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# Investigation of the electrosynthetic pathway of the aldol condensation of acetone

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## Abstract

The potential-controlled electrochemical aldol condensation of acetone to diacetone alcohol in a standard batch electrolysis set-up was studied in this work. It is confirmed that the reaction proceeds at the cathode and that, contrary to what is mentioned in earlier literature, water in the electrolyte has a disadvantageous effect on the reaction. Similar to the chemical reaction, the electrochemical reaction reaches a maximum yield when the equilibrium is reached. Separating the anode and cathode prevents cross-over and degradation of products, leading to a higher yield. Starting with pure acetone and support electrolyte, it was possible to obtain a diacetone alcohol concentration of 15 m% after two hours electrolysis in a divided set-up with a platinum electrode at -2.5 V. The concentration gradient throughout the electrolysis follows an exponential curve up to its equilibrium concentration.

### *Keywords:*

acetone condensation, diacetone alcohol, electrosynthesis

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## 1. Introduction

Acetone is the starting material to a broad range of products and intermediates [1, 2]. The aldol condensation of acetone initially produces 4-hydroxy-4-methyl-pentan-2-one, commonly known as diacetone alcohol (DAA) (see figure 1). Diacetone alcohol is an industrially useful and important product with a number of applications. It is used as a solvent in varnishes, paints, cellulose acetate lacquer, thinners and in cleaning compounds and is considered to be an environmentally friendly alternative to other materials such as acetone due to its much lower volatility [3]. It is also an intermediate to other industrially important products. The dehydration of diacetone alcohol yields mesityl oxide, a useful compound with various applications, but primarily it is the precursor of methyl isobutyl ketone (MIBK), a popular solvent used mainly in the paint and coating industry [4] and the largest volume aldol reaction product of acetone [2]. Heavier products from acetone such as phorone, isophorone and 3,5-xyleneol are formed by self-condensation or cross-condensation between the same or different ketones that are formed in the reaction and also find many applications. To optimize the yield of the desired product DAA, further condensation reactions have to be prevented without shifting the equilibrium towards the dehydration product mesityl oxide. A high-performance catalyst which not only gives high DAA yields, but also a high selectivity is required and thus, much attention has been given to the catalyst.

Conventionally, the aldol condensation of acetone is conducted using a homogeneous base catalyst such as NaOH and KOH [2, 5]. Some major drawbacks are associated with the homogeneity and basic nature of the catalysts. The strong bases require specific measures to prevent corrosion problems which leads to high capital costs. The homogeneity of the catalyst requires intense purification afterwards in which the catalyst often is destroyed. In the conventional process, phosphoric acid is added to neutralise the catalyst and stabilize DAA, after which DAA is recovered by evaporation and stripping of the acetone, which is then recycled [1, 6]. This neutralisation step must be accurately controlled as

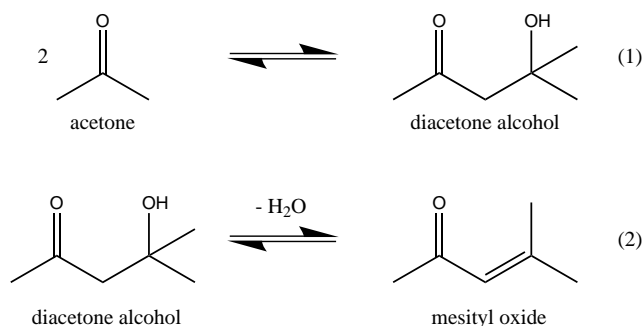


Figure 1: Aldol addition of acetone to diacetone alcohol (1) and dehydration of diacetone alcohol to mesityl oxide (2) to complete the aldol condensation. Reaction 1 is of interest in this work.

an excess of acid causes facile dehydration of DAA to MO [7]. The neutralisation process and subsequent purification steps by distillation entail a high cost and produce large amounts of waste streams. It has been estimated for these compounds that product purification, recovery and waste treatment account for 30 % of the selling price [8].

Because of the disadvantages inherent to the homogeneous catalysts, heterogeneous systems offer a viable alternative. Solid acid-base catalysts are becoming increasingly important in chemical and life science industry as they have many advantages over homogeneous liquid acid-base catalysts [8, 9]. Separation of the product stream is much easier, reducing purification costs and increasing catalyst life. They are more environmentally friendly than the homogeneous catalysts and are non-corrosive, making safe handling and disposal easier. Zeolites, oxides and ionic exchange resins make up about 80 % of the types of solid acid-base catalysts used in industrial processes while dehydration and condensation reactions most often use these types of catalysts [9]. Some commercial installations for the production of DAA use fixed-bed reactors employing solid alkaline catalysts such as Ba(OH)<sub>2</sub> and Ca(OH)<sub>2</sub>. However, self-condensation of acetone to diacetone alcohol is a reversible exothermic reaction which is equilibrium limited with the equilibrium strongly favouring acetone. (see table 1). To obtain a reasonable yield, commercial operations are conducted at 10-20

°C with typical residence times of 20-60 minutes. A lower temperature has a favourable effect on the equilibrium of the reaction, but results in slower kinetics, giving a maximum possible conversion of acetone of 15 % per pass at 15 °C [6]. Furthermore, many of the catalysts are susceptible to alkali dissolution and end up in the product stream.

Table 1: Equilibrium conversions of acetone to DAA [10].

Temperature (°C)	0	10	20	30
Conversion (wt%)	23.1	16.9	12.1	9.1

To meet the requirements of the toughening environmental regulations and economical demands of the industry, lots of attention has been focused on improving the catalyst of the reaction to increase the yield of diacetone alcohol or mesityl oxide. Different types of basic catalysts have been proposed for the condensation of acetone to diacetone alcohol, such as metal hydroxides [11, 12], metal oxides [11, 13–16] promoted with alkali or alkaline earth metal ions [17], mixed metal oxides [18, 19], layered double hydroxides [20, 21] and anionic and cationic exchange membranes [22–25]. Besides improving the catalyst, some research also focuses on a different reaction technique instead of conventional batch reactors or fixed-bed reactors, such as catalytic distillation [16, 23–26]. Nicol [24] concluded that catalytic distillation is the inferior option compared with the conventional separate reaction and distillation process for DAA production, Podrebarac et al. [23] came to a similar conclusion. Both mention factors attributed to the catalyst as the main cause, which is also concluded by Huang et al. [27]. Nicol further notes that the decoupled temperature and pressure dependence in the conventional process is a major advantage that the reactor costs will be minimal because of the mild reaction temperature and pressure.

The findings by Nicol, Podrebarac, Huang and others make way for an alternative production process for diacetone alcohol that combines the benefits of mild reaction conditions and heterogeneous catalysis, namely electrosynthe-

sis. Electrosynthesis uses electrons to activate molecules, making it a versatile and inherently environmentally friendly technique and therefore it is being considered as a "clean" and "green" process [28]. Electrosynthesis offers several important advantages to conventional synthetic methods, such as less aggressive process conditions (reactions can be carried out at ambient temperature and pressure), higher selectivity (precise control of reaction by control of electrode potential), ability to produce unstable or hazardous reagents in situ and less generation of pollutants and waste streams [29–31]. Though electrochemical processes often proceed in dilute solutions which require a purification afterwards to increase the concentration of the target product, its properties imply a much less profound and costly purification than the conventional chemical route [28]. Due to the increased selectivity (less byproducts, if any), the absence of a catalyst which has to be removed or regenerated and the readily reusable product stream a single separation step such as a simple distillation (in contrary to a complex rectification), membrane separation or absorption step can be sufficient. The advantages inherent to electrosynthesis make it an interesting and useful alternative: more than 100 processes have been piloted and more than 70 have been commercialised in the industry [29, 32].

The electrochemical aldol condensation has been investigated by Shono et al. [33]. They report the self- and cross-condensation of a small number of aldehydes at a platinum electrode in dimethylformamide (DMF) with a quaternary ammonium salt as supporting electrolyte. The reactions proceed at reduction potentials of -1.8 to -2.1 V vs. the saturated calomel electrode (SCE) with yields of about 75 %. Shono et al. suggest that the reaction proceeds indirectly through the formation of an electrogenerated base (EGB). Electrogenerated bases are most commonly radical anions, anions or dianions, which after formation initiate another reaction [30, 31]. A similar investigation was performed by Kumar et al. [34] who studied the aldol condensations of propanal with itself and with a small number of other aldehydes. They also used a platinum electrode, but the electrolyte consisted of 50 % DMF and 50 % water with KCl as supporting electrolyte. The reactions take place in a potential range of

-1.55 to -2.20 V vs. SCE with yields of 55 - 80 %. Kumar et al. also suggest that the reaction proceeds through the formation of an EGB, but propose a more detailed possible mechanism. The electrochemical aldol condensation of diacetone alcohol was also briefly investigated by Tsai et al. who reported the results in three papers [35–37]. Similar to Shono et al. and Kumar et al. these papers describe a preliminary investigation to the feasibility of the reaction, which confirms the possibility of the electrochemical pathway, but offers no information towards industrial development or implementation. In the first investigation [35], a solution of 4 M acetone in water with 2.5 M KCl was galvanostatically electrolysed, which resulted in millimolar concentrations of diacetone alcohol and cell potentials ranging from 3.2 to 5.2 V. When the acetone concentration was increased to 10 M in the set-up used, the potential further increased to 14 V. The high potentials correspond with a high energy consumption and the high concentration of support electrolyte requires thorough purification. These conditions, together with the low concentration of DAA that is obtained, are far from those that are required for an industrial feasible process. In the second investigation [37], pure acetone was galvanostatically electrolysed with lower concentrations of supporting electrolyte and lower cell potentials due to the lower current applied to the cell (though potentials up to 30 V are mentioned when the batch set-up is slightly altered and the inter-electrode distance approaches 2 cm). This resulted in a 2.8 % yield of DAA after a 2 hour run. Though a maximum begin concentration of reactants is desirable from a production point of view, such a low yield is insufficient when contemplating further industrial relevant development.

In this work a first investigation towards the efficiency of the production of diacetone alcohol from acetone by electrosynthesis is presented. This means an evaluation of the parameters that influence the reaction, such as the electrolyte composition, the electrolysis potential and the electrode material in regards to the yield of DAA while keeping the industrial viability in mind. Thus optimization towards a high yield and high selectivity in a reasonable time span is desirable, but with attention given to factors such as material cost, energy

consumption and simplicity of the reaction in regards to the set-up and further purification. Shono et al. and Kumar et al. have demonstrated the possibility of an electrochemical aldol condensation (albeit indirectly) and Tsai et al. have confirmed this for the aldol reaction of acetone to diacetone alcohol. Though, besides the confirmation, no further effort has been made towards the optimization of the reaction, especially with further industrial development in mind. This is shown by the fact that the reaction is conducted by galvanostatic electrolysis instead potentiostatic electrolysis with no attention given to the resulting potentials. This made it possible to perform the desired reaction but with very large potentials which connotes high energy costs or with very low yields. In this work, the electrolysis is potential-controlled. This way, an important factor that contributes to the viability is always taken into account.

## 2. Experimental

### 2.1. Chemicals

Acetone (HPLC grade,  $\geq 99.9$  % purity) was purchased from Biosolve BV (The Netherlands). The supporting electrolyte tetrabutylammonium perchlorate ( $n\text{-Bu}_4\text{NClO}_4$ , electrochemical analysis grade,  $\geq 99.0$  % purity) was purchased from Sigma-Aldrich (Belgium). The water used in this study was ultra-pure water ( $18.2 \text{ M}\Omega\cdot\text{cm}$ ) purified in the laboratory (Milli-Q, Millipore, USA).

### 2.2. Electrochemical experiments

The controlled-potential electrolysis experiments were conducted in a batch set-up in a conventional three-electrode configuration. A saturated Ag/AgCl was used as the reference electrode and a platinum sheet electrode ( $8 \text{ cm}^2$ ) was used as auxiliary electrode (all potentials in this work are reported versus Ag/AgCl). The potential was controlled by a VSP-300 potentiostat from Biologic (France). In the standard set-up the electrodes were placed in a glass recipient at a fixed inter-electrode distance, which was 1 cm between the working electrode and the reference electrode and 2 cm between the working electrode



and the auxiliary electrode. In the divided cell set-up, a glass container with a fritted glass disc bottom (4-15  $\mu\text{m}$  pores, 3 mm thick) was used to separate the cathode half-cell and anode half-cell. The resistance of this junction was found to be 100  $\Omega$ , which was accounted for. To prevent sampling errors due to local differences in electrolyte composition during the electrolysis, the cell was stirred thoroughly for 10 seconds before a sample was taken from the centre of the cell.

### *2.3. Analysis*

Analysis of the samples was performed by GC-FID (Thermo Scientific Trace 1300) on a polar capillary column (Restek RTX-Wax 30 m x 0.25 mm, PEG 0.25  $\mu\text{m}$ ). The carrier gas flow ( $\text{N}_2$ , 5.0 purity) was controlled at 1.0 ml/min. The temperature of the column was held constant at 40  $^\circ\text{C}$  for 3 minutes and then ramped to 200  $^\circ\text{C}$  at 40  $^\circ\text{C}/\text{min}$ . This gave excellent separation of the target products allowing easy quantification. High temperature favours the equilibrium of the reaction to acetone [10], leading to possible decomposition of DAA during the analysis. However, all samples were analysed 4 times with a corresponding standard deviation of less than 5 %. Calibration curves could be reproduced within the same standard deviation. Contrary to the expected effect of the high analysis temperature, a small amount of acetone is converted to diacetone alcohol during the GC analysis yielding 0.1 w% DAA in a blank sample. This is accounted for in the results.

## **3. Results and discussion**

### *3.1. Validation of the electrosynthetic pathway*

Prior to the investigation and optimization of the parameters that influence the reaction, a validation of the electrochemical aldol condensation was performed by means of a batch electrolysis in the standard set-up as described in section 2.2. Both the working and auxiliary electrode were platinum sheet electrodes of 8  $\text{cm}^2$ , the electrolyte consisted of 100 ml acetone with 0.1 M tetrabutylammonium perchlorate (TBAP). The potential was set at -2.5 V.

This potential was chosen similar to the potentials reported by Shono et al. [33] and Kumar et al. [34] and also considering that organic reductions often proceed in this potential range [30]. The experiment ran for seven hours and each hour a sample was taken from the cell. During the experiment, the solution turns from colourless to pale yellow and finally even a dark orange or brownish colour. Such a discolouration is also reported by Kumar et al. In all experiments, this discolouration was observed. This effect could not be directly assigned to a certain product in the GC-analysis results as there were no obvious correlations. To find the origin of this colour change, additional experiments in the same configuration were performed, but instead of homogenising the solution before sampling, local samples were taken close to the electrode (where the discolouration originates) and in the bulk. GC-analysis of these samples showed a positive correlation between mesityl oxide, the dehydration product of DAA and the amount of discolouration in the solution. To confirm this result and the cause of the colour change, UV-VIS-spectroscopy measurements were performed on the samples and compared to literature and analytical standards. Literature reports a mesityl oxide absorption peak at 235 nm (NIST) which shifts to 230-232 nm in hexane. Measurement of an analytical standard of mesityl oxide in heptane gave an absorption peak at 231 nm. Measurements of the samples in heptane gave a distinct absorption peak at 231.5 nm agreeing well with both the analytical standard and literature. These results confirm that mesityl oxide, though obtained in very small concentrations, is the cause of the discolouration of the solution during the experiments. Figure 2 shows the analysis results of the electrolysis experiment.

The concentration of DAA increases steadily over the time of the experiment, though with a less steep inclination after the first three hours. This is reflected in the formation rate of DAA which over the course of the entire experiment is  $2.20 \times 10^{-3}$  M/min., but is as high as  $4.01 \times 10^{-3}$  M/min. for the first 3 hours and as low as  $1.15 \times 10^{-3}$  M/min. for the last 3 hours. The selectivity towards DAA increases from 85 % after the first hour to 90 % after three hours and then remains about constant (selectivity calculated from relative peak area in GC-

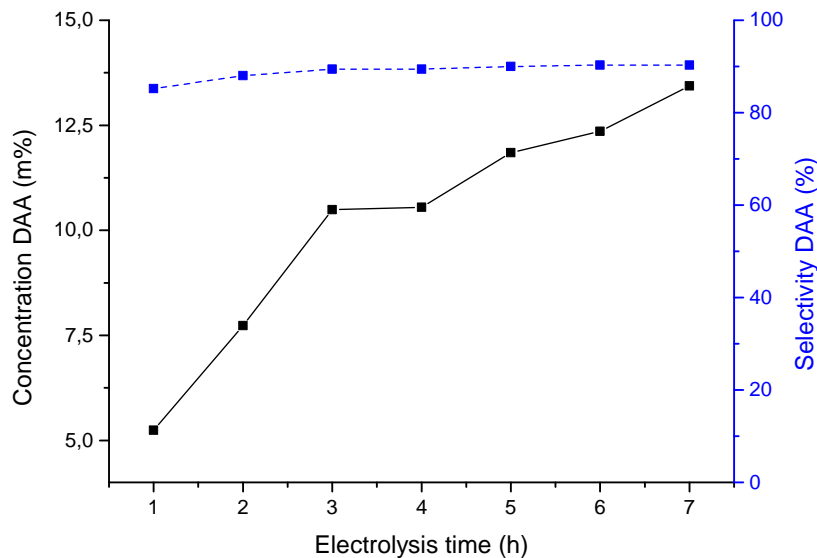


Figure 2: Concentration of DAA per hour (black squares connected by solid line, left y-axis) and corresponding selectivity (blue squares connected by dashed line, right y-axis) in a batch electrolysis in the standard set-up. Working electrode and auxiliary electrode: platinum sheet ( $8 \text{ cm}^2$ ), potential:  $-2.5 \text{ V}$ , runtime: 7 hours.

FID analysis). The final concentration of DAA after seven hours was  $13.4 \text{ m}\%$ . An experiment that ran under the same conditions for 32 hours showed that no significant increase in the concentration of DAA was noticeable after eight hours (results not shown). After two hours the concentration of DAA was  $7.7 \text{ m}\%$ , which is more than half of the final concentration. In further experiments, the runtime will be limited to two hours as then sufficient DAA has formed to evaluate the result.

### 3.2. Electrolysis potential

The first major parameter to be investigated is the electrolysis potential since it's directly linked to the energy requirement of the system. A high(er) potential implies a high(er) energy demand for the system and vice versa. A lower potential is thus desirable, but a lower potential means slower kinetics for

a process under electrical charge transfer control and hence a balance has to be found between the potential applied to the cell and the amount of product that can be formed in a certain time. Seven experiments were conducted with the potential varying from -1 V to -4 V in steps of 0.5 V. The current responses of the different experiments are plotted in figure 3.

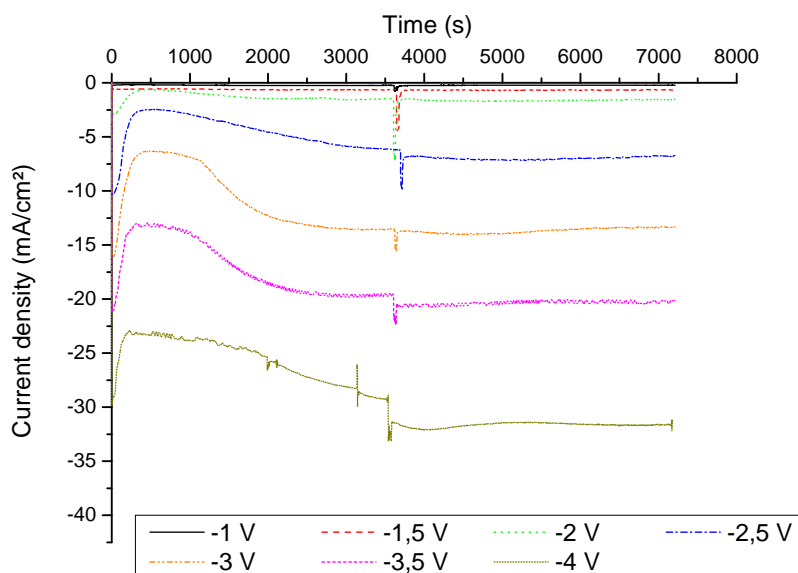


Figure 3: Current densities of separate batch electrolysis experiments at different potentials. Standard set-up, working electrode and auxiliary electrode: platinum sheet ( $8 \text{ cm}^2$ ), runtime: 2 hours.

It is immediately clear that the current density increases as the potential increases to a more negative value, i.e. for each potential step from -1 V to -4 the resulting current density is larger. All plots also display the same behaviour: a larger (cathodic) current in the beginning, which rapidly decreases to a minimum and then slowly increases to a steady value. The large current in the beginning is due to the abundance of electroactive species at the surface of the electrode, which can react immediately at the beginning of the experiment. After this immediate reaction, more molecules need to be transferred to the electrode from

the bulk and the current decreases to a minimum. A concentration gradient will drive molecules from the bulk to the electrode until the reaction is mass transfer-controlled and hence, the current slowly increases to a steady value. Since the solvent provides the electroactive species, there is no decrease of the current over time in the measured time frame as would be expected when using a small concentration of electroactive species due to the abundance of molecules in proximity of the electrode. At about one hour into the experiment, a sharp peak of the cathodic current toward more negative values can be discerned. The cause of this peak is the sampling procedure (see section 2.2). A sample was taken after one hour of electrolysis and at the end of the experiment and analysed as described in section 2.3.

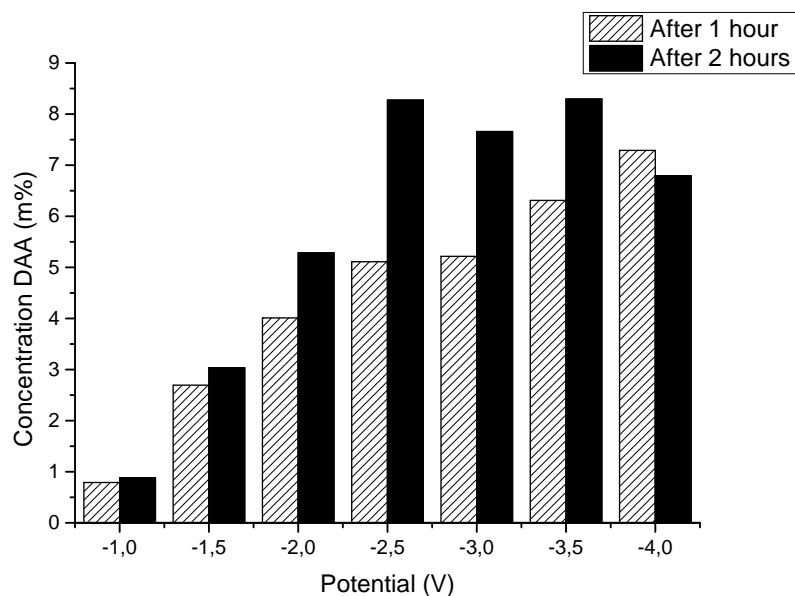


Figure 4: The concentration of DAA in separate experiments in the standard set-up with a different potential applied in each experiment, after one hour of electrolysis (hatched columns) and after two hours of electrolysis (black columns). Working electrode and auxiliary electrode: platinum sheet ( $8 \text{ cm}^2$ ), runtime: 2 hours.

Figure 4 shows the results of the analyses. The DAA concentration increases

as the potential increases to a larger negative value up to -2.5 V and then remains more or less constant up to -3.5 V, at -4 V the final concentration decreases a little. During the experiments, a discolouration is observed, going from a barely noticeable pale yellow colour at -1 V to a dark orange/brownish colour at -2.5 V, this discolouration is known to be caused by the formation of mesityl oxide (see section 3.1). At -3 V and further, the solution gets a very dark brown colour and at -4 V small amounts of precipitation become visible. Larger potentials give a larger drive for the reaction and faster kinetics but also give rise to several side reactions, as indicated by the increasing discolouration and decreasing selectivity towards DAA as shown in figure 5. The selectivity shows a maximum of about 95 % at -1.5 V and -2 V and decreases rapidly at higher potentials to a minimum of 70 % after 2 hours at -4 V.

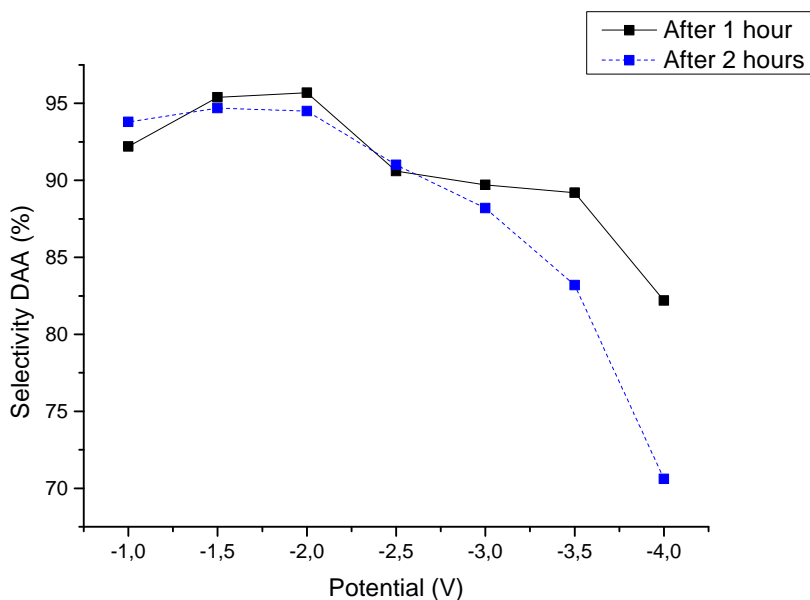


Figure 5: The selectivity towards DAA in separate experiments in the standard set-up with a different potential applied in each experiment, after one hour of electrolysis (black squares connected by solid line) and after two hours of electrolysis (blue squares connected by dashed line). Working electrode and auxiliary electrode: platinum sheet (8 cm<sup>2</sup>), runtime: 2 hours.

In addition, from [38] we know that, at potentials of -3 V and more negative, the boundary of the potential window of the supporting electrolyte is reached and its stability is compromised. The supporting electrolyte can then be reduced or oxidized itself and react with the solvent. The decrease in DAA concentration at -4 V can be the result of the competition of the side reactions or due to breakdown of the molecule by these reactions. It is also clear that in the first hour more DAA is formed than in the second hour of the electrolysis while this is not immediately visible in the current response. It is possible that products of the reaction or a side-reaction adsorb on the electrode and block the surface. From the analyses (not shown) it is also clear that more DAA converts to MO in the second hour, which logically follows from the fact that the DAA concentration increases as well (except for -4 V). When looking at the relative increments of the DAA concentration between the different experiments it is obvious that these are smaller than the relative increments of the corresponding current densities in figure 3, e.g. the current more than doubles between the -2 V and -2.5 V experiments while the final DAA concentration increases only by slightly more than 50 %. This is even more obvious at the higher potentials as the current keeps increasing, but the final concentration does not. This is a first indication of occurring side-reactions, which do not contribute to the formation of DAA. The extend of this effect can be seen by plotting the current efficiency of each experiment. Since the exact reaction mechanism is not known here, the current efficiency cannot be calculated by means of stoichiometric calculations. However, a measure for the current efficiency can be used by dividing the DAA concentration by the charge passed in the cell since both are connected through Faraday's law of electrolysis [39]. In this work this approximation is referred to as the current efficiency.

Figure 6 shows the current efficiency for each experiment. The current efficiency is always the highest in the first hour, which corresponds to the earlier noted observation that the increase in DAA concentration is less in the second hour than in the first hour. The ratios of the current efficiencies between the experiments stays the same for both hours with the maximum efficiency ob-

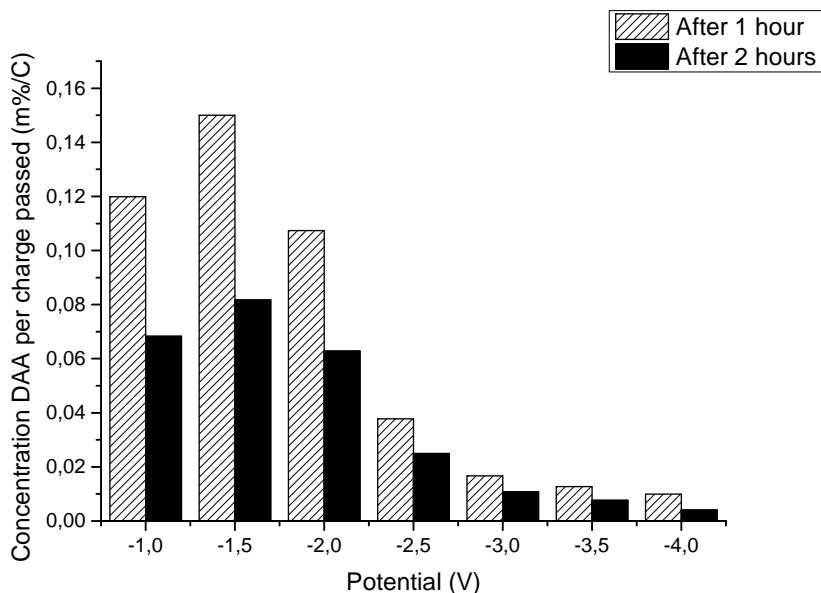


Figure 6: The DAA concentration per charge passed as a measure for current efficiency in separate experiments in the standard set-up with a different potential applied in each experiment, after one hour of electrolysis (hatched columns) and after two hours of electrolysis (black columns). Working electrode and auxiliary electrode: platinum sheet (8 cm<sup>2</sup>), runtime: 2 hours.

tained at -1.5 V. After 2 hours of electrolysis, -1 V and -2 V have a similar efficiency, which is about 20 % lower than the -1.5 V efficiency. The current efficiency decreases rapidly at potentials more negative than -2.5 V. From an energy-efficiency point of view -1.5 is the optimal potential as it has the highest current efficiency while from a production point of view -2.5 V is preferable since, compared to -1.5 V, it still has a significant increase in DAA concentration while not exhibiting the drawbacks of numerous side reactions and stability issues as encountered at potentials of -3 V and more negative. Combining both concerns, -2 V is the golden mean as the final DAA concentration is about halfway between -1.5 V and -2.5 V while the efficiency leans more towards the maximum of -1.5 V, additionally the selectivity towards DAA is also the highest



at this potential.

### 3.3. Influence of water in the electrolyte on the yield of DAA

The aldol addition or condensation can be catalysed by either an acid or a base [5] and thus, adding water to the electrolyte can be beneficial as the electrolysis of water generates in-situ acids and bases in the form of  $H^+$  and  $OH^-$ . The possible advantage of water in the electrolyte is also mentioned by Tsai et al. [37]. To investigate this effect, a series of experiments was conducted in the standard set-up with different amounts of ultrapure water added to the electrolyte in following concentrations: 0, 0.5, 1, 2, 5, 8, 10 and 12 m%. Figure 7 shows the results of the experiments. Acetone is a hygroscopic substance and always contains a small amount of water unless dried thoroughly. The acetone used in this work has a maximum water content of 0.1 %, thus the 0 m% described in the experiments contains this amount of water. To evaluate the influence of this tiny amount of water, an experiment with dried acetone (Extra Dry, Acroseal<sup>®</sup>,  $\geq 99.8\%$  pure,  $H_2O \leq 0.005\%$ , obtained from Acros) was conducted under inert atmosphere and in presence of molecular sieves (3A). The difference between the regular HPLC acetone and the dried acetone was negligible (results not shown).

In figure 7 it is clear that adding water does not have a beneficial effect for the production of DAA. The maximum DAA concentration is obtained when no water is added to the electrolyte. For any amount of water added, the resulting DAA concentration is significantly lower. The possible beneficial effect of the in-situ generated base in the form of  $OH^-$  is non-existent or much smaller than the disadvantageous effect of the water electrolysis. The electrolysis of the water is also observed visually during the experiment. The addition of water causes the formation of bubbles at the cathode and higher concentrations of water increase the amount of bubble formation, indicating the evolution of hydrogen on the cathode. Besides causing a competitive electrochemical reaction to the aldol addition of acetone (or to the generation of the required EGB), the water also slows down the rate of the chemical aldol addition of acetone [22, 26], which

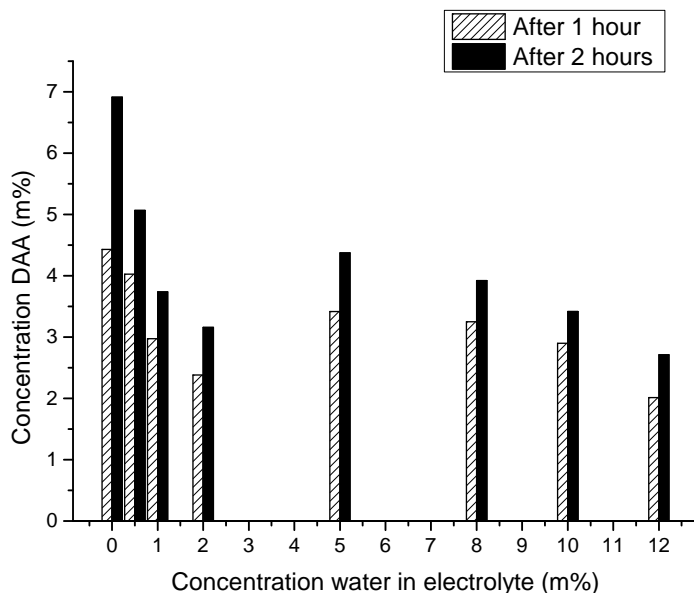


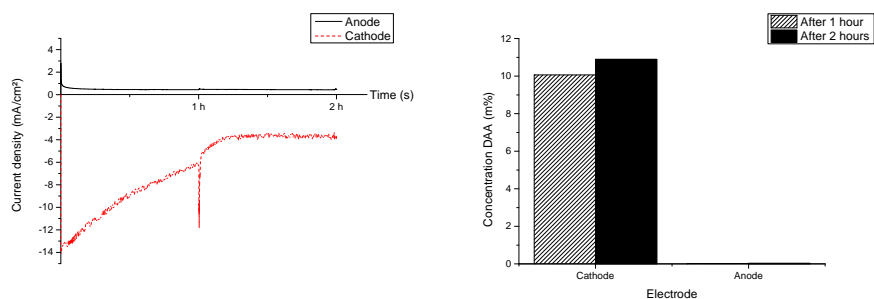
Figure 7: The concentration of DAA in separate experiments in the standard set-up with water added to the electrolyte, after one hour of electrolysis (hatched columns) and after two hours of electrolysis (black columns). Working electrode and auxiliary electrode: platinum sheet (8 cm<sup>2</sup>), potential: -2.5 V, runtime: 2 hours.

could be a possible additional inhibition for the reaction via the EGB. Tsai et al. propose reactions at both the cathode and anode for the indirect reaction via the electrolysis of water [35]. The effect of the addition of water described by Tsai et al. does not correspond with the results obtained in this work and the indirect reaction by the electrolysis of water is therefore disputed.

#### 3.4. Comparing the contribution of the anode and the cathode

Although the electrosynthetic aldol condensation is usually approached as purely an organic reduction, there are possible contributions of the anode to the reaction. In addition to the indirect reaction via the electrolysis of water, Tsai et al. also propose reactions at both the cathode and anode for the reaction via an EGB. Therefore, it is still interesting to investigate both electrodes separately to see the contribution of each towards the reaction through the formation of

an EGB. To this end two experiments were conducted in the divided set-up as described in 2.2 where the potential applied to the working electrode was  $-2.5$  V and  $+2.5$  V to investigate respectively the cathode and anode. Figure 8a shows the current responses of both experiments. The anodic current density peaks at about  $2.8$  mA/cm<sup>2</sup> in the beginning and quickly declines to  $1$  mA/cm<sup>2</sup> after which it steadily decreases over the course of two hours to less than  $0.5$  mA/cm<sup>2</sup> in the end. The cathodic current on the other hand, peaks at  $-14$  mA/cm<sup>2</sup> in the beginning, then decreases to about  $-4$  mA/cm<sup>2</sup> and remains constant around this value. As expected, the current response of the cathode is much larger than that of the anode. Again, the sharp peak due to the sampling after one hour is visible in both plots, though it is more pronounced in the cathode plot.



(a) Current densities.

(b) DAA production.

Figure 8: Current density of the anode (full line) and cathode (dashed line) in separate experiments (8a) and resulting DAA concentration after one hour (hatched columns) and two hours (black columns) (8b). Experiments in divided set-up with respectively  $-2.5$  V and  $+2.5$  V applied for the cathode and anode experiment, working electrode: platinum wire ( $0.156$  cm<sup>2</sup>), auxiliary electrode: platinum sheet ( $8$  cm<sup>2</sup>), runtime: 2 hours.

Figure 8b shows the results of the analyses from both experiments. The DAA concentration found in the anode experiment was  $0.1$  m%, which corresponds with the amount of DAA found in a blank acetone sample after analysis. Thus it can be concluded that the anode doesn't contribute to the formation of DAA. The current measured at the anode indicates that some reaction takes place, but in the analysis there wasn't a clear distinction of a possible product. At

the cathode, the formation of DAA is evident. The increase in concentration from one to two hours is very small, even less than what was observed during the potential experiments (see figure 4). It is possible that, similar to the pure chemical reaction, an equilibrium is reached. In the validation experiment (see 3.1) a final concentration of 13,4 m% was obtained, running this experiment for 32 hours showed no significant increase in the concentration, indicating a possible equilibrium. In this divided set-up, the equilibrium might be reached faster. The discrepancy in final concentration (11 m% vs. 13.4 m%) could be due to uncontrolled parameters such as the ambient temperature since the set-up is not temperature-controlled. Despite no increase in the DAA concentration in the second hour, the current density doesn't decrease to zero, but rather stays at a constant value. This means that either an equal amount of DAA is produced as there is converted to MO, other products or being broken down or that side-reactions with the EGB still proceed. As in the anode experiment, no clear distinction of one product was observed in the analysis. However, on the chromatograms of experiments that reached the equilibrium fast or in long experiments, more variation of the baseline (several very small peaks, not the noise) was observed. The resulting peaks were not pronounced and not separable enough to be identified, but they do indicate numerous products due to further condensation reactions and breakdown products.

### *3.5. Effect of the electrode material*

In the previous experiments platinum electrodes for both the working and auxiliary electrode were employed. Platinum was chosen as it has proven to have a good activity towards the electrochemical aldol condensation [33–37]. From section 3.4 it is clear that the reaction proceeds at the cathode. To investigate if the reaction is independent on the electrode material or if the material plays an important role in the generation of the EGB, two other materials beside platinum are tested as the cathode: gold and glassy carbon. The experiments were conducted in the divided set-up with a potential of -2.5 V applied to the working electrode.

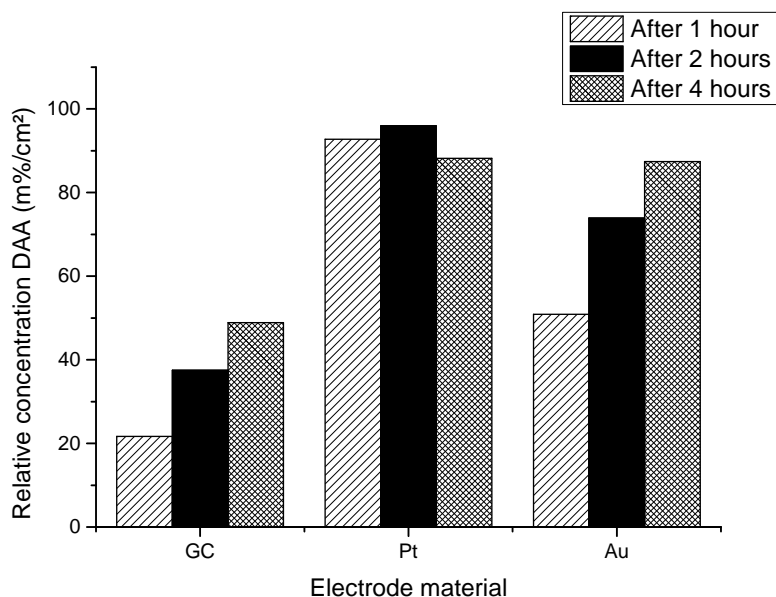


Figure 9: The relative DAA concentration after one hour (hatched columns), two hours (black columns) and four hours (double hatched columns) in separate experiments with different working electrodes: platinum wire ( $0.156 \text{ cm}^2$ ), glassy carbon disk ( $0.287 \text{ cm}^2$ ) and gold disk ( $0.133 \text{ cm}^2$ ), auxiliary electrode: platinum sheet ( $8 \text{ cm}^2$ ). Potential:  $-2.5 \text{ V}$ . Runtime: 4 hours.

Figure 9 shows the DAA concentration after one, two and four hours for each experiment. While for both gold and glassy carbon the concentration steadily increases over the 4 hours, for platinum the concentration remains about constant, even slightly decreasing after 4 hours. This corresponds to earlier observations described in section 3.1 and 3.4 that an equilibrium is reached. For gold this concentration is also reached after four hours, but for glassy carbon this concentration does not get reached in the same timespan, making it the least active material for this reaction. Though the same final concentration is obtained by both platinum and gold electrodes, platinum remains the better choice as it reaches this concentration in a much shorter timespan.

In figure 9 it is clear that in this set-up, for platinum, the maximum DAA concentration is reached within the first hour. To further investigate the course

of the reaction in the first hour, the experiment in section 3.5 for platinum was repeated and sample was taken each ten minutes. Figure 10 shows the analysis result. 0 minutes is not shown as this is the start of the experiment and no DAA has formed yet. The big increase between 10 and 20 minutes seems unlikely and is possibly due to experimental error. More important is that the concentration seems to increase to its final value with a declining increase. 80% of the final concentration is already reached after 30 minutes and after 50 minutes the maximum concentration is obtained. The data describes the course of an exponential curve: the concentration increases over the course of the reaction, but the increments between two measurements decrease. The selectivity towards DAA increases from 93 % after 10 minutes to 97 % after 20 minutes after which it remains constant. The reaction on platinum shows the same behaviour as gold or glassy carbon, but it proceeds much faster. An in-depth electrocatalysis investigation to optimize the catalyst (electrode material) can possibly even improve this, but this is not the scope of this work.

### *3.6. Reaction crossover and cell set-up*

During the experiments in the divided set-up (section 3.4 and 3.5) it was noticed that the resulting DAA concentration was higher than expected when compared to the standard (undivided) set-up, based on the surface to volume ratio. More specific a higher concentration per electrode surface area was reached in the same timespan compared to the standard set-up. This effect is also noticeable in the difference in formation rates of DAA between the two set-ups. In the standard set-up the formation rate was  $2.20 \times 10^{-3}$  M/min. (see section 3.1) while in the divided set-up the formation rate amounts to  $11.38 \times 10^{-3}$  M/min. after one hour and even to  $18.66 \times 10^{-3}$  M/min. if only the first 30 minutes are considered. To investigate this effect, two experiments were performed which were identical besides the set-up. The same two experiments were repeated with another working electrode. The working electrode was a platinum wire ( $0.156 \text{ cm}^2$ ) in the first two experiments and a platinum sheet ( $8 \text{ cm}^2$ ) in the other two, the auxiliary electrode in all experiments was a platinum sheet ( $8 \text{ cm}^2$ ).

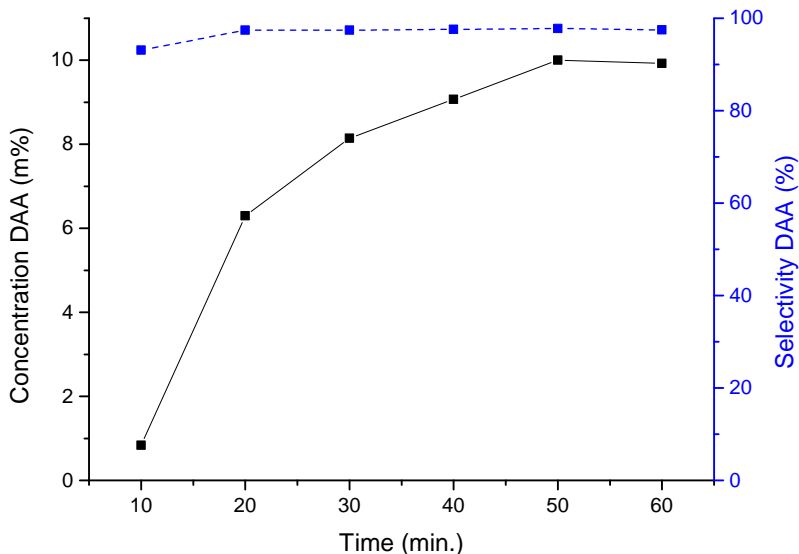


Figure 10: The DAA concentration (black squares connect by solid line, left y-axis) and corresponding selectivity (blue squares connected by dashed line, right y-axis) during a one hour experiment in the divided set-up, sampling each ten minutes. Working electrode: platinum wire ( $0.156 \text{ cm}^2$ ), auxiliary electrode: platinum sheet ( $8 \text{ cm}^2$ ), potential:  $-2.5 \text{ V}$ , runtime: 1 hour.

The surface to volume ratio was equal between two experiments with the same working electrode.

Figure 11 the distinct difference between the standard set-up and the divided set-up, which is the same for both electrodes: in both cases, the divided set-up leads to a higher DAA concentration. For the wire electrode (figure 11a) the difference in final concentration between the two set-ups is much larger and the increase after the first hour in the standard set-up is very small. Considering the results from previous experiments this is likely due to an experimental error. However, it is obvious that the divided set-up leads to better yields. This can likely be attributed to crossover from products, which has a negative effect on the DAA production. This can be products that are formed at the anode which

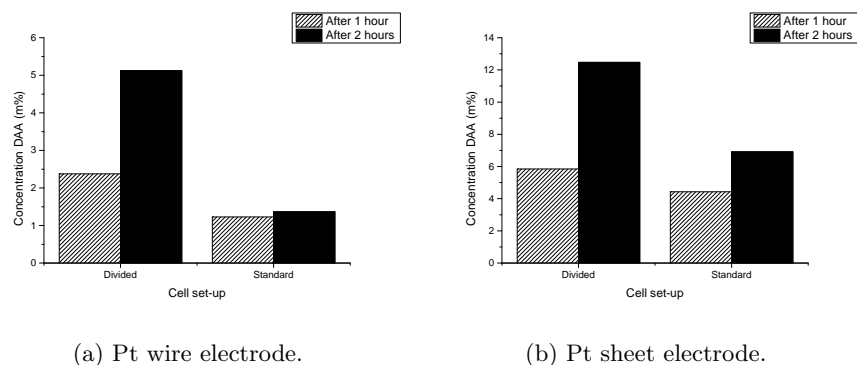


Figure 11: The absolute DAA concentration for the platinum wire electrode (11a) and the platinum sheet electrode (11b) after one hour (hatched columns) and two hours (black columns) in different set-ups: divided set-up and standard (undivided) set-up. Auxiliary electrode in both cases: platinum sheet (8 cm<sup>2</sup>). Potential: -2.5 V. Runtime: 2 hours.

breakdown DAA or it can be DAA itself which reacts at the anode or both. The exact cause is not clear, but the extend of it is and it can also be reproduced.

#### 4. Conclusions

Even though no thorough optimisation was done, it was possible to obtain DAA concentrations of 10-11 m% in the standard set-up up to 15 m% in the best case in the divided set-up in two hours of electrolysis. This is significantly more than the 2.8 % after two hours of galvanostatic electrolysis reported by Tsai et al. and similar to the commercial fixed-bed reactors operating at 15 °C. The parameters for this maximum concentration were a platinum working electrode, separation of both electrodes and -2.5 V potential applied, although a better trade-off between yield and current efficiency is obtained at -2 V. The potential-controlled electrochemical aldol condensation of acetone to diacetone alcohol was performed in a batch set-up. A number of parameters were screened. The results show that, contrary to the findings of Tsai et al., adding water to the electrolyte has a disadvantageous effect on the production of diacetone alcohol. The possibility of an indirect reaction via the electrolysis of water is hereby disputed. Furthermore it is confirmed that platinum is the most active for this



reaction and that the reaction proceeds exclusively via the cathode. However, it is also found that separation of the cathode and anode compartments of the cell prevent breakdown of diacetone alcohol and thus, have a beneficial effect on the production.

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