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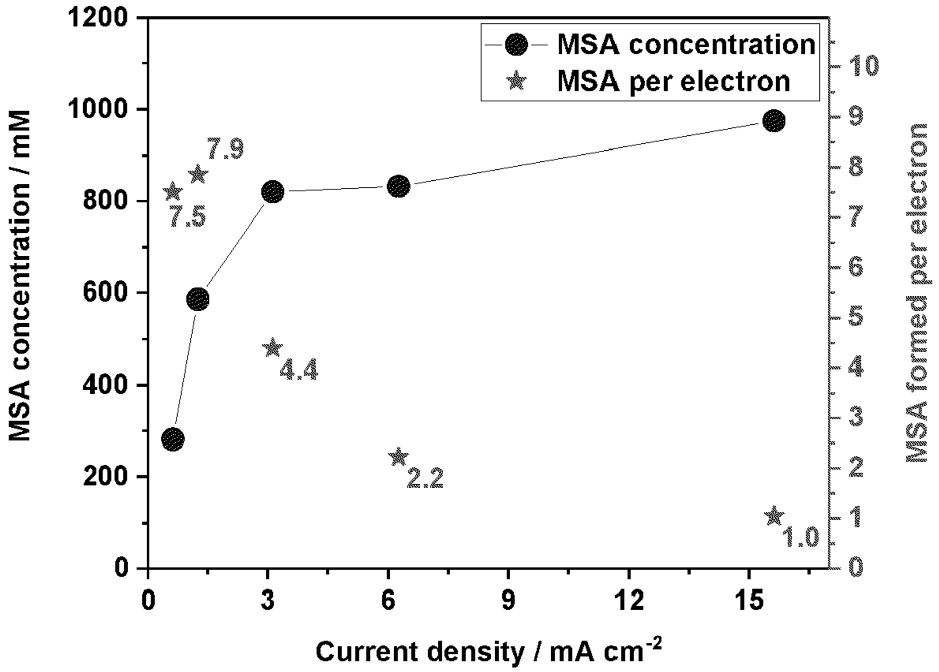
(54) PROCESS FOR THE PRODUCTION OF METHANE SULFONIC ACID

(57) The present invention relates to a process for the electrosynthetic production of methane sulfonic acid from methane and sulfur trioxide in oleum by electrolysis.

Figure 1



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Description

[0001] The present invention relates to a process for the production of methane sulfonic acid from methane and sulfur trioxide in oleum.

[0002] Selective methane functionalization is still one of the top challenges of chemical research due to its low reactivity compared to its oxidation products. However, being abundant and cheap it could be a great feedstock for a number of useful products that can either serve as fuels or be used in chemical industry.

[0003] In order to avoid the standard functionalization route via syngas formation various concepts including oxy-functionalization or coupling are under extensive investigation. Most of the very innovative developments, however, can still not meet the demands for an industrial application.

[0004] The two most recently developed processes that are used by industry are the oxidative methane coupling as developed at Linde and Siluria (US10047020B2) as well as the production of methanesulfonic acid (MSA) by BASF (WO 2018/146153).

[0005] Due to its unique properties, MSA is already used in some processes and demand is expected to increase further in the near future. The numerous advantages of MSA are: strongly acidic without being oxidizing, low vapor pressure and odorless, low toxicological risk, high solubility of its salts, high chemical stability and additionally it is biodegradable. All these characteristics make MSA attractive for use in e.g. the electronics industry for electroplating, for cleaning processes, for metal recycling, or in ionic liquids for a number of other processes.

[0006] For most of the production pathways described on the patent field, methane derivatives are used and then converted in multi-step redox reactions. This is not only unfavorable due to the number of reaction steps but also because side products are generated.

[0007] A more attractive pathway is the direct sulfonation of methane, which is known for more than twenty years. The sulfonation usually takes place in oleum and is initiated by a metal peroxo- or peroxosulfate species.

[0008] Early work on methane sulfonation led to the report of several radical initiators and additives for the activation of CH_4 to methane sulfonic acid (MSA) in fuming sulfuric acid. However, the reactions lack high yield and good selectivity. Additionally, the reaction mechanism is still not yet entirely understood. Obvious problems arise in order to scale up these processes such as additional catalytic routes for SO_2 conversion, excessively large reactors and extremely high temperatures. Methane sulfonic acid (MSA), in contrast to methyl bisulfate (MBS), is considered a high value-added product and a green acid (for example, non-oxidant, low vapor pressure, bio-degradable, and so on) with uses in the pharma, electronic and cleaning industry.

[0009] Basickes et al. (Basickes, Hogan, Sen, J. Am . Chem. Soc. 1996, 11, 13111- 13112) describe the radical-initiated functionalization of methane and ethane in fuming sulfuric acid. Temperatures of 90°C and above are necessary and the yield of MSA is low.

[0010] Mukhopadhyay and Bell (Organic Process Research & Development 2003, 7, 161-163) report the direct sulfonation of methane at low pressure to methanesulfonic acid in the presence of potassium peroxydisphosphate as the initiator. In order to activate the initiator, a temperature of 95°C is chosen and the conversion rate of SO_3 is below 30%.

[0011] Lobree and Bell (Ind. Eng. Chem . Res. 2001, 40, 736-742) also studied the $K_2S_2O_8$-initiated sulfonation of methane to methanesulfonic acid. A radical mechanism is described and high temperature as well as low concentrations of initiator are required in order to achieve modest conversion rates of SO_3.

[0012] US 2,493,038 describes the preparation of methane sulfonic acid from SO_3 and methane. US 2005/0070614 describes further methods for preparing methane sulfonic acid, and its application. The methods known in the prior art are in part complicated, cost-intensive, and lead to undesirable products because of the harsh conditions.

[0013] WO 2004/041399 A2 and US 7,119,226 B2 both suggest a radical pathway and chain reaction for the production of methane sulfonic acid. In general, radical chain reactions usually result in undesirable side products, which even manifest themselves as disturbing inhibitors in the production of alkane sulfonic acids, which may lead to termination of the actual reaction for preparing the alkane sulfonic acid and further to impurities, formation of side products and poor yields based on sulfur trioxide and methane.

[0014] WO 2018/146153 describes a method for the production of alkane sulfonic acids, especially methane sulfonic acid, from alkane, especially methane, in which a carbocation is assumingly formed as intermediate. However, said process is quite complicated and the reaction conditions and yields need further optimization.

[0015] It is thus the object of the present invention to provide an industrial process for the electrosynthetic production of methane sulfonic acid under improved conditions compared to thermochemical pathways.

[0016] In a first embodiment the problem is solved by an electrochemical process for the production of methane sulfonic acid (MSA) from methane and sulfur trioxide, wherein methane and fuming sulfuric acid are electrolyzed with at least one electrode as anode, preferably at least one BDD electrode or a resistant electrode made from another anode material such as FTO or Pt/Ir, ITO, ATO, lead, stainless steel, gold, and alloys thereof, in a pressurized reactor under a methane pressure in the range of at least 30 bar and at most 200 bar in a temperature range of 50°C to 120°C, preferably for a reaction time range which is adjusted depending on the current density and is preferably more than 2 hours, and the

MSA is separated from obtained reaction mixture, for instance by distillation or other suitable separation methods such as column chromatography, fractional freezing, ion chromatography, membrane separation.

[0017] In the inventive process, the current density at the anode is usually kept between 0.5 mA/cm^2 to 20 mA/cm^2 during current flow and can be varied in the progress of the reaction or even paused for a determined amount of time during the reaction so that times of current flow and current-less times may be changed in intervalls.

[0018] The pressure in the pressurized reactor is preferably kept in the range of 50 to 120 bar.

[0019] Furthermore, the reaction can be carried out at temperatures, where unselective and uncontrolled radical chain reactions do not take place as observed in the prior art where high temperatures are required. The inventive process can, for example, efficiently be carried out already at about 50°C or slightly higher. The addition of substances promoting the decomposition of any initiators to radicals or stabilizing said radicals, as used in the prior art, is not required in the inventive process as such initiators are not used in the inventive process. Particularly, no such substances are added in the invention. Such substances include metal salts {e.g., Pt, Hg, Rh). They show detrimental side effects of triggering side reactions, which can be avoided by the present invention.

[0020] Thus, the temperature in the pressurized reactor is preferably kept in a temperature range of 50°C to 100°C, and the reaction time in the pressurized reactor is usually kept between 3 and 24 hours, depending on the strength of the current density.

[0021] The reaction mixture in the pressurized reaction vessel is preferably agitated, advantageously with a high-speed stirrer in order to safeguard an intimate contact between the anode, the fuming sulfuric acid and the methane. Depending on the size and form of the stirrer and the design of the reactor, the stirring speed should be in the range of 600 rpm to 1800 rpm.

[0022] The above reaction condition of pressure and temperature influence the reaction results to some extent, but the kind of electrode and the applied current density have higher impact. Keeping the current density at a moderate strength, the yield of MSA can be increased whereas too high current density will first lead to an increase, but then to a decrease over the time. Thus, the strength of the current density has to be carefully adjusted to the electrolyzing time in order to obtain maximum yields. The use of a BDD-electrode is found to be of major advantage for the process. The inventors have found that the properties of the BDD electrode are of particular advantage:

- High selectivity towards MSA on the BDD-electrode
- BDD offers high corrosion stability
- BDD resist deactivation over a long period
- Chemically inert material prevents catalysis of unwanted side reactions

[0023] As an alternative electrode, any electrode fulfilling these properties, such as FTO or Pt/lr, ITO, ATO, lead, stainless steel, gold, and alloys thereof, depending on the actual conditions might also be used

[0024] The electrolyte is fuming sulfuric acid having a concentration of 20 to 30 wt.%. SO_3. However, other concentrations of concentrated sulfuric acid with SO_3 in a concentration up to 45 wt.%, or even higher up to 60 wt.% are also possible.

[0025] The present invention is further illustrated by the following Figures and Experimental Part. In the Figures, it is shown in:

Figure 1:	The dependency of the process on the current density for the formation of MSA
Figure 2:	The dependency of the concentration of MSA on the formation time in combination with the current density
Figure 3:	The dependency of the process on the methane pressure for the formation of MSA
Figure 4:	The dependency of the process on the temperature for the formation of MSA
Figure 5:	The separation of electrolysis step and methane pressurization
Figure 6:	The selectivity of a BDD electrode vs a Pt/lr electrode for the formation of MBS vs. MSA

[0026] As it can be seen in Figure 1, Very low current current densities already lead to high product concentration after only 3 hours reaction time. There is an optimum range for the applied current density. If current density is too low the reaction will be slowed down significantly. If current density is too high the product or active intermediate species will decompose. This is evident in the figure from the decrease in electron "turnover" with increasing current density. The decomposition reactions can for instance include total oxidation of methane or the oxygen evolution reaction. The number of MSA molecules generated per passed electron is in general higher at low current densities. This means that at the applied conditions a lower current density leads to the same or only slightly lower MSA yield than a higher current density however with a highly increased faradaic yield. Therefore, in this case lower current densities are favorable, as any higher current density would just lead to lost charge.

[0027] As shown in Figure 2, MSA concentration increases over time at all the current densities applied in shorter reaction times up to three hours. At reaction times longer than 3 hours, however, the current density will influence the yield significantly. At higher current density, the product as well as intermediate species can be decomposed faster which will lead to a decreased concentration compared to lower current densities. As the current density can also be adapted over the time this is actually an advantage as it gives room to find and tune an optimum setting between reaction kinetics and product or intermediate stability.

[0028] From Figure 3, it becomes evident that a high methane pressure is beneficial for high product concentration whereas lower pressure leads to a low concentration of MSA. In order to avoid a slow reaction rate due to a decreased methane partial pressure it would be of advantage to keep a high pressure during the whole reaction time, which could be realized in a continuously operating process of the invented method.

[0029] In Figure 4, the temperature dependence of product concentration is shown. Similar to current density it was found that an optimum temperature range exists for this reaction. If too low, the reaction will proceed slowly and if too high the concentration is decreased due to decomposition reactions or possibly undetected side reactions other than MBS formation.

[0030] As shown in Figure 5, the reaction can also take place if electrolysis and pressurization of the reactor are done in separate steps. After one hour of electrolysis of Oleum the reactor can be pressurized with methane immediately or after stirring without current for a time between 0 and 60 min in between. With increasing pause-time as intermediate stirring the concentration of MSA decreases. This shows that an active species is formed during electrolysis which decomposes slowly.

[0031] The comparison of BDD with Pt/Ir as anode material is shown in Figure 6. Although this is only a 30 min reaction it becomes evident that the selectivity towards MSA is higher using BDD. This does not only account for the selectivity with respect to SO_3 consumption but also to Coulomb selectivity. However, the presented method also works on Pt/Ir.

Experimental Part:

Chemicals and materials

[0032]

- BDD anodes, DIACHEM® Electrode Typ 52, from CONDIAS, which is an electrode with a boron doped diamond (BDD) active layer.
- Counter electrode wire, platinum/iridium - Pt90/Ir10, from Evochem
- Pt/Ir anodes from Goodfellow (Pt/Ir - 90/10 Foil)

Instruments

[0033]

- NMR analysis of the liquid phase with Bruker AV-300. Capillary DMSO-d_6 for reference.
- Electrochemical measurements with Gamry Interface 1010E potentiostat
- The autoclave was designed and built in-house (see Fig. 1 below). It is equipped with a pressure gauge (JUMO dTrans p30), and thermocouple (type K; protected by a Teflon hose). The autoclave material on the outside was stainless steel (1.4571) The H-type-cell design for electrochemical experiments was realized by a Teflon or glas inlet. The half cells were separated by a glass frit. The autoclave was heated via a heating jacket, controlled by a previously optimized PID controller. Sealing materials consisted of gold or Teflon.

General Experimental Procedure and Quantification

[0034] Every experiment was carried out in the electro-autoclave described above in a two electrode arrangement, i.e. working electrode and counter electrode. In a usual experiment both half-cells were filled with 3 ml each of oleum (20-30%), then the autoclave was closed and pressurized with methane at room temperature. After placing it in the heating block, electrodes were connected to the potentiostat and the autoclave was heated under stirring to the desired temperature. Once the temperature was reached and stabilized, the respective electrochemical experiment was started. After the pre-set reaction time the electrodes were disconnected from the potentiostat and the autoclave was placed in an ice water bath to cool down under stirring. Once room temperature was reached the gas phase was released. Then the autoclave was opened and stirred with 750 rpm for 5 min to remove residual gas from the liquid phase.

[0035] For quantification of MBS and MSA two NMR tubes were measured; one with the reaction solution (tube 1) and the other one with a mixture of a weighted amount of MBS and 1 ml of reaction solution (tube 2). The ratio R of MBS to MSA after reaction was determined from the first NMR tube. In equation 1 the definition of *R* is shown:

$$R = \frac{I_{1,MBS}}{I_{1,MSA}} = \frac{c_{MBS}}{c_{MSA}} = \frac{I_{2,MBS,reaction}}{I_{2,MSA}} \qquad \text{(Eq. 1)}$$

c_{MBS}	concentration of MBS after reaction	$I_{1,MSA}$	integral of MSA signal from NMR tube 1
c_{MSA}	concentration of MSA after reaction	$I_{2,MBS,reaction}$	contribution of MBS from reaction to integral of MBS signal from NMR tube 2
$I_{1,MBS}$	integral of MBS signal from NMR tube 1	$I_{2,MSA}$	integral of MSA signal from NMR tube 2

[0036] R was then used to calculate the contribution of MBS from the reaction to the NMR integral of MBS in the second tube, $I_{2,MBS,reaction}$, as this integral consists of the already present MBS from the reaction and the added MBS. After subtracting $I_{2,MBS,reaction}$ from the actual MBS integral from tube 2, $I_{2,MBS}$, the contribution of the added MBS to the integral, $I_{2,MBS,added}$, is obtained (eq. 2). Since this amount is known, it is used to calculate the MSA concentration after reaction, c_{MSA}, (eq. 3).

$$I_{2,MBS,added} = I_{2,MBS} - I_{2,MBS,reaction} \qquad \text{(Eq. 2)}$$

$$c_{MSA} = c_{MBS,added} * \frac{I_{2,MSA}}{I_{2,MBS,added}} \qquad \text{(Eq. 3)}$$

$I_{2,MBS,added}$	Share of added MBS to integral of MBS signal from NMR tube 2	$I_{2,MBS}$	Integral of MBS signal from NMR tube 2
$c_{MBS,added}$	concentration of MBS added to tube 2		

[0037] Then, knowing the actual MSA concentration, MBS concentration from reaction, c_{MBS}, can be simply calculated from the first NMR tube using eq. 1.

[0038] MSA generated per electron passed was calculated using eq. 4, with: charge, Q; molar amount of MSA, n_{MSA}; Faraday constant, F. Charge was obtained from integration of current over time.

$$MSA\ generated\ per\ electron = \frac{n_{MSA} * F}{Q} \qquad \text{(Eq. 4)}$$

Examples:

Example 1: Anodicallv induced Synthesis of MSA

[0039] In a 60 ml high pressure steel autoclave with an H-type cell glass inlet for electrochemical experiments where the two compartments were separated by a glass frit, 3 ml of fuming sulfuric acid (20-30%) were added to each cell compartment. The autoclave cap, where a boron-doped diamond anode and a platinum/iridium wire as a counter electrode were attached, was then carefully placed on the autoclave in a way that the electrodes were placed in the two compartments of the H-cell. After closing, the reactor was pressurized with 73 bar methane pressure at room temperature. The reactor was heated to 70 °C under stirring at 1200 rpm where a pressure of 90 bar was reached, then a current density of 3.125 mA/cm^2 was kept for 18000 seconds. Afterwards the autoclave was placed in an ice bath and cooled down to 25 °C before the pressure was released. The liquid sample was then analyzed by ^{1}H-NMR using sodium methyl sulfate as an internal standard for quantification. The concentration of MSA was 1.5 M, which is a yield of 24% based on SO_3. Per every electron passed, 4.7 molecules of MSA were generated. The concentration of by-product methyl bisulfate was 1.4 mM, resulting in a selectivity towards MSA of 99.9%.

Example 2: Anodicallv induced Synthesis of MSA

[0040] In a 60 ml high pressure steel autoclave with an H-type cell glass inlet for electrochemical experiments where the two compartments were separated by a glass fritt, 3 ml of fuming sulfuric acid (20-30%) were added to each cell compartment. The autoclave cap, where a boron-doped diamond anode and a platinum/iridium wire as a counter electrode were attached, was then carefully placed on the autoclave in a way that the electrodes were placed in the two compartments of the H-cell. After closing, the reactor was pressurized with 73 bar methane pressure at room temperature. The reactor was heated to 70 °C under stirring at 1200 rpm where a pressure of 90 bar was reached, then a current density of 1.25 mA/cm^2 was kept for 16 hours. Afterwards the autoclave was placed in an ice bath and cooled down to 25 °C before the pressure was released. The liquid sample was then analyzed by ^1H-NMR using sodium methyl sulfate as an internal standard for quantification. The concentration of MSA was 1.9 M, which is a yield of 32% based on SO_3. Per every electron passed, 4.9 molecules of MSA were generated. The concentration of by-product methyl bisulfate was 55 mM, resulting in a selectivity towards MSA of more than 97%.

Claims

1. Process for the electrosynthetic production of methane sulfonic acid (MSA) wherein methane and fuming sulfuric acid are electrolyzed with at least one electrode as anode that can be boron doped diamond or any other suitable electrode material in a pressurized reactor under a methane pressure in the range of at least 30 bar and at most 200 bar in a temperature range of 50°C to 120°C and a current density in a range of 0.5 mA/cm^2 to 20 mA/cm^2, preferably for a reaction time which is adjusted depending on the current density and is preferably more than 2 hours, and the MSA is separated from obtained reaction mixture by distillation or any other suitable separation method.

2. Process according to claim 1, wherein the pressure in the pressurized reactor is kept in the range of 50 to 120 bar.

3. Process according to claim 1 or 2, wherein the temperature in the pressurized reactor is kept in a temperature range of 50°C to 100°C.

4. Process according to any one of claims 1, 2 or 3, wherein the reaction time in the pressurized reactor is kept between 3 and 24 hours.

5. Process according to any one of claims 1, 2, 3 or 4 wherein the current density at the anode is kept between 0.5 mA/cm^2 to 20 mA/cm^2 during electrolysis.

Figure 1

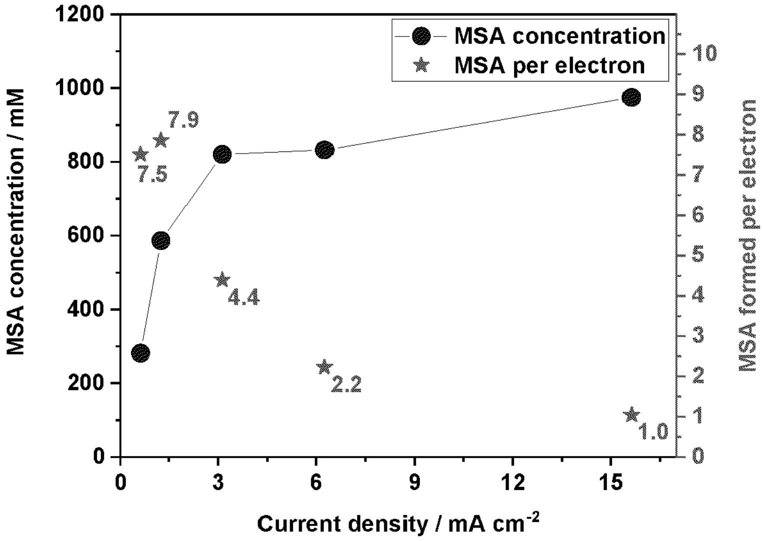


Figure 2

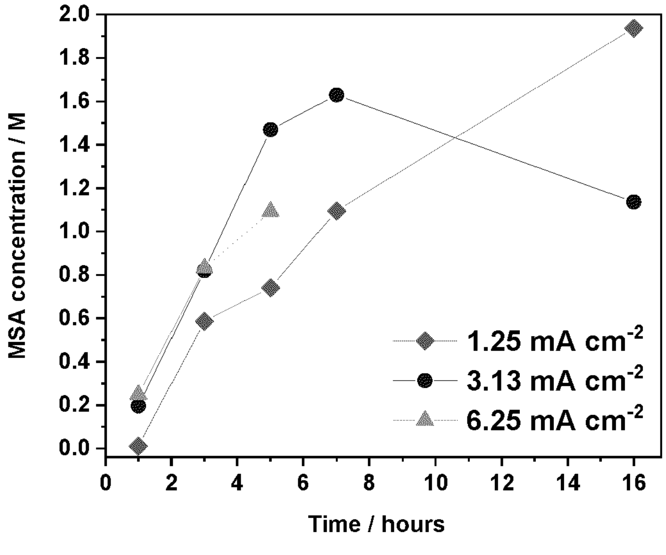


Figure 3

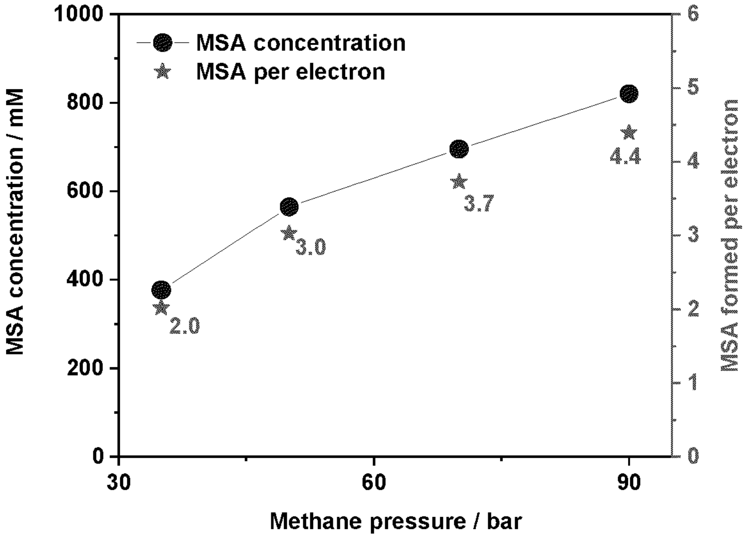


Figure 4

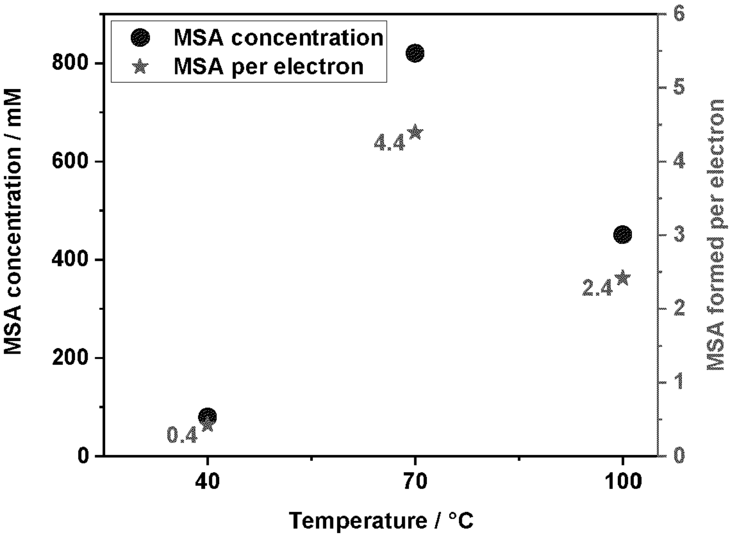
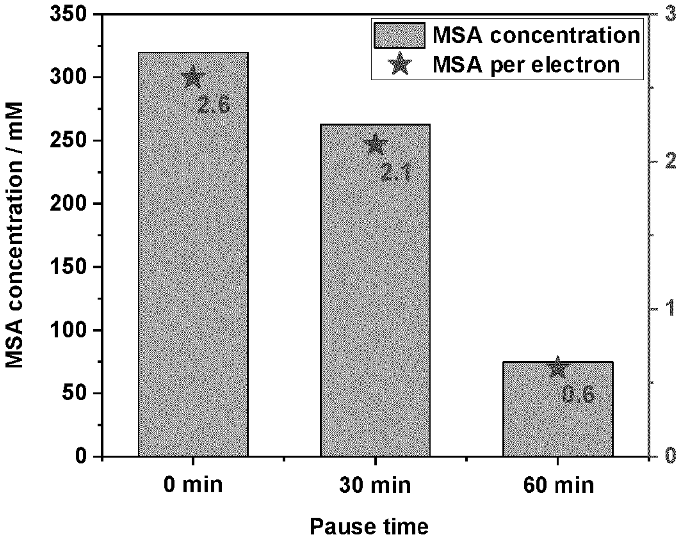


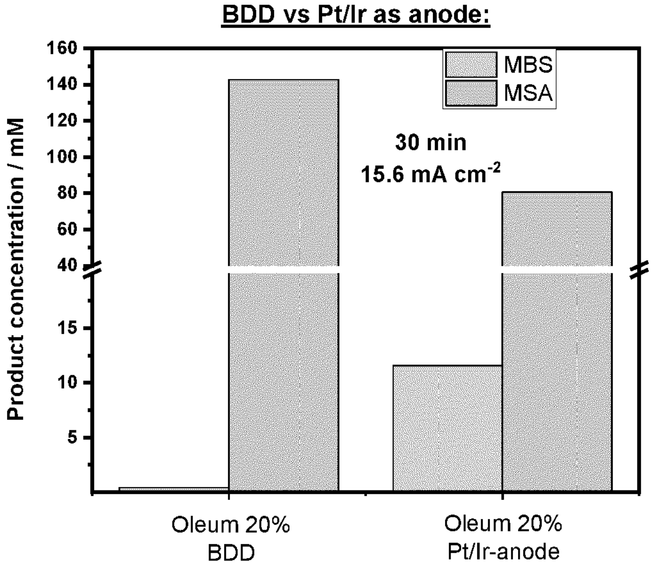
Figure 5



Experimental procedure to Fig. 5:

- 60 min Electrolysis of Oleum at 70 °C
- 0 to 60 min stirring at 70 °C without current flow (denoted as "Pause time" in the plot)
- 120 min stirring under CH_4 pressure at 70 °C without current flow

Figure 6



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EUROPEAN SEARCH REPORT

Application Number
EP 21 19 8115

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
X	US 2019/186026 A1 (SURENDRANATH YOGESH [US] ET AL) 20 June 2019 (2019-06-20) * the whole document * -----	1-5	INV. C25B3/07 C25B3/23 C25B3/29 C25B11/043 C07C303/06 C07C309/04
X	WO 2019/212835 A2 (RICHARDS ALAN K [US]) 7 November 2019 (2019-11-07) * the whole document * -----	1-5	
			TECHNICAL FIELDS SEARCHED (IPC)
			C25B C07C

1 The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
Munich	3 March 2022	Ritter, Thomas

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO.

EP 21 19 8115

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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2019186026 A1	20-06-2019	US 2019186026 A1	20-06-2019
		WO 2018031893 A1	15-02-2018
WO 2019212835 A2	07-11-2019	CA 3093412 A1	07-11-2019
		EP 3959192 A2	02-03-2022
		WO 2019212835 A2	07-11-2019

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For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

REFERENCES CITED IN THE DESCRIPTION

Patent documents cited in the description

- US 10047020 B2 **[0004]**
- WO 2018146153 A **[0004] [0014]**
- US 2493038 A **[0012]**
- US 20050070614 A **[0012]**
- WO 2004041399 A2 **[0013]**
- US 7119226 B2 **[0013]**

Non-patent literature cited in the description

- **BASICKES ; HOGAN ; SEN.** *J. Am . Chem. Soc.,* 1996, vol. 11, 13111-13112 **[0009]**
- **MUKHOPADHYAY ; BELL.** *Organic Process Research & Development,* 2003, vol. 7, 161-163 **[0010]**
- **LOBREE ; BELL.** *Ind. Eng. Chem . Res.,* 2001, vol. 40, 736-742 **[0011]**