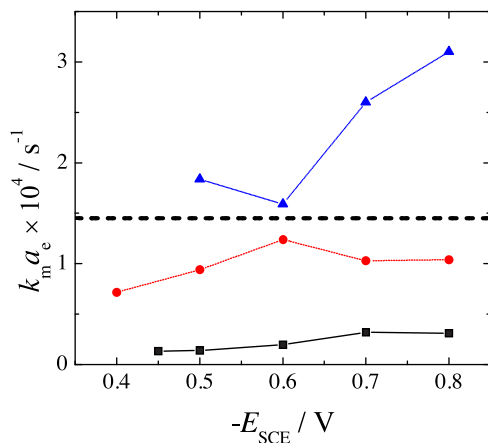


Fig. 8. Volumetric mass-transfer coefficient as a function of the potential calculated according to Eq. (22). (■): without application of ultrasound. (●): single phase system with application of ultrasound. (▲): biphasic system with application of ultrasound. Thick dashed line: theoretical value for the silent system calculated with Eq. (23).

According to Eq. (3), the limiting current density for the reduction of sulphur dioxide is

$$j_{\text{lim}}(t) = \frac{12}{2 + \beta_c} F k_m c(t) \quad (17)$$

and the mass balance for the sulphur production yields

$$\frac{dm(t)}{dt} = \frac{M}{4F} S \beta_c j_{\text{lim}}(t) \quad (18)$$

being S the electrode surface area. Combining Eqs. (16)–(18) and taking into account Eq. (14) is

$$\frac{dm(t)}{dt} = M Y_S k_m S c(0) \exp(-k_m a_e t) \quad (19)$$

The instantaneous value of the space time yield is defined as

$$\rho(t) = \frac{dm(t)}{V dt} \quad (20)$$

and its mean value is given by

$$\rho_{\text{mean}} = \frac{\int_0^t \rho(t) dt}{t} \quad (21)$$

Combining Eqs. (19)–(21) and solving results in

$$\rho_{\text{mean}} = \frac{M c(0) Y_S}{t} [1 - \exp(-k_m a_e t)] \quad (22)$$

For a rotating cylinder electrode under silent conditions, the mass-transfer coefficient can be calculated with the correlation proposed by Eisenberg et al. [23] according to

$$\text{Sh} = 0.0791 \text{Re}^{0.7} \text{Sc}^{0.356} \text{ for } 112 < \text{Re} < 1.62 \times 10^5 \quad (23)$$

The Sherwood number, Sh , the Reynolds number, Re , and the Schmidt number, Sc , are defined as

$$\text{Sh} = \frac{k_m d}{D} \quad (24)$$

$$\text{Re} = \frac{\omega d^2}{2\nu} \quad (25)$$

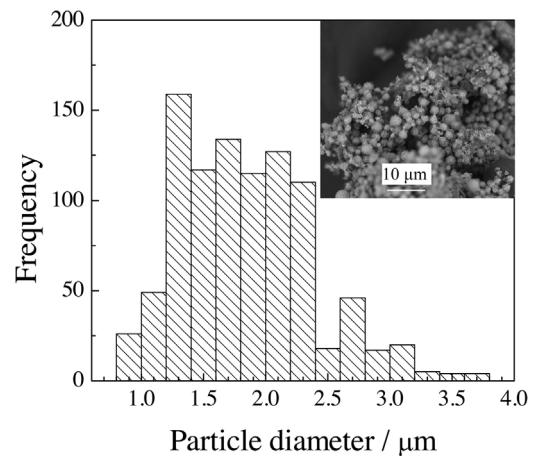


Fig. 9. Distribution of particle size in a sample of colloidal sulphur obtained with application of ultrasound in a single phase electrolyte. $\omega = 500$ rpm, $E_{\text{SCE}} = -0.5$ V. $T = 30^\circ\text{C}$. Inset: Scanning electron micrograph of colloidal sulphur. Magnification: $\times 5300$.

and

$$\text{Sc} = \frac{\nu}{D} \quad (26)$$

here D is the diffusion coefficient of sulphur dioxide, ν is the kinematic viscosity of the solution, ω is the rotation speed and d is the cylinder diameter. Table 1 summarizes the composition and physicochemical properties of the solution, which were measured in the laboratory [8]. Under working conditions the Reynolds number was 11842 and using Eq. (23) yields $k_m = 4 \times 10^{-5} \text{ m s}^{-1}$. Thus, the theoretical value of the volumetric mass-transfer coefficient may be estimated as $k_m a_e = 1.45 \times 10^{-4} \text{ s}^{-1}$.

Fig. 8 shows the volumetric mass-transfer coefficients as a function of the potential, which were calculated by using Eq. (22) with the mean space time yield given in the previous figures and with the values of molar yield towards sulphur as reported above. The values for the silent system, symbol ■, are always smaller than the theoretical one, shown as a thick dashed line because the surface area of the cathode is masked by the sulphur deposited. Likewise, it can be observed an increase in the volumetric mass-transfer coefficient as the potential becomes more negative, which can be attributed to the fact that hydrogen evolution enhances the mass-transfer coefficient by bubbled-induced convection. However, the values of $k_m a_e$ under silent conditions approach a maximum as the potential becomes more negative. Fig. 8 also shows that the application of ultrasound improves the volumetric mass-transfer coefficient in comparison with the silent case, being the effect more pronounced in the biphasic system. In the case of the single phase electrolyte the increase in the volumetric mass-transfer coefficient due to insonation is not enough to compensate for its diminution. This can be due to the fact that the thin and adherent layer of sulphidised products remains at the electrode surface generating a loss of surface area. However, in the biphasic case the combined action of ultrasound together with the presence of an additional gas phase improves the behaviour of the equipment corroborating that gas bubbles are extremely active in a sound field. Pollet et al. [24] proposed a Levich-like equation to calculate the limiting current in the presence of ultrasound in terms of horn-electrode distance, electrode geometry and ultrasonic intensity, but the equation is not applicable to the present case because of the different geometric configuration of the equipment.

5. Morphological characterization of colloidal sulphur

A drop of the suspension of sulphur particles obtained at $E_{SCE} = -0.5$ V, vs. SCE, together with a simultaneous application of ultrasound in the single phase electrolyte was placed on a glass slide and allowed to dry. The supporting electrolyte was extracted by adding a drop of distilled water and absorbing the solution with filter paper. This procedure was repeated four times. The residual sulphur powder was dried in a desiccator over silica gel and the size of the particles and the surface morphology were examined by scanning electron microscopy, SEM. Fig. 9 shows the histogram of the diameter of the particles, where it can be observed that the particle size is in the range of $0.9 \mu\text{m}$ to $3.1 \mu\text{m}$ with a mean value of $1.84 \mu\text{m}$ and a standard deviation of 0.54. The statistical analysis is based on a sample of 954 independent measurements of the particle size. The sulphur particles present a spheroidal shape, as shown in the inset of Fig. 9. The EDAX study of this sample revealed that sulphur was the only element in the powder, thus verifying the high purity of colloidal particles. These results are similar to those previously reported under silent conditions [7], showing that the application of ultrasound has not any influence on the shape, size and composition of sulphur particles.

6. Conclusions

The application of ultrasound improves the electro-synthesis of colloidal sulphur by reduction of sulphur dioxide. The current efficiency and selectivity for sulphur production are increased and the specific energy consumption is diminished. The effect of ultrasound is more marked in a biphasic system. The best values of space time yield were obtained at potentials more negative than -0.6 V. Therefore, the use of ultrasound can be recognised as an appropriate strategy to detach the sulphur deposited at the cathode increasing the performance of the electrochemical reactor in comparison with the behaviour without insonation. However, the properties of colloidal sulphur are not influenced by ultrasound treatment.

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