



Simplified approach for an enhanced electrochemical hydrogenation of carbonyl compounds

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ABSTRACT

In this study, a method for the electrochemical hydrogenation of various carbonyl compounds was developed, with a particular emphasis on industrial applicability and scalability. Each parameter—including current density, solvent, solvent ratio, electrolyte, proton concentration, electrode material and structure, as well as substrate concentration—was systematically investigated for its impact on yield and selectivity. Isophorone served as a model compound, facilitating the transition from the corresponding enone to the ketone. Additionally, the applicability of the system was expanded to include the hydrogenation of other enones such as methacrylates, ketones, and aldehydes. The method employs nickel foam electrodes and a simple electrolyte mixture of water: methanol (1:1) with 0.5 M sulfuric acid. Notably, the current density used is relatively high at 90 mA/cm², enhancing the industrial attractiveness of the process.

1. Introduction

Hydrogenations reactions constitute one of the major classes of processes found in chemical manufacturing. Common hydrogenation methods are associated with energy intensive conditions, such as high pressure and elevated temperature [1]. Additionally, super stoichiometric amounts of hydrogen as well as the use of transition metal catalysts are typically necessary, e.g. ruthenium for the hydrogenation of ketones and enones [2]. The combination of harsh process conditions and precious metal catalysts results in high costs for state of the art hydrogenation processes. Given the utmost importance of hydrogenation technology for production of chemicals, more energy efficient and sustainable methods are strongly desired in chemical industry. The field of electro-organic synthesis is currently experiencing increased attention from both, academia and industry because it is considered as a green and cost-efficient future technology [3–5]. The combination of synthetic electrochemistry with catalytically active electrodes is ideally suited for combining the sustainability of electrochemical transformations with the potential of catalysis to control reactivity and selectivity. Therefore, electrochemistry provides a highly attractive waste-free alternative for

such transformations as the electrons required for the redox process are directly supplied by the applied electrical current[6–9]. The inherent safety, scalability and unique reactivity make electrosynthesis to an outstanding approach [10–13]. An alternative to conventional hydrogenation processes is the electrochemical hydrogenation reaction. In electrochemical hydrogenations, hydrogen is generated in-situ by cathodic reduction of hydrogen sources such as hydrazine, ammonium chloride or water [14]. Water represents the optimal hydrogen source, due to inherent safety and low associated costs. The applicability of electrochemical hydrogenation processes has so far been limited by the necessity of employing complex electrodes modified with metal catalysts in addition to the need for hazardous and expensive additives, e.g., stoichiometric amounts of reducing agents. Commonly employed metal catalysts utilized in electrochemical hydrogenation reaction include manganese base-metal, Pt/Ru coatings, or Raney nickel. Additionally, substrate activation via organic catalysts has been reported, e.g. hexamethylphosphoramide [15–21]. One reported approach involves the hydrogenation of carbonyl compounds to secondary alcohols using carbon-based electrodes under potentiostatic conditions, with ammonia serving as the hydrogen source. Another study reports the hydrogenation of aldehydes employing manganese complexes, which enable the

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Nomenclature

Abbreviations

BDD	Boron-doped diamond
DSA	Dimensionally stable anode
GC	Gas chromatography
MS	Mass spectrometry
SEM	Scanning electron microscope

Symbols

A	Ampere
j	Current density
V	Voltage

electrochemical hydrogenation using phenol as proton donor [22]. The hydrogenation of cyclohexanone and enones derivatives in specific was demonstrated with a range of different electrochemical set-ups [19,23]. Mahdavi et al. reported a selective hydrogenation of the double bond in cyclic enones to the corresponding saturated ketones by the use of fractal-powder nickel or nickel boride cathodes in a divided cell setup [19]. The highest yield and selectivity were obtained at a current density of 3 mA/cm², using 0.1 M NaCl and H₃BO₃ as additives. Vilar et al. reported the hydrogenation of α,β -unsaturated ketones in an undivided setup using a sacrificial nickel-rod anode and NH₄Cl as supporting electrolyte [23]. By in-situ coating of several base cathode materials (Cu, Fe, Ni) with the dissolving nickel anode, saturated ketones were obtained in high yield and selectivity from the corresponding cyclic enones [23]. In a recent study by Tortajada et al., a combination of nickel foam electrodes with sulfuric acid as the electrolyte was found to convert enones to ketones selectively under potentiostatic conditions [24]. Additionally, significant advancements have been made in the electrochemical hydrogenation of nitriles to amines. Utilizing high current densities and a nickel foam cathode in a methanol-water mixture, high yields were achieved [25]. The aim of this work was the development of a simple, sustainable and efficient method for the selective hydrogenation of enones to saturated ketones and carbonyl compounds to the

corresponding alcohols. The focus of this study is to enhance existing methods for the electrochemical hydrogenation of enones, prioritizing the practicality of the process. Initially, we examine the configuration of the electrochemical setup, aiming for a straightforward design that operates under galvanostatic conditions without the need for a third reference electrode, thereby simplifying the process. Additionally, we address the challenges associated with reaction parameters, advocating for the use of a practical and safe hydrogen source, such as water, and the implementation of readily available electrode materials like nickel foam. Noteworthy, nickel foam electrodes are common electrodes and used in alkaline media wherein they form at the surface NiOOH as active anode [26–30]. The study also aims to utilize high current densities, making the method more appealing for a straightforward industrial setting.

2. Materials and methods

2.1. Analysis

Analysis of the reaction mixtures was performed with GC–MS using internal standard calibration to determine the product yield. All reported results are the average of at least three repetitions with the standard deviation given as the margin of error.

2.2. Electrochemical cells

Electrochemical screening cells (divided) from IKA-Werke GmbH & Co. KG, Staufen, Germany, were utilized, along with the corresponding reaction setup for the magnetic stirrer. The screening cells are equipped with magnetic stir bars. The power supply used was the HMP4040 programmable laboratory power supply (32 V, 10A, 384 W) from Rohde & Schwarz GmbH & Co. KG, Munich, Germany. This set-up was described in detail before [31].

3. Results

Following preliminary work by Tortajada et al., a method was envisioned allowing the electrochemical production of ketones from

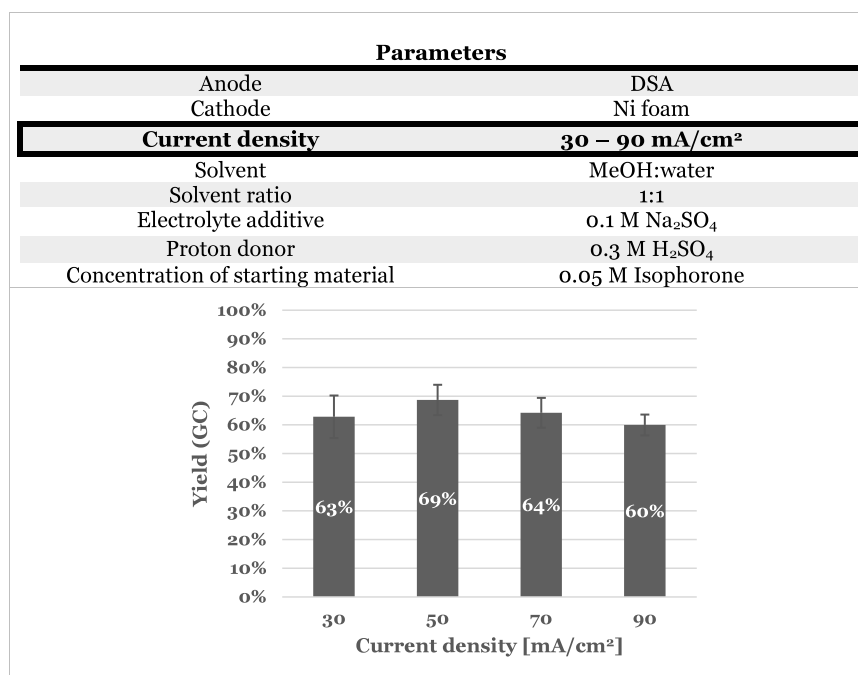


Fig. 1. Effect of the employed current density on the yield of 2. DSA was used as the anode and nickel foam as the cathode. NafionTM 424 served as a separator and the concentration of 1 was 0.05 M. The sulfuric acid concentration was 0.3 M.

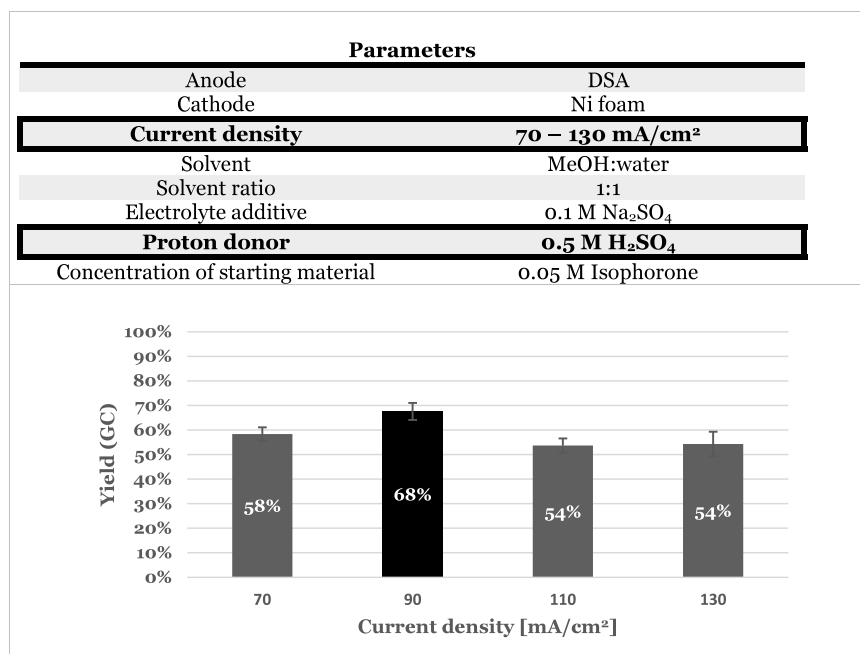


Fig. 2. Effect of current density on the yield of **2** at higher sulfuric acid concentration (0.5 M). DSA was used as the anode and nickel foam as the cathode. NafionTM 424 served as a separator and the concentration of **1** was 0.05 M.

α,β -unsaturated enones with high selectivity [24]. Isophorone **1** was chosen as a test compound. A combination of sulfuric acid and sodium sulfate was used as the halogen-free electrolyte. Relying on halogen-free electrolytes prevents the generation of undesired process gases at the anode, e.g. chlorine. As the solvent, a methanol water mixture was selected to ensure sufficient solubility of the substrate, in addition to providing sufficient amounts of activated hydrogen, with water being the best hydrogen source regarding economic and safety aspects. A NafionTM 424 membrane was selected as a separator to facilitate the transfer of protons generated at the anode to the cathodic compartment, thereby maintaining an acidic pH in the catholyte to provide sufficient protons for the hydrogenation reaction. As described above, readily available nickel foam exhibited an outstanding catalytic activity in electrochemical hydrogenation as observed in other reports [25]. High current density and galvanostatic conditions were applied to develop a practical electrochemical hydrogenation method.

3.1. First optimization – influence of current density and concentration of sulfuric acid

The first optimization started with the postulated methanol and water ratio of 1:1 and current density of 50 mA/cm². This current density refers to the geometric current density of the nickel foam. In every experiment 579 C were applied, which corresponds 8 F. Besides sulfuric acid (0.3 M), sodium sulfate was added in order to increase the conductivity for applying these high current densities [25]. Nickel foam was utilized as the cathode, while DSA served as anode. The study employed the proposed range of starting current densities from the literature as a baseline [25,27]. A yield of 69 % for **2** was observed in the initial trial (Fig. 1). To investigate the relationship between current density and yield, a lower current density of 30 mA/cm² was tested, resulting in a decrease to 63 % yield. Conversely, increasing the current density proved ineffective with 64 % and 60 % yield at 70 mA/cm² and 90 mA/cm², respectively.

Following the reaction, a caustic pH was observed in the catholyte for several of the conducted experiments. This observation is consistent with an imbalanced proton concentration in the electrolyte resulting in rapid proton consumption and too slow replenishment at the anode. In

order to mitigate the loss in proton concentration at the cathode potentially resulting in losses of electrochemical activity, the current density screening was repeated with an increased concentration of sulfuric acid.

The obtained results with an increased sulfuric acid concentration are depicted in Fig. 2. At higher sulfuric acid concentration, the highest yield for **2** of 68 % was achieved at a current density of 90 mA/cm². The current density of 70 mA/cm² lead to 58 % yield. Notably, higher current densities of 110 and 130 mA/cm² exhibited a decreasing yield, with both yielding 54 %. With a higher availability of protons, the optimal current density for maximizing the yield of **2** is greater than observed at lower concentrations. Consequently, the decision was made to proceed with a current density of 90 mA/cm² in conjunction with a sulfuric acid concentration of 0.5 M.

To confirm the dependence of the reaction on applying an electrical current, an experiment was conducted without electrical current, utilizing the developed parameters. No conversion was observed, thus demonstrating the process depending on electrochemical activation.

3.2. Investigation of the influence of electrolyte

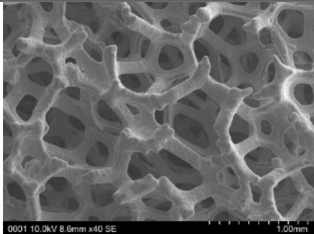
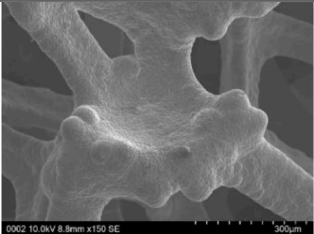
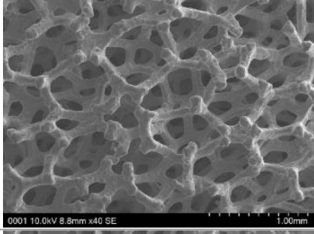
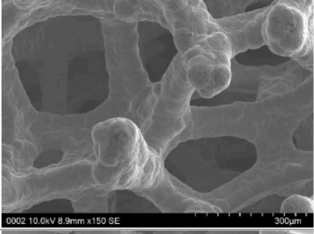
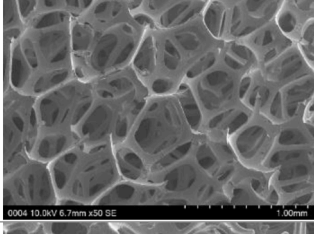
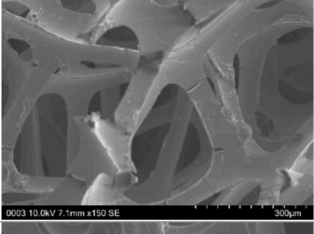
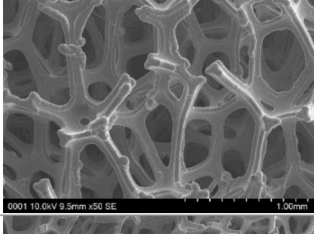
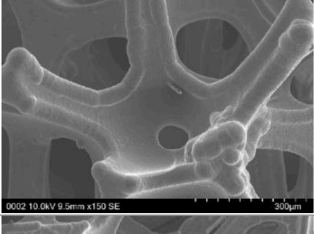
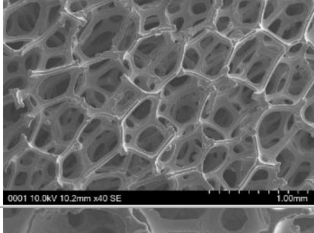
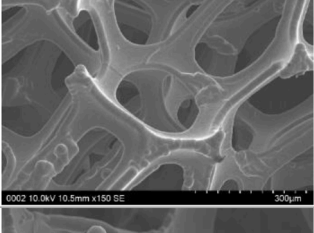
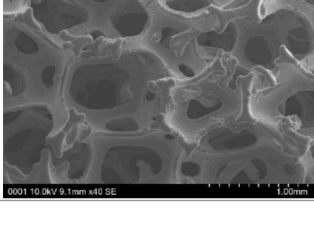
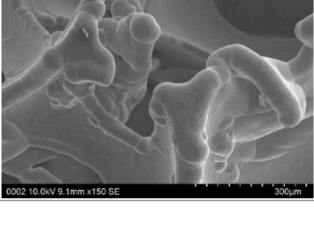
With basic process parameters in hand, the subsequent optimization aimed at increasing the yield of **2**. Additionally, the goal was to acquire sufficient knowledge about the reaction. Various parameters were investigated, e.g. the supporting electrolyte, co-solvents, solvent mixture and cathode material and structure.

To examine the influence of sodium sulfate as an additive, experiments were performed under the optimal conditions of 90 mA/cm² and a sulfuric acid concentration of 0.5 M, excluding sodium sulfate. No loss in yield was obtained when excluding sodium sulfate (68 % yield with sodium sulfate vs. 71 % without sodium sulfate). Consequently, sodium sulfate was removed as additional supporting electrolyte, simplifying the reaction conditions to three base chemicals.

The next step was to investigate the influence of the solvent on the reaction efficiency. A series of experiments were conducted using various organic co-solvents, e.g. acetonitrile, THF, and ethanol. The solvents were selected based on the miscibility with water as the hydrogen source. These experiments were conducted under conditions

Table 1

SEM images of different nickel-foam electrodes at 1.00 mm and 300 microns magnification. Further information from the supplier can be found in the supporting information.

No.	SEM picture 1 mm	SEM picture 300 μ m
1		
2		
3		
4		
5		
6		

of 90 mA/cm² and a concentration of 0.5 M sulfuric acid. As illustrated in Fig. 4, switching to other co-solvents resulted in a significant decrease in the yield of **2** compared to methanol. Ethanol emerged as the most promising alternative, yielding approximately 28 % of **2**. Additionally, it was observed that the use of the alternative co-solvents led to undesired side reactions in the cell, e.g. coating of the electrode. The overall recovery of reactants and products, assessed using a GC internal standard

method, was found to be below 40 %. This observation highlights that methanol not only dramatically enhances the yield but also effectively suppresses side reactions like polymerizations.

To investigate the influence of the organic co-solvent in more detail, experiments were conducted varying the methanol content in the mixture. A decrease in yield was observed with any changes to the co-solvent concentration in the reaction mixture (see Fig. 5). Using a

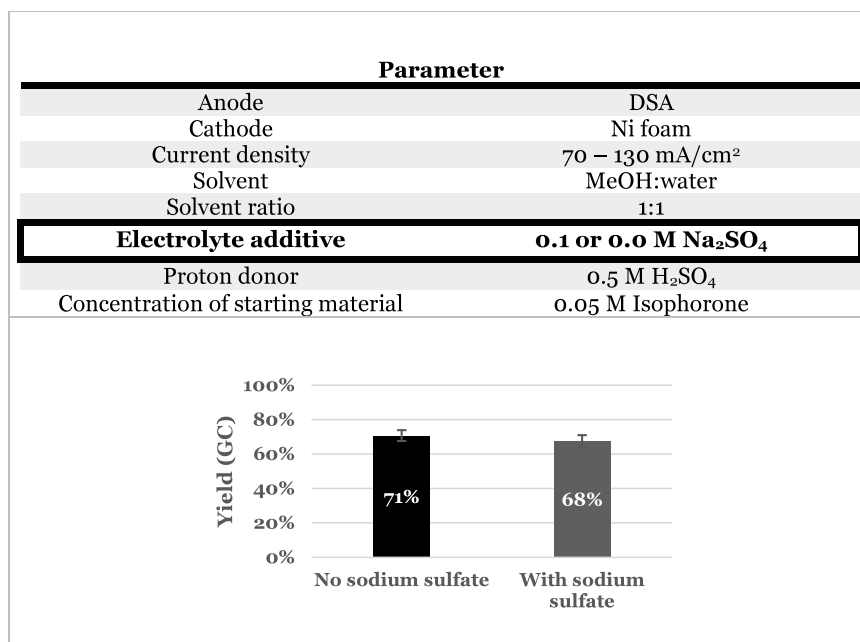


Fig. 3. Effect of sodium sulfate as a secondary electrolyte on the yield of **2** at a current density of 90 mA/cm². DSA was used as the anode and nickel foam as the cathode. Nafion™ 424 served as a separator and the concentration of **1** was 0.05 M. The sulfuric acid concentration was 0.5 M. Tested were conditions without sodium sulfate and sodium sulfate concentration of 0.1 M.

higher water content (1:2 methanol to water ratio) resulted in a yield of 56 % for **2**. The standard deviation was significantly higher compared to the initial mixture. This observation can be attributed to the insufficient solubility of isophorone (**1**) in the reaction mixture. Conversely, with an increased methanol concentration of 2:1 methanol:water, a yield of 46 % was obtained, showing that sufficient amounts of the hydrogen source water are crucial for the reaction. Additionally, a significant loss in reproducibility was found reflected by the significantly increased standard deviation across three experiments (see Fig. 5). Thus, the initial solvent system comprising a 1:1 mixture of methanol and water was confirmed as the optimal choice. The formulation provides the necessary solubility for the reactant while also delivering sufficient water to serve as the optimal hydrogenation donor.

3.3. Influence of the used electrode material

Copper was reported as suitable material for electrochemical hydrogenation reactions on other structural motives [32–34]. In addition to copper foam, copper mesh was tested to compare the geometric structures alongside the metallic properties. Using copper as the cathode material resulted in a significant loss in yield for **2** compared to nickel. Additionally, the copper mesh exhibited significantly inferior performance compared to copper foam, yielding 14 % versus 30 % of **2**.

The observation suggests that the metal properties play an important role in the electrochemical hydrogenation reaction. Additionally, it highlights the importance of the surface activity. The hydrogenation reaction most likely occurs directly at the electrode rather than by hydrogen formation and subsequent hydrogenation reaction.

Given that copper proved to be inferior to nickel foam, the next experiments focused on cobalt as an alternative to nickel. Cobalt was selected due to the isoelectronic characteristics with nickel and overall strong redox-active catalytic properties of cobalt. Both cobalt foam and cobalt-nickel foam were evaluated to elucidate the performance dependence on varying nickel content in the cathode material. It was found that the performance improved with increasing nickel content in the cathode foam. Compared to pure cobalt foam yielding 46 % of **2**, use of the nickel-cobalt foam resulted in an increase in yield to 68 %, while the highest yield of 71 % was obtained with pure nickel foam. This

suggests that nickel possesses superior features in catalysing the electrochemical hydrogenation reaction of **1**.

In order to delineate the effect of electrode morphology and surface properties, a series of different nickel foams were investigated, varying in mesh size, and nickel content. Additionally, SEM images were taken to analyse the geometric structure and surface properties. The SEM images show significant differences in both the surface structure, mesh size, and cavities (see Table 1, number supplied by IKA was used in previous optimization efforts). Typical for foam-type structures overlap of individual meshes was found. Type 1 (IKA) exhibits a smooth surface with round, bulky edges. The skeleton structures of Foam 3 are significantly more delicate and have a coarse surface with sharp-edges and cracks. The mesh size and cavities are tighter than those of the other foams. Foam 4 has a smooth, rounded surface. Furthermore, the edges of the skeleton structures protrude, creating a depression in the individual skeletons. The mesh size is larger than observed in the other foam materials.

Foam 5 has a similar surface structure to Foam 4. However, the skeletons are more delicate, resulting in smaller cavities. Foam 6 features a smooth, rounded surface structure and appears cartilaginous. The properties mentioned are derived from various manufacturing characteristics. For example, the difference between type 4 and 6 is the larger pore size of 6, 1.2 mm compared to 0.8 respectively. Details regarding the manufacturing process and additional characterization based on supplier information are provided in the supporting information.

The analysed nickel-foams were employed under optimized conditions to elucidate the impact of surface structure on reaction performance. Overall, comparable yields of **2** were obtained for the nickel-foams number 1, 2, and 4–6. Interestingly, nickel-foam number 3 with the coarse and cracked surface structure exhibited significantly lower performance with a yield of 30 % for **2**. The best results were obtained with nickel-foam number 6 yielding 77 % **2** under the optimized conditions. Given that hydrogenation likely occurs directly at the electrode surface, the surface properties determine the overall activity of the electrode material. Differences stemming from the manufacturing process, e.g. the coarse and cracked surface of electrode material 3, can have a direct impact on available surface area and thus efficiency of the

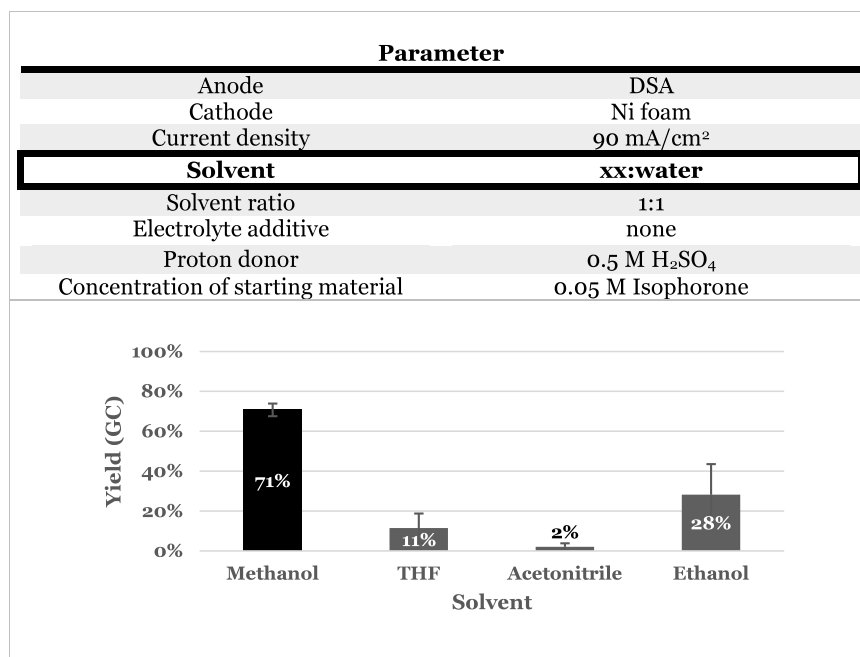


Fig. 4. Effect of the co-solvent on the yield of **2** at a current density of 90 mA/cm². DSA was used as the anode and nickel foam as the cathode. NafionTM 424 served as a separator and the concentration of **1** was 0.05 M. The sulfuric acid concentration was 0.5 M. The investigated solvents were employed in a ratio of 1:1 with water.

electrochemical hydrogenation. As a last step we doubled the educt concentration of **1** from 0.05 to 0.1 M and investigate the influence. However, the yield was slightly decreased from 77 % to 71 % yield of **2**. A higher concentration was not investigated due to solubility issues of the educt.

This observation prompted further investigations to elucidate the relationship between the electrode structure and the corresponding yield, specifically regarding the mechanism of electrochemical hydrogenation. CV measurements were conducted to determine whether substrate hydrogenation occurs directly at the electrode or is facilitated by hydrogen reduction. The CV results clearly indicate that direct

reduction is feasible. However, the potential for proton reduction is significantly lower.

Based on these findings and insights from the literature, it is envisioned that the hydrogenation proceeds via metal hydride formation at the electrode surface [25,35]. This supports the conclusion that the electrode structure significantly influences the yield. For detailed information, please refer to the supporting information.

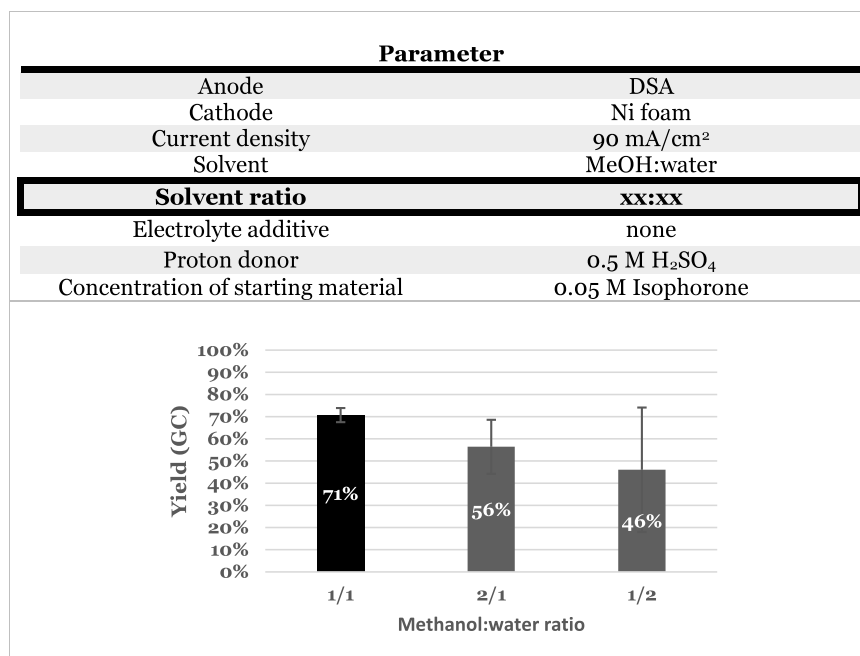


Fig. 5. Effect of the methanol concentration on the yield of **2** at a current density of 90 mA/cm². DSA was used as the anode and nickel foam as the cathode. NafionTM 424 served as a separator and the concentration of **1** was 0.05 M. The sulfuric acid concentration was 0.5 M.

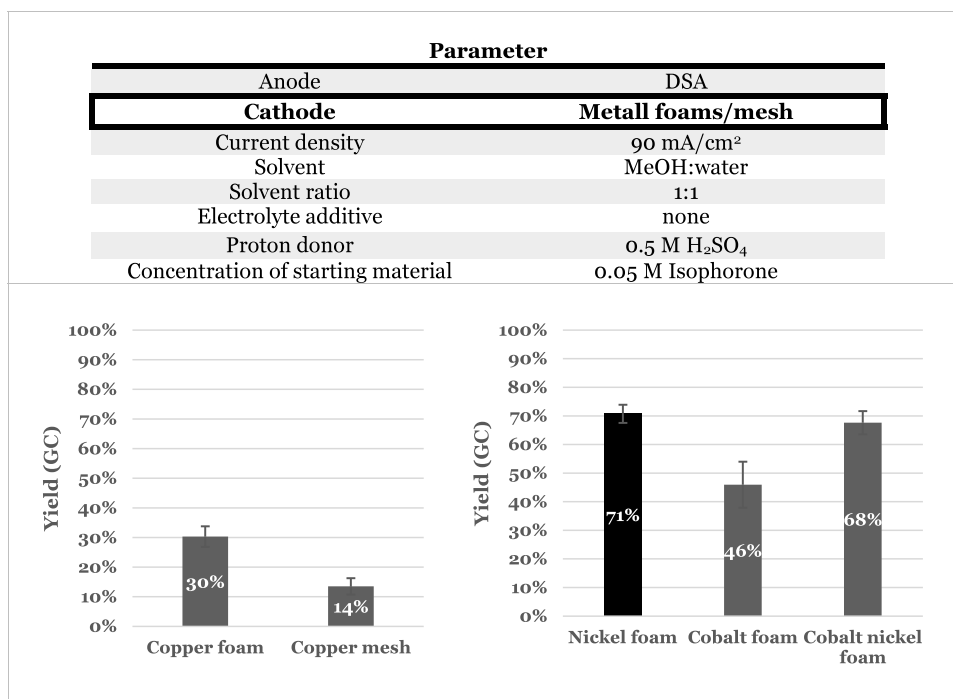


Fig. 6. Effect of the cathode material on the yield of **2** at a current density of 90 mA/cm². DSA was used as the anode. Nafion™ 424 served as a separator and concentration of **1** was 0.05 M. The sulfuric acid the concentration was 0.5 M and a 1:1 methanol to water mixture was used as the solvent.

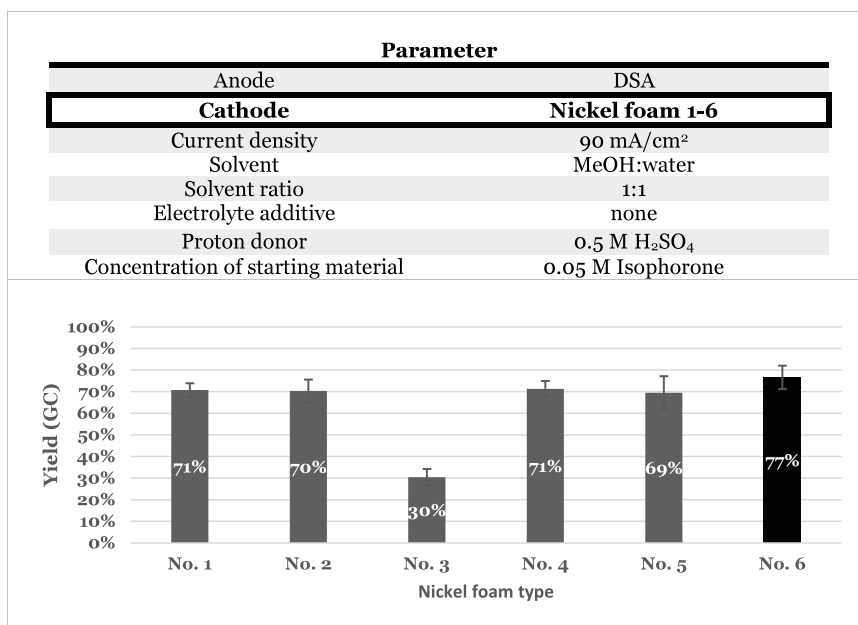


Fig. 7. Effect of different Nickel-foam types (see Table 1) onto yield of **2** at a current density of 90 mA/cm². DSA was used as the anode. Nafion™ 424 served as a separator and the concentration of **1** was 0.05 M. The sulfuric acid concentration was 0.5 M and a 1:1 methanol to water mixture was used as the solvent.

3.4. Transfer of the method developed to various carbonyl structural motifs

With the optimized conditions in hand, we turned our interests towards broadening the applicability of the developed electrochemical hydrogenation process. Therefore, the hydrogenation of a range of enones, ketones, and aldehydes was investigated. For this experiment row, the lower concentration of 0.05 M educt was chosen to avoid solubility issues. The method's effectiveness on other enone structures was demonstrated for cyclohexenone, which was converted to

cyclohexanone in 51 % yield. To investigate other industrially relevant enones besides isophorone, two methacrylates were included in the study. Butyl methacrylate was hydrogenated to isobutyrate **13** in 58 % yield, while the corresponding benzyl derivative **14** yielded only 9 % of the hydrogenated product. This discrepancy may be attributed to the more lipophilic nature of the benzyl derivative, resulting in lower solubility in the polar mixture, corroborating the lower yields observed in isophorone experiments with higher water content. These findings demonstrate that ester-containing enone structures can be hydrogenated using the developed method. Based on the obtained results, it was

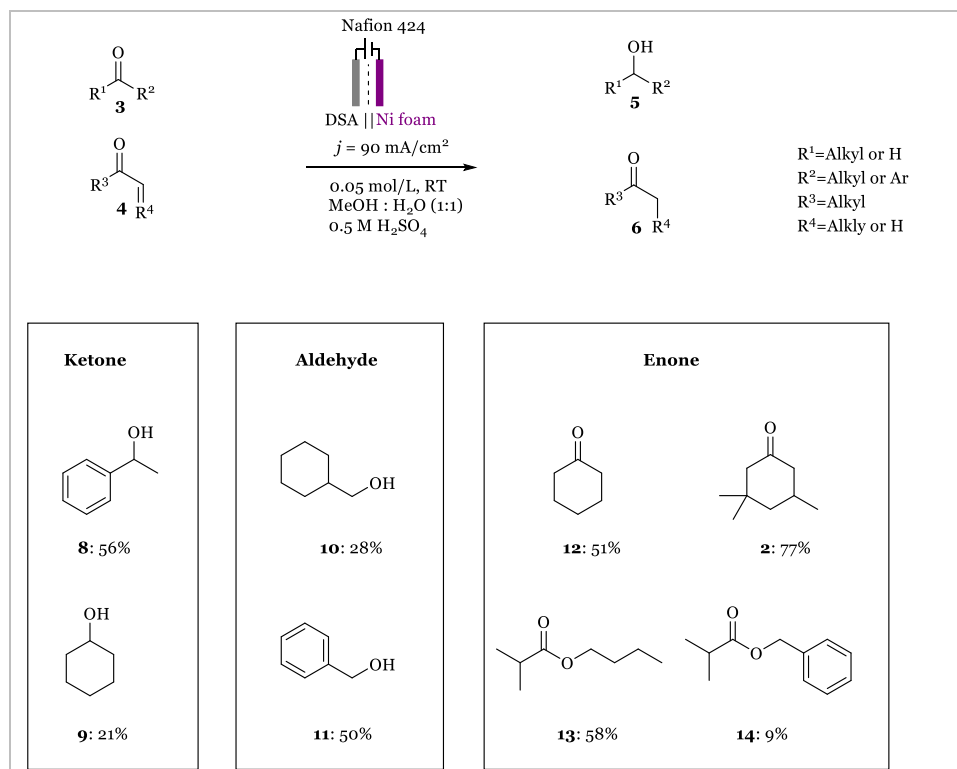


Fig. 8. The yields (GC) of different structure motifs are illustrated. The optimized conditions with 90 mA/cm^2 , MeOH:water 1:1, 0.5 M H_2SO_4 and the type 6 nickel foam was used. Different carbonyl substrates were hydrogenated including ketones, enones and aldehydes.

hypothesized that the developed method can be extended to the hydrogenation of isolated carbonyl structures in the absence unsaturation. Testing cyclic non-conjugated ketones resulted in the formation of the corresponding alcohols **9** with lower yields of 21 %, respectively.

In contrast, aromatic conjugation of the ketone resulted in approved yields, e.g. 56 % for the hydrogenation of acetophenone to **8**. Similar results were obtained for aldehydes. The yield of benzaldehyde to benzylalcohol **11** was found to be higher at 50 %, compared to 28 % for the non-aromatic cyclohexancarboxaldehyde to **10** (Figs. 3, 6, 7 and 8).

4. Conclusions

In conclusion, a practical method for the electrochemical hydrogenation of carbonyl compounds including enones, aldehydes and ketones was established. The streamlined system is characterized by a high current density of 90 mA/cm^2 and galvanostatic conditions. Detailed understanding of the influence of proton concentration, additives, and the solvent combination on the process allowed for improvement of the hydrogenation and extension to a range of different substrates. Notably, methanol significantly affects the yield of the ketone and the selectivity of the reaction. Sulfuric acid emerged as the sole conductivity enabling material required in the electrolyte, with proton concentration being a critical parameter influencing both yield and increasing the optimal operating current density. The choice of cathode material was identified as a key factor not only for yield enhancement, but also for suppressing side reactions, such as the formation of polymer films, thereby increasing reaction selectivity. Additionally, the geometric structure of the electrodes was found to be crucial for improving the process efficiency. The obtained insights serve as a valuable takeaway for the design of future electro-organic processes that may occur directly at the electrode surface. Overall, a new electrochemical method for key structural motifs was developed. The method, based on a simplified two electrode system, demonstrates high efficiency through elevated current densities and the utilization of bulk chemicals as electrolytes. This approach is not

only efficient but also serves as a valuable framework for the development of electrochemical hydrogenation techniques for other structures, highlighting the significance and impact of the investigated parameters.

CRediT authorship contribution statement

Laura Lennartz: Writing – review & editing, Writing – original draft, Methodology, Investigation. **Vera Beier:** Writing – review & editing, Writing – original draft, Methodology, Investigation, Formal analysis. **Jan B. Metternich:** Writing – review & editing, Writing – original draft, Methodology. **Patrik Stenner:** Writing – review & editing, Writing – original draft, Supervision, Conceptualization. **Siegfried R. Waldvogel:** Writing – review & editing, Writing – original draft, Supervision, Project administration, Investigation, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at [doi:10.1016/j.electacta.2025.147542](https://doi.org/10.1016/j.electacta.2025.147542).

Data availability

The data will be available in the supporting information.

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