Alternating Current Electrolysis for the Electrocatalytic Synthesis of Mixed Disulfide via Sulfur–Sulfur Bond Metathesis towards Dynamic Disulfide Libraries

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chem_201904948_sm_m miscellaneous_information.pdf
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1. General Information

1.1 Generic

All reactions were carried out under atmospheric conditions. The used solvents were distilled prior to use or were purchased in high purity (HPLC grade). Commercially available chemicals were used without further purification, non-commercially available chemicals (di-n-dodecyl disulfide) were synthesised by literature-known procedures.

Electrolysis were executed in undivided or divided cells under constant current (drawings/photos see Figure S1 and Figure S2). Therefore, a laboratory power supply from Tenma 72-10480 Digital-Control DC Power Supply (0-30 V, 3 A) or Aim TTI MX100T Triple Output Multi-Range DC Power Supply (35 V, 3 A) were used. The switching of the electrode polarisation was accomplished by a custom-made device built by the electronics workshop of the Oldenburg University. The \( t_1 \) (pulse time) and \( t_2 \) (quiet time) can be adjusted independently while the current is controlled by the power supply.

As electrode materials platinum plates (dimensions (H x W x D): 35 mm x 10 mm x 0.5 mm, purity: min. 99.95%), glassy carbon plates (dimensions (H x W x D): 35 mm x 10 mm x 3 mm), carbon roving (6k, 400 tex), copper (Cu-DHP according to EN CW 024 A, dimensions (H x W x D): 35 mm x 10 mm x 0.5 mm) and stainless steel (material number: 1.4571 according to EN 10027-2, dimensions (H x W x D): 35 mm x 10 mm x 0.5 mm) were utilised.

Thin layer chromatography (TLC) was performed with prefabricated plates by Macherey-Nagel (silica gel 60, F254 fluorescence indicator). For development, the TLC plate was deployed in KMnO\(_4\) dip (9.00 g KMnO\(_4\), 60.0 g K\(_2\)CO\(_3\), 1.0 mL acetic acid, 900 mL demineralized H\(_2\)O) and dried carefully with a heat gun afterwards (250 °C). Purification of the crude products was conducted by flash column chromatography using silica gel 60 (40-63 µm, 230-400 mesh) from Macherey-Nagel.

\(^1\)H and \(^{13}\)C NMR spectra were recorded on a Bruker Fourier 300HD spectrometer utilising preset pulse programs. The measurements were performed at room temperature. The chemical shifts are given in parts per million (ppm). Calibration was done by referring to the residual solvent signal (CDCl\(_3\): \(^1\)H NMR: 7.26 ppm, \(^{13}\)C NMR: 77.16 ppm)\(^2,3\) in relation to tetramethylsilane. The multiplicity of the signal is reported in singlet (s), doublet (d), triplet (t), quartet (q) or multiplet (m).

High resolution mass spectra were recorded on a Thermo Scientific DFS spectrometer using electron ionization (EI) at an energy of 70 eV. GCMS measurements were performed on a Shimadzu GCMS-QP2020. As capillary column an Optima 5 HT from Macherey-Nagel was used (length: 30 m, inner diameter: 0.25 mm, film thickness: 0.25 µm).

The ionisation was accomplished by electron impact (EI) with an energy of 70 eV. Detailed information of the GCMS parameters can be found in Table S1-Table S3. GC-FID measurements were carried out on a Shimadzu GC-2010 Plus gas chromatograph with an Optima 5 MS capillary column from

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\(^2\) H. Bychkov, V. G. Rzhevskii, A. F. Gorshkova, I. A. Tkachenko, and V. V. Bychikov, "EPR Microwave Spectroscopy," American Institute of Physics, Woodbury, NY, 1963.

\(^3\) M. P. Krätschmer, "High-Resolution Nuclear Magnetic Resonance Spectroscopy," John Wiley & Sons, Inc., New York, 1978.
**Macherey-Nagel** (length: 15 m, inner diameter: 0.25 mm, film thickness: 0.25 µm). Further information of the GC parameters are summarised in Table S4 and Table S5. In both cases, *n*-dodecane was added as internal standard (ISTD) for normalization of the peak heights for comparability and in reaction optimization.

### 1.2 GCMS and GC-FID Parameters

| **Table S1:** GC parameters for GCMS measurements. |
|---------------------------------------------------|
| **GC parameters** | **Details** |
| Injection mode | Split |
| Injection volume | 1.0 µL |
| Split ratio | 20.0 |
| Injection temperature | 300 °C |
| Carrier Gas | Helium |
| Flow Control Mode | linear velocity, 40.0 cm/s |
| Column oven temperature | 100 °C, hold time: 2 min |
| RAMP1 | rate: 50 °C/min, final temperature: 250 °C, hold time: 0 min |
| RAMP2 | rate: 5 °C/min, final temperature: 280 °C, hold time: 0 min |
| RAMP3 | rate: 15 °C/min, final temperature: 350 °C, hold time: 0 min |
| Total run time | 15.67 min |

| **Table S2:** MS parameters for total ion current (TIC) GCMS measurements. |
|---------------------------------------------------|
| **MS parameters** | **Details** |
| measuring mode | scan, m/z range: 50.00 - 600.00 |
| Ion source temperature | 230 °C |
| Interface temperature | 280 °C |
| Solvent cut time | 3.8 min |
| Start time | 3.81 min |
| End time | 15.66 min |
Table S3: MS parameters for selected ion monitoring (SIM) GCMS measurements.

| MS parameters            | Details                                                                 |
|--------------------------|-------------------------------------------------------------------------|
| measuring mode           | selected ion measurement (SIM)                                          |
| selected m/z ratios      | 170.00, 178.00, 198.00, 204.00, 212.00, 228.00, 218.00, 230.00, 224.00,  |
|                          | 232.00, 238.00, 246.00, 290.00, 248.00, 254.00, 262.00, 278.00, 310.00,  |
|                          | 316.00, 324.00, 340.00, 402.00                                          |
| Ion source temperature   | 230 °C                                                                  |
| Interface temperature    | 280 °C                                                                  |
| Solvent cut time         | 3.8 min                                                                 |
| Start time               | 3.81 min                                                                |
| End time                 | 15.66 min                                                               |

Table S4: GC parameters of method A for GC-FID measurements.

| GC parameters            | Details                                                                 |
|--------------------------|-------------------------------------------------------------------------|
| Injection mode           | Split                                                                   |
| Injection volume         | 1.0 µL                                                                  |
| Split ratio              | 20.0                                                                    |
| Injection temperature    | 280 °C                                                                  |
| Carrier Gas              | Helium                                                                  |
| Flow Control Mode        | linear velocity, 40.0 cm/s                                              |
| Column oven temperature  | 100 °C, hold time: 3 min                                               |
| RAMP1                    | rate: 60.0 °C/min, final temperature: 280 °C, hold time: 14 min        |
| Total run time           | 20.00 min                                                               |
| FID temperature          | 300 °C                                                                  |
| FID makeup gas           | Nitrogen                                                                |
| Makeup flow              | 30.0 mL/min                                                             |
| FID hydrogen flow        | 40.0 mL/min                                                             |
| FID air flow             | 400.0 mL/min                                                            |
Table S5: GC parameters of method B for GC-FID measurements.

| GC parameters         | Details                                      |
|-----------------------|----------------------------------------------|
| Injection mode        | Split                                        |
| Injection volume      | 1.0 µL                                       |
| Split ratio           | 20.0                                         |
| Injection temperature | 300 °C                                       |
| Carrier Gas           | Helium                                       |
| Flow Control Mode     | linear velocity, 40.0 cm/s                   |
| Column oven temperature| 100 °C, hold time: 2 min                    |
| RAMP1                 | rate: 50 °C/min, final temperature: 250 °C, hold time: 0 min |
| RAMP2                 | rate: 5 °C/min, final temperature: 280 °C, hold time: 0 min |
| RAMP3                 | rate: 15 °C/min, final temperature: 340 °C, hold time: 0 min |
| Total run time        | 15.00 min                                    |
| FID makeup gas        | Nitrogen                                     |
| Makeup flow           | 30.0 mL/min                                  |
| FID hydrogen flow     | 40.0 mL/min                                  |
| FID air flow          | 400.0 mL/min                                 |

1.3 Electrochemical Setup

1.3.1 Drawings and Photos of the Used Electrolysis Cells

Figure S1: Drawing of the undivided electrolysis cell (left), photo of electrolysis cell with electrodes (right).
Figure S2: Top: Drawing of the divided electrolysis cell; left side: frontal view, right side: side view. Bottom: Photo of the divided electrolysis cell equipped with platinum (left compartment) and glassy carbon electrode (right compartment).
1.3.2 Alternating Current

Equation for the estimation of cumulated charge:

\[ Q_{\text{cum}} = \frac{t_1}{t_1 + t_2} \cdot t_3 \cdot \frac{I}{n \cdot F} \]

- \( Q_{\text{cum}} \): cumulated charge,
- \( t_1 \): pulse time in seconds,
- \( t_2 \): quiet time in seconds,
- \( t_3 \): total electrolysis time in seconds,
- \( I \): current in ampere,
- \( n \): amount of substance in mole,
- \( F \): Faraday’s constant.

**Figure S3**: Schematic profile for alternating current.
2. Experimental Section

2.1 General Procedures (GP)

2.1.1 General Procedure 1: Direct Current (DC) Electrolysis

Both compartments of the divided cell were equipped with a magnetic stirring bar and charged with 988 mg (3.00 mmol) TBABF₄. The supporting electrolyte was diluted with 10 mL CH₃CN in each compartment. Afterwards, 1.0 equiv. (109 mg, 0.500 mmol) of diphenyl disulfide (1), 1.0 equiv. (95.1 µL, 0.500 mmol) of di-n-butyl disulfide (2) and 1.0 equiv. (0.5 mL, 0.500 mmol) of n-dodecane (1.0 M in CHCl₃) were added in both compartments. At last, the platinum electrodes were immersed into the solution (1 cm²) and constant current was applied. The determination of the yield or the ratio in disulfide distribution was accomplished by GC-FID or GCMS analysis.

2.1.2 General Procedure 2: Alternating Current (AC) Electrolysis

Both compartments of the divided cell were equipped with a magnetic stirring bar and charged with 988 mg (3.00 mmol) TBABF₄. The supporting electrolyte was diluted with 10 mL CH₃CN in each compartment. Afterwards, 1.0 equiv. (109 mg, 0.500 mmol) of diphenyl disulfide (1), 1.0 equiv. (95.1 µL, 0.500 mmol) of di-n-butyl disulfide (2) and 1.0 equiv. (0.5 mL, 0.500 mmol) of n-dodecane (1.0 M in CHCl₃) were added in both compartments. At last, the electrodes (first compartment platinum, second compartment glassy carbon) were immersed into the solution (1 cm²) and a constant current with an alternation in electrode polarisation of 5 s (t₁ = 4 s pulse time, t₂ = 1 s quiet time) was applied. The determination of the yield or the ratio in disulfide distribution was accomplished by GC-FID or GCMS analysis.
2.2 Direct Current Electrolysis of Diphenyl Disulfide (1) and Di-n-butyl Disulfide (2) in an Undivided Cell

\[
\text{DC, } I = 10 \text{ mA}
\]

In an undivided cell 321 mg (3.02 mmol) LiClO\(_4\) were dissolved in 10 mL CH\(_3\)CN followed by the addition of 218 mg (0.998 mmol, 1.0 equiv.) diphenyl disulfide (1) and 0.2 mL (1.05 mmol, 1.0 equiv.) di-n-butyl disulfide (2). The cell was equipped with two platinum electrodes and the reaction mixture was electrolysed for 15 min (0.1 F·mol\(^{-1}\)). After electrolysis, 0.5 mL (0.500 mmol, 0.50 equiv.) of n-dodecane solution (1.0 M in CHCl\(_3\)) was added for GC analysis. The reaction solution was diluted with Et\(_2\)O and afterwards the addition of 20 mL water and 5.0 mL brine was executed. The phases were separated, the aqueous phase was extracted three times with 15 mL Et\(_2\)O and the combined organic layer was dried with Na\(_2\)SO\(_4\). The suspension was filtered, the solvent was removed under reduced pressure and the crude product was purified by column chromatography on silica gel (eluent: n-pentane). The product 7 was obtained as colourless liquid with contaminations of di-n-butyl disulfide (2) (corrected yield: 0.839 mmol, 42%, GC yield: 0.990 mmol, 50%).\(^{4}\)

\(^{1}\)H NMR (500 MHz, CDCl\(_3\)) \(\delta = 7.57 - 7.52\) (m, 2H), 7.32 (t, \(J = 7.7\) Hz, 2H), 7.22 (t, \(J = 7.4\) Hz, 1H), 2.75 (t, \(J = 7.3\) Hz, 2H), 1.70 - 1.63 (m, 2H), 1.46 - 1.36 (m, 2H), 0.89 (t, \(J = 7.4\) Hz, 3H) ppm.

\(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \(\delta = 137.8, 129.1, 127.5, 126.8, 38.8, 31.0, 21.8, 13.8\) ppm.

The analytical data are in accordance with the literature.\(^{4}\)

2.3 Direct Current Electrolysis of a Two Disulfides Matrix in a Divided Cell

\[
\text{DC, } I = 10 \text{ mA}
\]

Due to similar ratios of fronts in TLC, a complete separation by column chromatography of di-n-butyl disulfide (2) and product 7 could not be achieved. The corrected yield was determined by integral ratios in the \(^{1}\)H NMR spectra.
According to GP1, both compartments of the divided cell were charged with 988 mg (3.00 mmol) TBABF₄, 10 mL CH₃CN, 109 mg (0.500 mmol, 1.0 equiv.) diphenyl disulfide (1), 95.1 µL (0.500 mmol, 1.0 equiv.) di-n-butyl disulfide (2) and 0.5 mL (0.500 mmol, 1.0 equiv.) n-dodecane solution (1.0 M in CHCl₃) as internal standard. The solution was electrolysed at a constant current of 10 mA. After the consumption of 0.1 F·mol⁻¹, 0.5 F·mol⁻¹, 1.0 F·mol⁻¹, 2.0 F·mol⁻¹, 3.0 F·mol⁻¹ and 4.0 F·mol⁻¹ samples of both compartments were taken for GC-FID analysis. The results are summarized in Table S6 for the cathode and in Table S7 for the anode compartment. For a comparison to the alternating current electrolysis in conversion of 1 and yield of 7 see Figure S13.

Table S6: Results of GC-FID analysis in the cathodic cell compartment.

| Qcum / F·mol⁻¹ | conversion of 1 | yield of 7 |
|---------------|----------------|------------|
| 0.1           | 59%            | 57%        |
| 0.5           | 66%            | 51%        |
| 1.0           | 72%            | 46%        |
| 2.0           | 82%            | 34%        |
| 3.0           | 88%            | 26%        |
| 4.0           | 91%            | 19%        |

Table S7: Results of GC-FID analysis in the anodic cell compartment.

| Qcum / F·mol⁻¹ | conversion of 1 | yield of 7 |
|---------------|----------------|------------|
| 0.1           | 57%            | 56%        |
| 0.5           | 60%            | 52%        |
| 1.0           | 67%            | 47%        |
| 2.0           | 75%            | 38%        |
| 3.0           | 82%            | 31%        |
| 4.0           | 87%            | 25%        |

2.4 Thiolate mediated exchange reaction

![Thiolate mediated exchange reaction diagram](image-url)
In a round-bottom flask 16.5 mg (0.125 mmol, 0.25 equiv.) of sodium thiophenolate were dissolved in 1.0 mL water and 9.0 mL CH₃CN. Afterwards, 109 mg (0.500 mmol, 1.0 equiv.) diphenyl disulfide (1) and 95.1 µL (0.500 mmol, 1.0 equiv.) di-n-butyl disulfide (2) were added. The resulting solution was stirred at room temperature. After 8 min, 40 min, 80 min, 161 min, 241 min, 322 min and 1520 min samples were taken for GC-FID analysis. The results are summarized in Table S8. A comparison between the thiolate mediated exchange reaction and the alternating current electrolysis in yield of product 7 is presented in Figure S4.

Table S8: Results of the GC-FID analysis for thiolate mediated exchange reaction.

| t     | yield of 7 |
|-------|------------|
| 8 min | 0%         |
| 40 min| 1%         |
| 80 min| 3%         |
| 161 min| 6%       |
| 241 min| 11%       |
| 322 min| 11%       |
| 1520 min| 15%      |

Figure S4: Comparison of the yield in product 7 by thiolate mediated exchange reaction (red) versus the alternating current electrolysis (black). The numbers in parenthesis for the black circles representing the cumulated charge $Q_{cum}$. 
2.5 Alternating Current Electrolysis of a Two Disulfides Matrix in a Divided Cell

According to GP2 both compartments of the divided cell were charged with 988 mg (3.00 mmol) TBABF₄, 10 mL CH₃CN, 109 mg (0.500 mmol, 1.0 equiv.) diphenyl disulfide (1), 95.1 µL (0.500 mmol, 1.0 equiv.) di-n-butyl disulfide (2) and 0.5 mL (0.500 mmol, 1.0 equiv.) n-dodecane solution (1.0 M in CHCl₃) as internal standard. The solution was electrolyzed with different electrode materials at a constant current of 10 mA. After the consumption of 0.08 F·mol⁻¹, 0.4 F·mol⁻¹, 0.8 F·mol⁻¹, 1.6 F·mol⁻¹, 2.4 F·mol⁻¹ and 3.2 F·mol⁻¹ samples of both compartments were taken for GC-FID analysis. The results for the different solvents are summarized in Table S9 and Table S10. For a comparison to the direct current electrolysis in conversion of 1 and yield of 7 see Figure S13.

**Table S9:** Results of GC-FID analysis in the platinum electrode cell compartment.

| \( Q_{\text{cum}} / \text{F·mol}^{-1} \) | conversion of 1 | yield of 7 |
|-----------------------------|----------------|-----------|
| 0.08                        | 51%            | 55%       |
| 0.4                         | 55%            | 58%       |
| 0.8                         | 56%            | 57%       |
| 1.6                         | 58%            | 55%       |
| 2.4                         | 58%            | 54%       |
| 3.2                         | 58%            | 52%       |

**Table S10:** Results of GC-FID analysis in the glassy carbon electrode cell compartment.

| \( Q_{\text{cum}} / \text{F·mol}^{-1} \) | conversion of 1 | yield of 7 |
|-----------------------------|----------------|-----------|
| 0.08                        | 38%            | 39%       |
| 0.4                         | 58%            | 56%       |
| 0.8                         | 59%            | 56%       |
| 1.6                         | 60%            | 54%       |
| 2.4                         | 58%            | 54%       |
| 3.2                         | 59%            | 51%       |
2.6 Electrode material screening

According to GP2 both compartments of the divided cell were charged with 988 mg (3.00 mmol) TBABF₄, 10 mL CH₃CN, 109 mg (0.500 mmol, 1.0 equiv.) diphenyl disulfide (1), 95.1 µL (0.500 mmol, 1.0 equiv.) di-n-butyl disulfide (2) and 0.5 mL (0.500 mmol, 1.0 equiv.) n-dodecane solution (1.0 M in CHCl₃) as internal standard. The solution was electrolyzed with different electrode materials at a constant current of 10 mA. After the consumption of 0.08 F·mol⁻¹, 0.4 F·mol⁻¹, 0.8 F·mol⁻¹, 1.6 F·mol⁻¹, 2.4 F·mol⁻¹ and 3.2 F·mol⁻¹ samples of both compartments were taken for GC-FID analysis. The results for the different solvents are summarized in Table S11.

| Electrode material | Qcum / F·mol⁻¹ | conversion of 1 | yield of 7 |
|--------------------|----------------|----------------|------------|
| Pt                 | 0.4            | 55%            | 58%        |
| GC                 | 0.4            | 58%            | 56%        |
| carbon roving<sup>a</sup> | 0.8            | 54%            | 55%        |
| stainless steel (1.4571)<sup>b</sup> | 0.4            | 30%            | 29%        |
| Cu-DHP<sup>b,c</sup> | 4.0            | 9%             | <1%        |

<sup>a</sup> Higher cumulated charge was needed. <sup>b</sup> Corrosion of the electrode surface. <sup>c</sup> Formation of 7 only in traces (less than 1%).

2.7 Solvent Screening

According to GP2 both compartments of the divided cell were charged with 988 mg (3.00 mmol) TBABF₄, 10 mL solvent, 109 mg (0.500 mmol, 1.0 equiv.) diphenyl disulfide (1), 95.1 µL (0.500 mmol, 1.0 equiv.) di-n-butyl disulfide (2) and 0.5 mL (0.500 mmol, 1.0 equiv.) n-dodecane solution (1.0 M in CHCl₃) as internal standard. The solution was electrolysed at a constant current of 10 mA. After the consumption of 0.08 F·mol⁻¹, 0.4 F·mol⁻¹, 0.8 F·mol⁻¹, 1.6 F·mol⁻¹, 2.4 F·mol⁻¹ and 3.2 F·mol⁻¹ samples of
both compartments were taken for GC-FID analysis. The results for the different solvents are summarized in Table S12.

**Table S12: Results of solvent investigations, determined by GC-FID analysis.**

| Solvent / electrode | \( Q_{\text{cum}} / \text{F-mol}^{-1} \) | conversion of 1 | yield of 7 |
|---------------------|----------------------------------------|----------------|-------------|
| \( \text{CH}_3\text{CN} / \text{Pt} \) | 0.8                                    | 68%            | 56%         |
| \( \text{CH}_3\text{CN} / \text{GC} \) | 0.8                                    | 64%            | 59%         |
| \( \text{MeOH} / \text{Pt} \)     | 3.2                                    | 10%            | 18%         |
| \( \text{MeOH} / \text{GC} \)     | 3.2                                    | 27%            | 35%         |
| \( \text{DMF} / \text{Pt} \)      | 3.2                                    | 29%            | 49%         |
| \( \text{DMF} / \text{GC} \)      | 3.2                                    | 41%            | 47%         |
| \( \text{DMA} / \text{Pt} \)      | 3.2                                    | 29%            | 29%         |
| \( \text{DMA} / \text{GC} \)      | 3.2                                    | 35%            | 38%         |

2.8 Influence of Pulse and Quiet Time in Alternating Current Electrolysis

According to GP2 both compartments of the divided cell were charged with 988 mg (3.00 mmol) TBABF₄, 10 mL CH₃CN, 109 mg (0.500 mmol, 1.0 equiv.) diphenyl disulfide (1), 95.1 µL (0.500 mmol, 1.0 equiv.) di-n-butyl disulfide (2) and 0.5 mL (0.500 mmol, 1.0 equiv.) n-dodecane solution (1.0 M in CHCl₃) as internal standard. The solution was electrolysed at a constant current of 10 mA with different pulse \( t_1 \) and quiet times \( t_2 \) in the range from seconds to milliseconds. After the consumption of 0.08 F·mol⁻¹, 0.4 F·mol⁻¹, 0.8 F·mol⁻¹, 1.6 F·mol⁻¹, 2.4 F·mol⁻¹ and 3.2 F·mol⁻¹ samples of both compartments were taken for GC-FID analysis. The results are summarized in Table S13.
Table S13: Investigation on the influence of pulse and quiet time in alternating current electrolysis, determined by GC-FID analysis.

| $t_1$ | $t_2$ | Electrode / $Q_{cum}$ | conversion of 1 | yield of 7 |
|-------|-------|-----------------------|-----------------|------------|
| 4 ms  | 1 ms  | Pt / 2.4 F·mol$^{-1}$  | 55%             | 60%        |
|       |       | GC / 3.2 F·mol$^{-1}$  | 0%              | 5%         |
| 40 ms | 10 ms | Pt / 1.6 F·mol$^{-1}$  | 61%             | 55%        |
|       |       | GC / 3.2 F·mol$^{-1}$  | 50%             | 45%        |
| 400 ms| 100 ms| Pt / 0.8 F·mol$^{-1}$  | 68%             | 56%        |
|       |       | GC / 0.8 F·mol$^{-1}$  | 61%             | 63%        |
| 4 s   | 1 s   | Pt / 0.8 F·mol$^{-1}$  | 68%             | 56%        |
|       |       | GC / 0.8 F·mol$^{-1}$  | 64%             | 59%        |
| 40 s  | 10 s  | Pt / 0.4 F·mol$^{-1}$  | 53%             | 59%        |
|       |       | GC / 0.4 F·mol$^{-1}$  | 62%             | 56%        |

2.9 Excess Amount of One Disulfide

According to GP2 both compartments of the divided cell were charged with 988 mg (3.00 mmol) TBABF$_4$, 10 mL CH$_3$CN, 109 mg (0.500 mmol, 1.0 equiv.) diphenyl disulfide (1), different equivalents (from 1.0 up to 5.0 equiv.) di-n-butyl disulfide (2) and 0.5 mL (0.500 mmol, 1.0 equiv.) n-dodecane solution (1.0 M in CHCl$_3$) as internal standard. The solution was electrolysed at a constant current of 10 mA. After the consumption of 0.08 F·mol$^{-1}$, 0.4 F·mol$^{-1}$, 0.8 F·mol$^{-1}$, 1.6 F·mol$^{-1}$, 2.4 F·mol$^{-1}$ and 3.2 F·mol$^{-1}$ samples of both compartments were taken for GC-FID analysis. The results are summarized in Table S14.
Table S14: Influence of excess amount of one disulfide, determined by GC-FID analysis.

| equiv. Bu₂S₂ | Electrode / Q_{cum} | conversion of 1 | yield of 7 |
|--------------|----------------------|-----------------|------------|
| 1.0          | Pt / 1.6 F·mol⁻¹     | 68%             | 54%        |
|              | GC / 1.6 F·mol⁻¹     | 65%             | 57%        |
| 2.0          | Pt / 1.6 F·mol⁻¹     | 73%             | 83%        |
|              | GC / 1.6 F·mol⁻¹     | 75%             | 77%        |
| 3.0          | Pt / 1.6 F·mol⁻¹     | 88%             | 84%        |
|              | GC / 1.6 F·mol⁻¹     | 83%             | 89%        |
| 4.0          | Pt / 1.6 F·mol⁻¹     | 86%             | 90%        |
|              | GC / 1.6 F·mol⁻¹     | 87%             | 91%        |
| 5.0          | Pt / 1.6 F·mol⁻¹     | 90%             | 96%        |
|              | GC / 1.6 F·mol⁻¹     | 88%             | 98%        |

2.10 Control Experiments

2.10.1 Two Disulfides Matrix

![Diagram of reaction](image)

In an undivided cell 988 mg (3.00 mmol) TBABF₄ were dissolved in 10 mL CH₃CN followed by the addition of 218 mg (1.00 mmol, 1.0 equiv.) diphenyl disulfide (1), 0.2 mL (1.02 mmol, 1.0 equiv.) di-n-butyl disulfide (2) and 1.0 mL (1.00 mmol, 1.0 equiv.) n-dodecane solution (1.0 M in CHCl₃) as internal standard. The resulting solution was stirred for 2 h in absence of electricity and a sample for GCMS analysis was taken. The formation of the unsymmetrical disulfide 7 was not observed.
2.10.2 Six Disulfides Matrix

In an undivided cell 990 mg (3.01 mmol) TBABF$_4$ were dissolved in 10 mL CH$_3$CN followed by the addition of 109 mg (0.500 mmol, 1.0 equiv.) diphenyl disulfide (1), 95.1 µL (0.500 mmol, 1.0 equiv.) di-n-butyl disulfide (2), 114 mg (0.495 mmol, 0.99 equiv.) dicyclopentyl disulfide (3), 206 mg (0.511 mmol, 1.0 equiv.) di-n-dodecyl disulfide (4), 123 mg (0.499 mmol, 1.0 equiv.) di-p-tolyl disulfide (5), 143 mg (0.500 mmol, 1.0 equiv.) Bis(p-methoxyphenyl) disulfide (6) and 0.5 mL (0.500 mmol, 1.0 equiv.) n-dodecane solution (1.0 M in CHCl$_3$) as internal standard. The resulting solution was stirred for 1 h in the absence of electricity and a sample for GCMS analysis was taken. Afterwards, the cell was equipped with two platinum electrodes and the solution was electrolysed for 30 min at a constant current of 10 mA. A second sample for GCMS analysis was prepared after electrolysis.

The formation of the unsymmetrical disulfides 11, 12 and 21 (19 and 20 in traces) could be observed in the absence of electricity by GCMS analysis (see Figure S5). After electrolysis for 30 min, all unsymmetrical disulfides could be detected by GCMS analysis of the second sample (Figure S6).
Figure S5: GCMS analysis of the control experiment in absence of electricity for 1 h (total ion current mode).

The numbers in parenthesis express the [M]+ ion masses.

Figure S6: GCMS analysis of the control experiment after DC electrolysis for 30 min (total ion current mode).

The numbers in parenthesis express the [M]+ ion masses.
2.10.3 Further Investigations on the Self-Formation of Unsymmetrical Disulfide 11

The self-formation of the unsymmetrical disulfide 11 was investigated by variation of the reaction vessel material and the reaction conditions. Therefore, 109 mg (0.499 mmol, 1.0 equiv.) diphenyl disulfide (1) and 123 mg (0.499 mmol, 1.0 equiv.) di-p-tolyl disulfide (5) were dissolved in 10 mL CH₃CN, followed by the addition of 0.5 mL (0.500 mmol, 1.0 equiv.) n-dodecane solution (1.0 M in CHCl₃) as internal standard. The resulting solution was stirred for 1 h in absence of electricity and a sample for GCMS analysis was taken. The results are summarized in Table S15.

Table S15: Investigation on the self-formation of unsymmetrical disulfide 11.

| Reaction vessel      | Reaction conditions               | GCMS yield of unsymmetrical disulfide in relation to ISTD<sup>a</sup> |
|----------------------|-----------------------------------|---------------------------------------------------------------------|
| soda-lime glass vial | air atmosphere                    | 118%                                                                |
| soda-lime glass vial | light exclusion, air atmosphere   | 6%                                                                  |
| Borosilicate 3.3 round bottom flask | inert atmosphere               | 83%                                                                |
| Borosilicate 3.3 vial | air atmosphere                    | 76%                                                                |
| PTFE vessel<sup>b</sup> | air atmosphere                   | 14%                                                                |
| PTFE vessel<sup>b</sup> | air, addition of 1 g crushed borosilicate 3.3 glass | 22%                                                                |

<sup>a</sup> The yield was determined by GCMS measurements. Therefore, the integral of the unsymmetrical disulfide 11 was related towards the integrals of the internal standard. <sup>b</sup> For GCMS analysis, a self-made vial made from PTFE was used (to avoid any possible glass induced formation of the unsymmetrical disulfides).
2.11 Three and Six Disulfides Matrix

2.11.1 Three Disulfides Matrices

2.11.1.1 Mixture A

According to GP2 both compartments of the divided cell were charged with 988 mg (3.00 mmol) TBABF₆, 10 mL CH₃CN, 109 mg (0.500 mmol, 1.0 equiv.) diphenyl disulfide (1), 95.1 µL (0.500 mmol, 1.0 equiv.) di-n-butyl disulfide (2), 201 mg (0.499 mmol, 1.0 equiv.) di-n-dodecyl disulfide (4) and 0.5 mL (0.500 mmol, 1.0 equiv.) n-dodecane solution (1.0 M in CHCl₃) as internal standard. The solution was electrolysed at a constant current of 10 mA. After 0.15 F·mol⁻¹, 0.30 F·mol⁻¹, 0.45 F·mol⁻¹ and 0.80 F·mol⁻¹ samples of both compartments were taken for GCMS analysis. The steady-state in the disulfide distribution was reached after 0.80 F·mol⁻¹. The GCMS analyses are shown in Figure S7 for the platinum electrode and in Figure S8 for the glassy carbon electrode compartment.

![Graph](image)

**Figure S7:** GCMS analysis of the three disulfides matrix (mixture A, platinum electrode compartment) after AC electrolysis for 80 min (total ion current mode). The numbers in parenthesis express the [M]⁺ ion masses.
2.11.1.2 Mixture B

According to GP2 both compartments of the divided cell were charged with 988 mg (3.00 mmol) TBABF₄, 10 mL CH₃CN, 115 mg (0.500 mmol, 1.0 equiv.) dicyclohexyl disulfide (3), 123 mg (0.500 mmol, 1.0 equiv.) di-ᵦ-tolyl disulfide (5), 143 mg (0.500 mmol, 1.0 equiv.) Bis(ᵦ-methoxyphenyl) disulfide (6) and 0.5 mL (0.500 mmol, 1.0 equiv.) n-dodecane solution (1.0 M in CHCl₃) as internal standard. The solution was electrolysed at a constant current of 10 mA. After 0.15 F·mol⁻¹, 0.30 F·mol⁻¹, 0.45 F·mol⁻¹ and 0.80 F·mol⁻¹ samples of both compartments were taken for GCMS analysis. The steady-state in the disulfide distribution was reached after 0.80 F·mol⁻¹. The GCMS analyses are shown in Figure S9 for the platinum electrode and in Figure S10 for the glassy carbon electrode compartment.
Figure S9: GCMS analysis of the three disulfides matrix (mixture B, platinum electrode compartment) after AC electrolysis for 80 min (total ion current mode). The numbers in parenthesis express the [M]$^+$ ion masses.

Figure S10: GCMS analysis of the three disulfides matrix (mixture B, glassy carbon electrode compartment) after AC electrolysis for 80 min (total ion current mode). The numbers in parenthesis express the [M]$^+$ ion masses.
2.11.2 Six Disulfides Matrix

According to GP2 both compartments of the divided cell were charged with 988 mg (3.00 mmol) TBABF₄, 10 mL CH₃CN, 109 mg (0.500 mmol, 1.0 equiv.) diphenyl disulfide (1), 95.1 µL (0.500 mmol, 1.0 equiv.) di-n-butyl disulfide (2), 115 mg (0.500 mmol, 1.0 equiv.) dicyclohexyl disulfide (3), 201 mg (0.499 mmol, 1.0 equiv.) di-n-dodecyl disulfide (4), 123 mg (0.500 mmol, 1.0 equiv.) di-p-tolyl disulfide (5), 143 mg (0.500 mmol, 1.0 equiv.) Bis(p-methoxyphenyl) disulfide (6) and 0.5 mL (0.500 mmol, 1.0 equiv.) n-dodecane solution (1.0 M in CHCl₃) as internal standard. The solution was electrolysed at a constant current of 10 mA. After 0.15 F·mol⁻¹, 0.30 F·mol⁻¹, 0.45 F·mol⁻¹, 0.80 F·mol⁻¹ and 1.60 F·mol⁻¹ samples of both compartments were taken for GCMS analysis. The steady-state in the disulfide
distribution was reached after 1.60 F·mol\textsuperscript{-1}. The GCMS analyses are shown in Figure S11 for the platinum electrode and in Figure S12 for the glassy carbon electrode compartment. Furthermore, for the resolution of overlaid components in the gas chromatogram measurements in selected ion monitoring (SIM) mode were performed (see appendix Figure S15). In addition, high resolution mass spectra were recorded for the identification of all disulfides.

**HRMS (EI+) m/z [M]⁺**

- m/z [M]⁺ calcd for C\textsubscript{8}H\textsubscript{18}S\textsubscript{2} (2) 178.0844, found 178.0842;
- m/z [M]⁺ calcd for C\textsubscript{10}H\textsubscript{14}S\textsubscript{2} (7) 198.0531, found 198.0524;
- m/z [M]⁺ calcd for C\textsubscript{10}H\textsubscript{20}S\textsubscript{2} (9) 204.1001, found 204.1002;
- m/z [M]⁺ calcd for C\textsubscript{11}H\textsubscript{16}S\textsubscript{2} (14) 212.0688, found 212.0695;
- m/z [M]⁺ calcd for C\textsubscript{11}H\textsubscript{16}OS\textsubscript{2} (15) 228.0637, found 228.0632;
- m/z [M]⁺ calcd for C\textsubscript{12}H\textsubscript{10}S\textsubscript{2} (1) 218.0218, found 218.0214;
- m/z [M]⁺ calcd for C\textsubscript{12}H\textsubscript{22}S\textsubscript{2} (3) 230.1157, found 230.1159;
- m/z [M]⁺ calcd for C\textsubscript{12}H\textsubscript{16}S\textsubscript{2} (8) 224.0688, found 224.0687;
- m/z [M]⁺ calcd for C\textsubscript{13}H\textsubscript{12}S\textsubscript{2} (11) 232.0375, found 232.0377;
- m/z [M]⁺ calcd for C\textsubscript{13}H\textsubscript{18}S\textsubscript{2} (17) 238.0844, found 238.0850;
- m/z [M]⁺ calcd for C\textsubscript{14}H\textsubscript{14}S\textsubscript{2} (5) 246.0531, found 246.0533;
- m/z [M]⁺ calcd for C\textsubscript{16}H\textsubscript{30}S\textsubscript{2} (13) 290.2096, found 290.2095;
- m/z [M]⁺ calcd for C\textsubscript{13}H\textsubscript{12}OS\textsubscript{2} (12) 248.0324, found 248.0330;
- m/z [M]⁺ calcd for C\textsubscript{13}H\textsubscript{18}OS\textsubscript{2} (18) 254.0794, found 254.0798;
- m/z [M]⁺ calcd for C\textsubscript{14}H\textsubscript{14}OS\textsubscript{2} (21) 262.0481, found 262.0487;
- m/z [M]⁺ calcd for C\textsubscript{14}H\textsubscript{14}O\textsubscript{2}S\textsubscript{2} (6) 278.0430, found 278.0433;
- m/z [M]⁺ calcd for C\textsubscript{16}H\textsubscript{30}S\textsubscript{2} (10) 310.1783, found 310.1783;
- m/z [M]⁺ calcd for C\textsubscript{18}H\textsubscript{36}S\textsubscript{2} (16) 316.2253, found 316.2251;
- m/z [M]⁺ calcd for C\textsubscript{19}H\textsubscript{32}S\textsubscript{2} (19) 324.1940, found 324.1938;
- m/z [M]⁺ calcd for C\textsubscript{19}H\textsubscript{32}OS\textsubscript{2} (20) 340.1889, found 340.1882;
- m/z [M]⁺ calcd for C\textsubscript{24}H\textsubscript{50}OS\textsubscript{2} (4) 402.3348, found 402.3342.
**Figure S11:** GCMS analysis of the six disulfides matrix (platinum electrode compartment) after AC electrolysis for 160 min (total ion current mode). The numbers in parenthesis express the \([M]^+\) ion masses.

**Figure S12:** GCMS analysis of the six disulfides matrix (glassy carbon electrode compartment) after AC electrolysis for 160 min (total ion current mode). The numbers in parenthesis express the \([M]^+\) ion masses.
2.11.2.1.1 Expanding from Two Disulfides Matrix to Six Disulfides Matrix

According to GP2 both compartments of the divided cell were charged with 988 mg (3.00 mmol) TBABF₄, 10 mL CH₃CN, 109 mg (0.500 mmol, 1.0 equiv.) diphenyl disulfide (1), 95.1 µL (0.500 mmol, 1.0 equiv) di-n-butyldisulfide (2) and 0.5 mL (0.500 mmol, 1.0 equiv.) n-dodecane solution (1.0 M in CHCl₃) as internal standard. For a stepwise expansion of the matrix, the solution was electrolysed in each step at a constant current of 10 mA. After 15 min (0.15 F·mol⁻¹) samples of both compartments were taken for GCMS analysis, the next disulfide was added and the expanded matrix was electrolysed subsequently for 15 min (0.15 F·mol⁻¹). The described procedure was performed for didodecyl disulfide (4; 201 mg, 0.500 mmol, 1.0 equiv.), dicyclohexyl disulfide (3; 0.11 mL, 0.500 mmol, 1.0 equiv.) di-p-tolyl disulfide (5; 123 mg, 0.500 mmol, 1.0 equiv.) and Bis(p-methoxyphenyl) disulfide (6; 143 mg, 0.500 mmol, 1.0 equiv.). In each step, the expected formation of the unsymmetrical disulfides was observed. The GCMS analysis are shown in the appendix (Figure S16-Figure S20).

2.11.2.1.2 Mixing the Three Disulfides Containing Matrices A and B Towards Six Disulfides Matrix

For the mixing of both three disulfides matrices A and B, 5.0 mL of mixture A and 5.0 mL of mixture B were added in both cell compartments of the divided cell. The solution was electrolysed at a constant current of 10 mA. After 0.15 F·mol⁻¹, 0.80 F·mol⁻¹ and 1.60 F·mol⁻¹ samples of each compartment were

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Note: The three disulfide matrices A and B were mixed directly before electrolysis (1-3 min). Prior mixing of the matrices (for example one day before electrolysis) showed in initial experiments the self-formation of all 21 disulfides without applying electric current due to residues of active species in matrices A and/or B. Another possibility for removal of the active species in the three disulfides matrices is a filtration over a small plug of silica gel prior electrolysis (for example in a Pasteur pipette).
taken for GCMS analysis. In both compartments the formation of all 21 disulfides analog to the six disulfide matrix was observed (see appendix Figure S21 and Figure S22).

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Appendix

Comparison between DC and AC electrolysis

Figure S13: Comparison between DC and AC electrolysis in yield of mixed disulfide 7 and conversion of 1.

Selected Ion Monitoring GCMS Analysis of the Six Disulfides Matrix

Figure S14: Full spectrum of the selected ion monitoring chromatogram (platinum electrode compartment, 160 min (1.6 F-mol⁻¹)).
Figure S15: Peak resolution of overlaid disulfide peaks in total ion current chromatogram by using selected ion monitoring measurement mode.
GCMS Analysis for Matrix Expanding

Note: The depicted figures herein represent the analytical results from the glassy carbon electrode compartment. The results of the platinum electrode compartment are not represented because the same observations were made (in comparison).

Figure S16: GCMS analysis for matrix expanding (starting with disulfides 1 and 2).

Figure S17: GCMS analysis for matrix expanding (after addition of disulfide 4 and AC electrolysis for 15 min).
Figure S18: GCMS analysis for matrix expanding (after addition of disulfide 3 and AC electrolysis for 15 min).

Figure S19: GCMS analysis for matrix expanding (after addition of disulfide 5 and AC electrolysis for 15 min).
Figure S20: GCMS analysis for matrix expanding (after addition of disulfide 6 and AC electrolysis for 15 min).

GCMS Analysis for Matrix Mixing

Figure S21: GCMS analysis for mixing of matrices A and B (after AC electrolysis for 15 min, platinum electrode compartment).
Figure S22: GCMS analysis for mixing of matrices A and B (after AC electrolysis for 15 min, glassy carbon electrode compartment).

Figure S23: Mass spectra (EI(+), 70 eV) of unsymmetrical disulfide 7.
Figure S24: Mass spectra (El(+), 70 eV) of unsymmetrical disulfide 8.

Figure S25: Mass spectra (El(+), 70 eV) of unsymmetrical disulfide 9.
**Figure S26**: Mass spectra (El(+), 70 eV) of unsymmetrical disulfide 10.

**Figure S27**: Mass spectra (El(+), 70 eV) of unsymmetrical disulfide 11.
Figure S28: Mass spectra (El(+), 70 eV) of unsymmetrical disulfide 12.

Figure S29: Mass spectra (El(+), 70 eV) of unsymmetrical disulfide 13.
Figure S30: Mass spectra (EI(+), 70 eV) of unsymmetrical disulfide 14.

Figure S31: Mass spectra (EI(+), 70 eV) of unsymmetrical disulfide 15.
Figure S32: Mass spectra (El(+), 70 eV) of unsymmetrical disulfide 16.

Figure S33: Mass spectra (El(+), 70 eV) of unsymmetrical disulfide 17.
Figure S34: Mass spectra (El(+), 70 eV) of unsymmetrical disulfide 18.

Figure 35: Mass spectra (El(+), 70 eV) of unsymmetrical disulfide 19.
Figure S36: Mass spectra (EI(+), 70 eV) of unsymmetrical disulfide 20.

Figure S37: Mass spectra (EI(+), 70 eV) of unsymmetrical disulfide 21.