



POLİTEKNİK DERGİSİ

*JOURNAL of POLYTECHNIC*

ISSN: 1302-0900 (PRINT), ISSN: 2147-9429 (ONLINE)

URL: <http://dergipark.org.tr/politeknik>



# Low-voltage hydrogen production from formic acid: The role of different electrolysis parameters

## *Formik asitten düşük voltajlı hidrojen üretimi: Farklı elektroliz parametrelerinin rolü*

*Yazar(lar) (Author(s)): Özgü YÖRÜK<sup>1</sup>, Duygu UYSAL<sup>2</sup>, Özkan Murat DOĞAN<sup>3</sup>*

*ORCID<sup>1</sup>: 0000-0001-7768-0313*

*ORCID<sup>2</sup>: 0000-0002-8963-6026*

*ORCID<sup>3</sup>: 0000-0003-3801-3141*

**To cite to this article:** Yörük Ö., Uysal D. and Doğan Ö. M., “Low-Voltage Hydrogen Production From Formic Acid: The Role of Different Electrolysis Parameters”, *Journal of Polytechnic*, 28(6): 1853-1864, (2025).

**Bu makaleye şu şekilde atıfta bulunabilirsiniz:** Yörük Ö., Uysal D. ve Doğan Ö. M., “Low-Voltage Hydrogen Production From Formic Acid: The Role of Different Electrolysis Parameters”, *Politeknik Dergisi*, 28(6): 1853-1864, (2025).

**Erişim linki (To link to this article):** <http://dergipark.org.tr/politeknik/archive>

**DOI:** 10.2339/politeknik.1655878

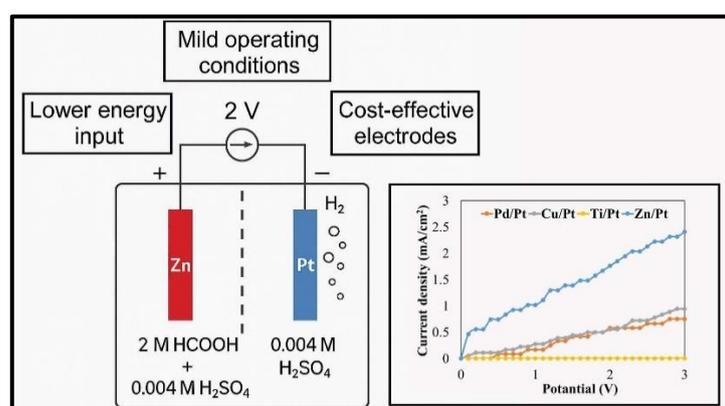
# Low-Voltage Hydrogen Production From Formic Acid: The Role of Different Electrolysis Parameters

## Highlights

- ❖ The Zn/Zn electrodes outperformed Pd/Pt, achieving four times higher current density.
- ❖ Electrolysis at 2 V and 50°C produced pure hydrogen at the cathode with 92% Faradaic efficiency.
- ❖ H<sub>2</sub>SO<sub>4</sub> enabled the highest current density of 5.18 mA/cm<sup>2</sup> at 1 V, proving its effectiveness in electrolysis.
- ❖ The study highlights the use of cost-effective Zn electrodes and mild conditions for H<sub>2</sub> production.

## Graphical Abstract

This study investigated formic acid electrolysis using Pd/Pt and Zn/Zn electrodes, with Zn/Zn outperforming Pd/Pt. Under optimized conditions (2 V, 50°C), pure hydrogen was produced at 0.4 mL·min<sup>-1</sup> with 92% Faradaic efficiency, demonstrating a cost-effective, sustainable approach.



**Figure.** Schematic diagram of the experimental system

## Aim

The aim of this study is to investigate the electrolysis of formic acid for hydrogen production, focusing on optimizing electrolysis conditions, evaluating the effect of different electrode materials, and assessing the impact of parameters such as voltage and temperature.

## Design & Methodology

Experiments were conducted using a basic electrolysis cell to evaluate parameter effects on current density, followed by a two-chamber membrane cell to analyze gas composition. Optimal conditions were identified, and various electrode materials were tested under different electrolytes.

## Originality

This study highlights the efficient electrolysis of formic acid at low voltage and mild conditions using affordable electrodes, offering a sustainable alternative for hydrogen production.

## Findings

This study demonstrates that formic acid electrolysis enables efficient hydrogen production at low voltage (2 V) and mild temperature (50°C), with Zn/Pt electrodes achieving high current density and 92% Faradaic efficiency.

## Conclusion

This study demonstrates the successful electrolysis of formic acid using a Zn/Pt electrode pair, achieving efficient hydrogen production at low voltage and temperature, with high Faradaic efficiency and promising cost-effectiveness for large-scale applications.

## Declaration of Ethical Standards

The author(s) of this article declare that the materials and methods used in this study do not require ethical committee permission and/or legal-special permission.

# Low-Voltage Hydrogen Production From Formic Acid: The Role of Different Electrolysis Parameters

*Araştırma Makalesi / Research Article*

Özgü YÖRÜK<sup>1\*</sup>, Duygu UYSAL<sup>2</sup>, Özkan Murat DOĞAN<sup>3</sup>

<sup>1\*,2,3</sup> Gazi University, Faculty of Engineering, Chemical Engineering Department, Ankara, Turkey

(Geliş/Received : 11.03.2025 ; Kabul/Accepted : 14.04.2025 ; Erken Görünüm/Early View : 26.04.2025 )

## ABSTRACT

This study investigates the electrolysis of formic acid for hydrogen production, focusing on the effects of various parameters and materials. In the first phase, experiments were conducted using a single-compartment electrolysis cell with Pd/Pt electrodes at 20°C. The effect of formic acid concentration, electrolytes, and electrode materials on current density was analyzed. The highest current density (5.18 mA/cm<sup>2</sup> at 1 V) was achieved with H<sub>2</sub>SO<sub>4</sub> as an electrolyte. The Zn/Zn electrode pair significantly outperformed Pd/Pt, yielding four times higher current density. In the second phase, electrolysis conditions for hydrogen production at low voltage (2 V) and temperature (50°C) were optimized. Pure hydrogen was obtained at the cathode, confirming the successful hydrogen production under these conditions. Faradic efficiency reached 92% at 2 V, with a high hydrogen production rate. The use of cost-effective Zn electrode, along with mild electrolysis conditions, enhances the practicality and sustainability of the process. These findings highlight that formic acid electrolysis is a promising and efficient method for pure hydrogen production, offering an economical and sustainable alternative for hydrogen generation.

**Keywords:** Formic acid, hydrogen, electrolysis, Faradic efficiency.

## Formik Asitten Düşük Voltajlı Hidrojen Üretimi: Farklı Elektroliz Parametrelerinin Rolü

### ÖZ

Bu çalışma, hidrojen üretimi amacıyla formik asidin elektrolizini incelemekte olup, çeşitli parametrelerin ve malzemelerin etkilerine odaklanmaktadır. İlk aşamada, 20°C'de Pd/Pt elektrotlar kullanılarak tek bölmeli bir elektroliz hücresinde deneyler gerçekleştirilmiştir. Formik asit konsantrasyonu, elektrolit türleri ve elektrot malzemelerinin akım yoğunluğu üzerindeki etkisi analiz edilmiştir. En yüksek akım yoğunluğu (1 V'ta 5,18 mA/cm<sup>2</sup>), elektrolit olarak H<sub>2</sub>SO<sub>4</sub> kullanıldığında elde edilmiştir. Zn/Zn elektrot çifti, Pd/Pt'ye kıyasla dört kat daha yüksek akım yoğunluğu sağlayarak önemli bir üstünlük göstermiştir. İkinci aşamada ise, düşük voltaj (2 V) ve sıcaklık (50°C) koşullarında hidrojen üretimi için elektroliz şartları optimize edilmiştir. Katotta saf hidrojen elde edilerek bu koşullarda başarılı bir hidrojen üretimi doğrulanmıştır. 2 V'ta Faradik verim %92'ye ulaşmış ve yüksek bir hidrojen üretim hızı sağlanmıştır. Uygun maliyetli Zn elektrot kullanımı ve yumuşak elektroliz koşulları, sürecin uygulanabilirliğini ve sürdürülebilirliğini artırmaktadır. Bu bulgular, formik asit elektrolizinin saf hidrojen üretimi için ekonomik ve sürdürülebilir bir alternatif sunduğunu ve umut vadeden, verimli bir yöntem olduğunu ortaya koymaktadır.

**Anahtar Kelimeler:** Formik asit, hidrojen, elektroliz, Faradik verim.

### 1. INTRODUCTION

Currently, the majority of hydrogen is derived from fossil fuels. This is primarily due to the accessibility, abundance, and lower cost of fossil fuel-based processes [1, 2]. However, as fossil fuel reserves continue to deplete rapidly, not only will production costs rise, but the long-term sustainability of human development will also be at risk [3]. Therefore, the exploration of alternative, renewable pathways for hydrogen production has become increasingly critical to ensure both energy security and environmental sustainability [4].

Today, various methods are available for hydrogen production [5-7]. One of these methods, water electrolysis, requires a relatively high theoretical cell voltage and energy consumption, prompting the search for alternative feedstocks [8-10]. Alcohols such as methanol and ethanol have been considered as potential

substitutes since their electrolysis requires significantly lower voltages than water, leading to reduced energy consumption during hydrogen production [11-13]. In this context, formic acid has emerged as a promising alternative, as its electrolysis also requires lower voltages compared to water, offering potential advantages in terms of energy efficiency and hydrogen production rates.

Formic acid (HCOOH) is a versatile organic compound extensively utilized in various industrial applications due to its unique chemical properties. It is primarily synthesized through two main processes: the oxidation of methanol and the reaction of carbon monoxide with sodium hydroxide [14, 15]. This compound plays a crucial role in multiple sectors, including agriculture, where it serves as a preservative for silage and livestock feed; in the leather industry, where it is used in the tanning process; in the food industry, where it acts as a

\*Sorumlu Yazar (Corresponding Author)  
e-posta : ozguyoruk@gazi.edu.tr

preservative; and in the chemical sector as a solvent [16]. Additionally, formic acid is a key precursor in the production of formate salts, esters, and other industrial chemicals. Despite its broad utility, large quantities of waste byproducts associated with formic acid are generated, particularly in industries such as agriculture, leather production, and textiles [17]. In these sectors, significant waste arises from the use of formic acid in various processes, including preservation, tanning, and dyeing, resulting in spent acids, chemical effluents, and residual byproducts [18, 19]. The proper management and disposal of these wastes are critical to minimizing their environmental impact [20]. Therefore, utilizing formic acid and its solutions for hydrogen production offers two major benefits: pollution mitigation and clean energy generation [19, 21, 22].

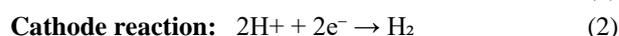
Hydrogen production from formic acid is typically achieved through thermal/catalytic decomposition or electrochemical methods. In thermal dehydrogenation, metal catalysts such as Pt, Pd, and Ru facilitate the decomposition of formic acid into H<sub>2</sub> and CO<sub>2</sub> [23-25]. Alternatively, different catalysts can promote dehydration, leading to CO and water formation. Early studies on formic acid decomposition over heterogeneous catalysts, dating back to the 1930s, did not focus on catalyst optimization or CO evolution from side reactions [26, 27]. Most research was conducted in the gas phase at temperatures above 100°C or required an inert carrier gas, adding complexity to practical applications. To address this, liquid-phase dehydrogenation has gained interest, with research exploring both noble and non-noble metal nanoparticles for improved catalytic performance [28, 29]. Numerous studies have been conducted on hydrogen production from formic acid and the studies conducted for the dehydrogenation method have focused on developing highly active and stable catalysts for selective H<sub>2</sub> and CO<sub>2</sub> production under mild conditions [30, 31]. Various metal complexes including Ru [32, 33], Rh [34, 35], Fe [36-38] and Ir [38-40] have been extensively investigated. In addition to metal complexes, carbon materials have also been widely studied as catalyst supports due to their stability in acidic and basic media, tunable porosity, adjustable hydrophilicity, and ability to incorporate heteroatoms [41, 42]. Their structural versatility allows for further functionalization, enhancing catalytic performance [42]. However, designing efficient and selective heterogeneous catalysts for this process remains a significant challenge [27, 43].

In electrochemical methods, formic acid undergoes direct electrolysis using suitable electrode materials and electrolytes to generate hydrogen [21]. These methods enable formic acid to serve as a portable hydrogen source and a hydrogen carrier in fuel cells [44]. Among the hydrogen production methods from formic acid, electrolysis stands out for its low energy consumption [27, 45]. In electrochemical processes, formic acid is directly decomposed into hydrogen and carbon dioxide using appropriate electrode materials and electrolytes.

This method consumes up to 31% less energy than conventional water electrolysis, making it a promising option for sustainable hydrogen production [46].

Aqueous formic acid solutions have been explored for hydrogen production through catalytic decomposition and electrolysis using solid polymer electrolytes. If these solutions can be directly used for hydrogen generation via electrolysis, the required energy or power input would theoretically be lower than that of water electrolysis, making the process more cost-effective [19, 47-49].

The electrochemical reactions for the electrolysis of formic acid solutions primarily occur as follows [20, 50, 51]:



In this process, formic acid undergoes electrochemical decomposition, producing hydrogen and carbon dioxide. While hydrogen is obtained in pure form at the cathode compartment, carbon dioxide gas is released from the anode compartment [52, 53]. To prevent the mixing of gases, electrolysis cells with membrane-separated anode and cathode compartments are used [54]. This method not only enables the production of pure hydrogen but also allows the direct collection of pure carbon dioxide from the anode, offering a significant advantage.

The theoretical potential required for water electrolysis is 1.23 V, while for formic acid electrolysis, it is 0.25 V. However, due to factors such as overpotential in real experimental conditions, the process occurs at a higher voltage [53, 55]. Nevertheless, it still requires a lower potential compared to water electrolysis. This indicates that formic acid could enable hydrogen production with lower energy input, which may contribute to more economical hydrogen generation under certain conditions.

Formic acid, derived from renewable sources such as biomass, presents a sustainable pathway for hydrogen production. Its electrolysis can be conducted at low temperatures and atmospheric pressure, minimizing energy consumption while enabling direct hydrogen generation, making it an efficient method [56-58]. Electrochemical approaches offer high selectivity and process control, with performance significantly influenced by electrode materials [52, 59]. Current research focuses on enhancing the efficiency of formic acid electrolysis through the development of advanced electrode and catalyst materials [44, 53, 60, 61]. In particular, innovative catalysts such as graphene-supported metal nanoparticles improve reaction kinetics, increase hydrogen production efficiency, and contribute to the economic feasibility of the process [44, 62-65].

Although hydrogen production via formic acid electrolysis offers several advantages, certain drawbacks must also be considered. The catalysts used in the electrolysis process often contain precious metals such as

palladium (Pd) or platinum (Pt), making high costs a limiting factor for large-scale commercial applications [66-68]. Additionally, the source of formic acid is a critical factor; if derived from fossil fuels, the process may lose its low-carbon emission advantage [49]. Energy efficiency varies depending on the electrode materials and system design, highlighting the need for the development of more efficient and cost-effective electrodes. Furthermore, the gradual degradation and corrosion of electrodes during electrolysis pose significant challenges for long-term system durability, increasing maintenance requirements and overall operational costs [69, 70]. Besides all this, an increase in temperature is anticipated to improve the kinetics of CO<sub>2</sub> reduction, increase CO<sub>2</sub> diffusivity, while simultaneously decrease CO<sub>2</sub> solubility [71, 72]. However, the impact of temperature on the performance of formic acid processing in an aqueous electrolyte has been insufficiently explored to date.

Until now, many studies have explored hydrogen production from formic acid via catalytic and electrochemical methods, most focus on catalyst development or reaction mechanisms rather than practical system efficiency. Previous research has primarily examined noble metal catalysts or specific operating conditions without a comprehensive evaluation of cost-effective electrode materials, anode compositions, or electrolysis cell designs. In this study, we systematically investigate the impact of economical electrode choices, anode material selection, temperature variations, and electrolyte conditions on hydrogen production efficiency. Our findings indicate that material selection and process parameters significantly influence overall performance, highlighting the importance of reducing both material costs and energy consumption, emphasizing the need for a cost-effective yet efficient approach to hydrogen production [73]. Additionally, by evaluating different electrolysis cell configurations, we provide novel insights into optimizing hydrogen production rates. These aspects distinguish our study from previous works and contribute to the development of a more sustainable, economically viable hydrogen production process.

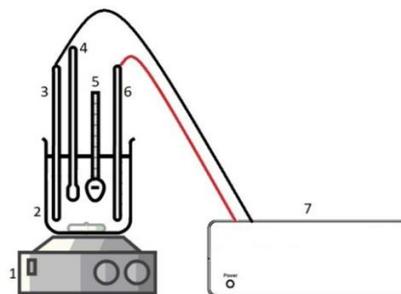
## 2. MATERIAL and METHOD

### 2.1. Experimental Systems

Experiments on the electrolysis of formic acid for hydrogen production were conducted using two different electrolysis cells. In the first stage, a basic 0.25 L electrolysis cell (Fig. 1) was used to investigate the effects of various parameter changes on current density.

The system operated with continuous stirring at 50.26 rad/s (480 RPM) using a magnetic stirrer with a heating function. The distance between electrodes was adjusted to approximately 1 cm. The current density was determined by varying the applied voltage, utilizing a power source unit (GW Instek brand, PSP-405 model) connected to the electrode. Electrolysis process was

performed under increasing temperature conditions ranging from 20°C to 80°C, as well as at a constant temperature of 20°C, to assess the system's response. Under atmospheric conditions, the boiling point of the formic acid solutions used is around 100.8°C [74]. At higher temperatures, water molecules would evaporate, leading to deviations in the diffusion-controlled process and a decrease in current values [75].

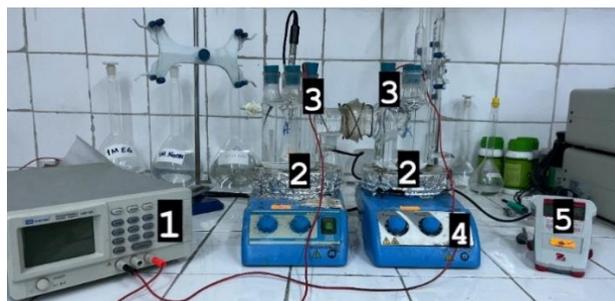


**Figure 1.** Single-compartment electrolysis cell experimental setup: (1) Magnetic stirrer with heating function, (2) Electrolysis cell, (3) Cathodic electrode, (4) pH measurement device, (5) Thermometer, (6) Anodic electrode, (7) Power source.

Therefore, temperatures above 80°C were not tested. Additionally, to prevent concentration variations due to evaporation, the electrolysis cell was sealed with parafilm, allowing the evaporated solution to condense back into the system.

To evaluate the impact of formic acid concentration on current density and determine the optimal solution concentration, experiments were conducted using tap water and six different concentrations of formic acid solutions. Various metal electrodes in plate and cylindrical forms, with active surface areas ranging from 7 to 19 cm<sup>2</sup>, were utilized. The selected electrode materials, commercially available, included Platinum (Pt), Palladium (Pd), Zinc (Zn), Copper (Cu), Stainless Steel (SS), Aluminum (Al), Lead (Pb), Graphite (C), and Titanium (Ti). The experiments were performed under both acidic and basic conditions. In this context, sulfuric acid (H<sub>2</sub>SO<sub>4</sub>), hydrochloric acid (HCl), and potassium hydroxide (KOH) were used as electrolytes to examine the impact of electrolyte type on the electrolysis of formic acid. In all experiments, pure commercial formic acid was used.

In the second stage, a specially designed two-chamber electrolysis cell constructed from Pyrex glass was utilized, featuring separate anode and cathode sections separated by a membrane [76]. The experimental setup, illustrated in Fig. 2, maintained the optimal parameters identified in the first stage. The main objective was to examine the gas composition produced. Each chamber held 750 mL of liquid, giving a total volume of 1500 mL. To ensure uniform solutions, continuous stirring and temperature regulation were provided by heated magnetic stirrer (VELP Scientifica ARE model). The anode and cathode chambers were connected by a removable, shielded spherical neck.



**Figure 2.** Two- chamber electrolysis cell system (1: DC power source, 2: electrolysis cell, 3: electrode connection point, 4: heated magnetic stirrer, 5: pH meter)

In the second phase of the study, a membrane-based electrolysis system was used, maintaining the parameter values that yielded the greatest current density in the simple electrolysis cell. The anode chamber contained a solution of 2 M formic acid and 0.004 M  $\text{H}_2\text{SO}_4$ , while the cathode chamber contained 0.004 M  $\text{H}_2\text{SO}_4$  solution. Both solutions were stirred at 480 rpm during the entire experiment, the temperature was kept at 50°C. Based on the results obtained from the simple electrolysis cell, a Pt electrode, which demonstrated the highest current density, was selected as the cathode for hydrogen evolution. The anode electrode was varied in the experiments, and commercial Zn/Pt, Pd/Pt, Cu/Pt, and Ti/Pt electrode pairs were used.

## 2.2. Membrane Activation

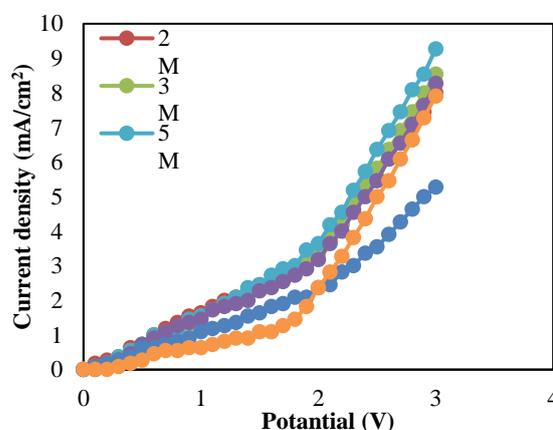
In this study, a commercially available Nafion membrane, known for its proton conductivity and thermal stability, was utilized. Nafion membranes act as cation-exchange membranes and have active sites with a negative charge, facilitating  $\text{H}^+$  ion transport [77]. Their structure comprises a hydrophobic perfluorinated backbone and hydrophilic sulfonic acid groups [78]. The hydrophilic regions enable proton and water transport, while the hydrophobic backbone provides structural stability and water insolubility. Water molecules in the membrane create weak interactions with protons, facilitating ion movement from the anode to the cathode. To enhance performance, Nafion membranes require activation through acid treatment, which increases water content and conductivity [79]. While activation improves proton permeability, it does not alter surface morphology or functional groups [80]. Various activation methods for Nafion membranes are described in the literature [81-84]. In this study, the membrane was activated by immersing it in a 2 M  $\text{H}_2\text{SO}_4$  solution for 24 hours, followed by rinsing in distilled water for another 24 hours [85]. This procedure was found to enhance proton conductivity while preserving the membrane's structural integrity [73, 85]. The hydrogen peroxide treatment commonly used in some studies was not preferred in this work due to its potential to generate highly reactive radicals that may degrade the membrane structure and reduce proton conductivity [86, 87].

## 3. RESULTS AND DISCUSSION

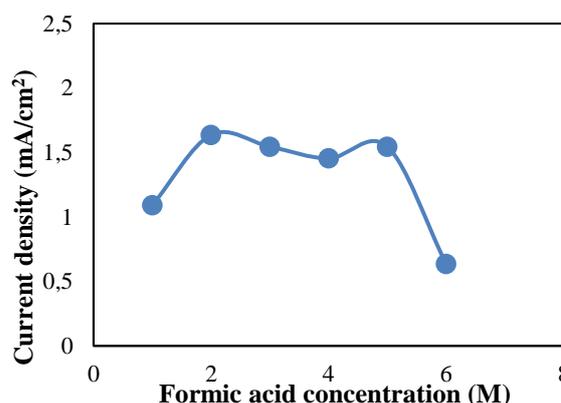
### 3.1. Single-Compartment Electrolysis Cell Experiments

#### 3.1.1. Effect of solution concentration

During the experiments, the solution temperature was consistently maintained at 20°C. A palladium (Pd) plate ( $5.5 \times 1$  cm) was utilized as the anode, while a platinum (Pt) plate of the same dimensions was employed as the cathode. The electrolysis was performed under potential-controlled conditions, where varying potentials were applied to the electrodes, and the corresponding current density values were recorded. The relationship between potential and current density for different concentrations of formic acid solutions, stirred at 480 RPM and maintained at 20°C, is presented in Fig. 3. Additionally, the changes in current density with concentration at a constant voltage of 1 V is shown in Fig. 4.



**Figure 3.** Current density change at constant temperature of 20°C for formic acid solutions of different concentrations

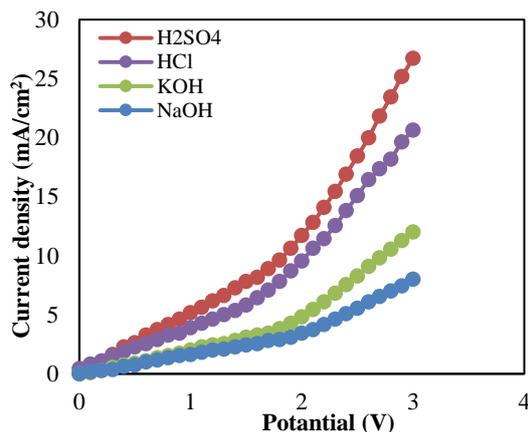


**Figure 4.** Current density change with concentration at 1 V constant voltage

At a constant voltage of 1 V, the highest current density was observed at a 2 M formic acid concentration among all concentrations. Since the highest current density (1.7  $\text{mA}/\text{cm}^2$  at 1 V) was obtained with 2 M formic acid, further parameter studies in the study were continued with the 2 M concentration.

### 3.1.2. Effect of electrolyte type

The electrolysis of formic acid was studied in different electrolyte environments and at varying pH levels. While the onset potential in the electrooxidation of formic acid was not significantly affected by pH, the product distribution was directly dependent on the pH. In this study, the effects of NaOH and KOH were examined as electrolytes for working under basic conditions, while the effects of H<sub>2</sub>SO<sub>4</sub> and HCl were investigated for working under acidic conditions. The impact of different electrolytes on current density was presented in Fig. 5.



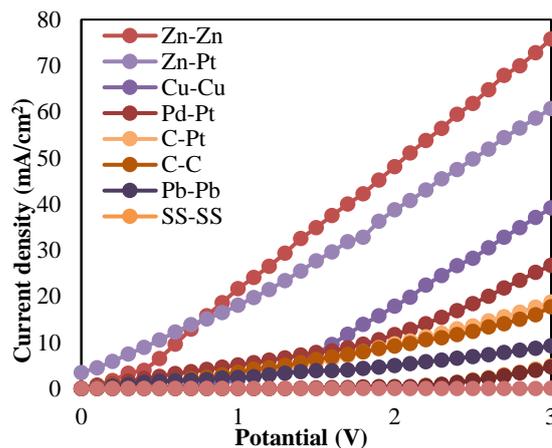
**Figure 5.** Effect of different electrolytes on current density

In experiments conducted using a Pd/Pt electrode pair with the addition of 10 mL of 1 M base and acid to a 2 M formic acid solution, the highest current density value was obtained when H<sub>2</sub>SO<sub>4</sub> was used. The electrochemical modification of the solution was investigated in an alkaline environment with 1 M NaOH and KOH solutions separately in the 2 M formic acid solution, but lower current density values were obtained compared to the acid-based solutions (for 1 V: NaOH: 1.63 mA/cm<sup>2</sup>, KOH: 2 mA/cm<sup>2</sup>). This suggests that under basic conditions, the electrochemical reconfiguration of formic acid using the Pd/Pt electrode pair is not suitable compared to acidic conditions [88].

For acidic conditions, the electrochemical reconfiguration of solutions formed by adding 10 mL of 1 M H<sub>2</sub>SO<sub>4</sub> and HCl solutions separately to the 2 M formic acid solution was investigated, resulting in higher current density values (for 1 V: H<sub>2</sub>SO<sub>4</sub>: 5.18 mA/cm<sup>2</sup>, HCl: 3.91 mA/cm<sup>2</sup>). In this case, the highest current density for acidic conditions was observed with H<sub>2</sub>SO<sub>4</sub>.

### 3.1.3. Effect of different electrode materials

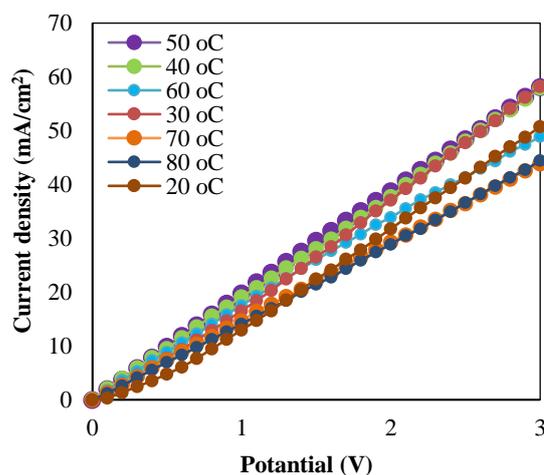
The current densities for different electrodes in the electrolysis of formic acid were investigated. In this context, the performance of electrode pairs such as Pd/Pt, Zn/Zn, Cu/Cu, SS/SS, Al/Al, Pb/Pb, C/C, Ti/Ti, Zn/Pt, and C/Pt were examined in the electrolysis of formic acid for a 2 M solution. The experiments used a solution composed of 2 M HCOOH and 1 M H<sub>2</sub>SO<sub>4</sub>. In experiments conducted at a stable temperature of 20°C, the impacts of various electrode materials pairs on the electrolysis of formic acid, as shown in Fig. 6.



**Figure 6.** Impact of various electrode pairs on current density  
The highest current density at a constant voltage of 1 V was obtained with the Zn/Zn electrode pair. At a constant voltage of 1 V, the Zn electrode pair can yield 4 times higher current density compared to the Pd/Pt electrode pair. Based on these results, the decision was made to use Zn/Zn as the electrode in the later stages of the study.

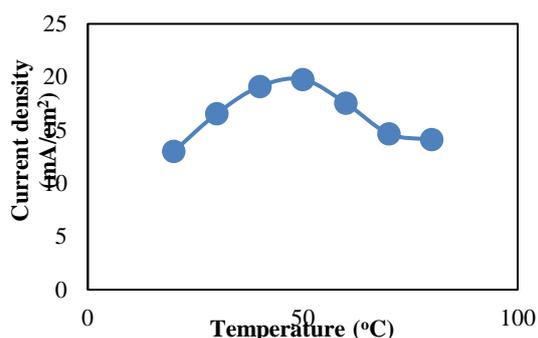
### 3.1.4. Effect of temperature

The electrolysis of a 2 M HCOOH and 1 M H<sub>2</sub>SO<sub>4</sub> solution with the Zn/Zn electrode pair was studied at various temperatures, as shown in Fig. 7, which illustrates the impact of different temperatures on current density. The experiments were performed between 20°C and 80°C, and the change in current density over time was observed at these temperatures. The highest current density was achieved at 50°C. Higher temperatures were avoided due to concerns regarding system safety and cost [89]. Based on these findings, a working temperature of 50°C was selected for the subsequent experiments.



**Figure 7.** Effect of temperature changes on current density

Fig. 8 displays how current density changes with temperature at a constant voltage of 1 V. As the temperature increases, the current density rises, reaching its maximum at 50°C. Based on these findings, 50°C was determined as the operating temperature for the further stages of the study.



**Figure 8.** Variation of current density with temperature under a constant voltage of 1 V

### 3.2. Two-Chamber Electrolysis Cell Experiments

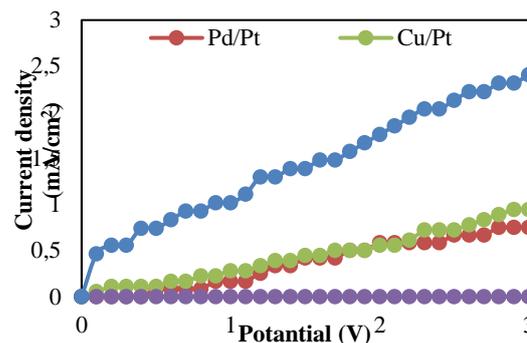
The working concentration of FA was determined to be 2 M based on the results from the single-compartment electrolysis cell experiments and was maintained throughout the two-chamber electrolysis cell experiments. Each experiment was conducted at 50°C with a stirring rate of 480 rpm. The pH of the environment in the anode compartment containing FA was measured as 2.4.

#### 3.2.1. The role of different anode materials in the electrolysis process

Due to the acidic environment in PEM electrolyzers, noble metals are essential as catalysts for both the anode and cathode [90]. Noble metal oxides, such as  $\text{IrO}_2$  and  $\text{RuO}_2$ , are typically used as anode catalysts, while more stable noble metals like platinum (Pt) and palladium (Pd) are preferred for the cathode [73, 91]. To enhance hydrogen production efficiency in two-chamber electrolysis cell, where the cathode electrode, a commercially available Pt electrode with proven catalytic activity and stability, was kept constant, while the anode electrode was varied to test different combinations. In this context, zinc/platinum (Zn/Pt), copper/platinum (Cu/Pt), titanium/platinum (Ti/Pt), and palladium/platinum (Pd/Pt) electrodes were tested in an acidic environment to determine the impacts of different anode electrodes on current density and, directly, hydrogen production. The impact of various anode electrodes on current density is shown in Fig. 9.

The Zn/Pt electrolyte pair yielded the highest current values. At 2 V, Pd and Cu showed almost the same current density, but the Zn electrode produced a 33% higher current density compared to the Pd and Cu electrode pairs.

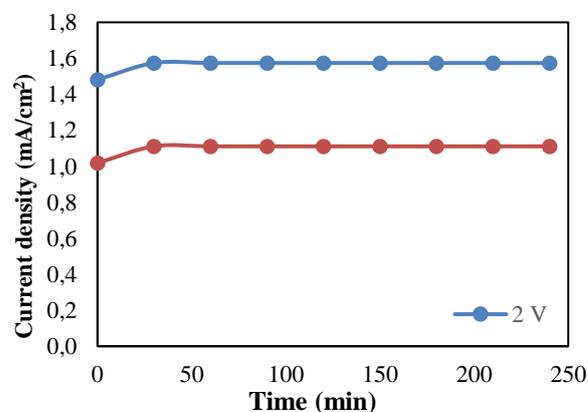
The enhanced current density seen with the Zn electrode, in comparison to Pd and Cu, is due to various factors. Zn exhibits lower overpotential for the hydrogen evolution reaction (HER), enhancing its electrochemical efficiency [92, 93]. Its surface reactivity facilitates proton reduction more effectively. Partial dissolution of Zn in the electrolyte creates a dynamic surface that promotes hydrogen evolution [73, 94]. Additionally, Zn provides a more favorable electron transfer rate at the electrode-electrolyte interface, accelerating reaction kinetics [89, 95].



**Figure 9.** The effect of different anode materials on current density

#### 3.2.2. Long-term performance test of Zn electrode

When selecting the potential range for the study, it was anticipated that increasing the potential would enhance the reaction rate on the electrode surface, leading to a rise in current density. However, excessively high potentials were also considered to potentially induce side reactions and cause damage to the electrode surface. Additionally, applied high potentials could result in gas bubble formation on the electrode surface, leading to a transition from homogeneous to heterogeneous reactions. Therefore, a 4-hour long-term performance test was conducted in a two-chamber electrolysis cell to evaluate the Zn electrode pair performance in the electrolysis of formic acid. Fig. 10 presents the current density curves obtained under constant voltages of 1 V and 2 V during the experiment.



**Figure 10.** Long-term (4-hr) performance curve of Zn electrode pair

The current density at 1V increased by approximately 10% in the first 30 minutes, stabilizing after one hour with no significant decrease observed until the completion of the experiment. At 2V, the current density showed an initial rise of about 6%, followed by stabilization after one hour with no noticeable decline.

However, by the end of the performance test, signs of electrode surface wear were detected. This wear was attributed to the gradual reduction of the active surface area and the depletion of formic acid over time [89, 95].

To further investigate this effect, Zn test was conducted to determine the amount of dissolved Zn in the electrolyte using gravimetric analysis.

### 3.2.3. Gravimetric determination of Zn electrode

A gravimetric analysis was performed to determine the Zn loss from the electrode during the electrolysis process. The method involves precipitating zinc as ammonium zinc phosphate, which is then converted to zinc pyrophosphate for constant weighing [96, 97]. In this process, the solution containing zinc ions is treated with concentrated HCl, heated, and diluted with water. After adding  $\text{NH}_4\text{Cl}$  and acetic acid, the solution is heated in a water bath, followed by the addition of  $(\text{NH}_4)_2\text{HPO}_4$  and  $\text{NH}_3$ . Precipitation occurs when the solution turns yellow, and the precipitate is allowed to mature in a water bath

that pure  $\text{H}_2$  was obtained from the cathode chamber using a Nafion XL membrane with formic acid in a two-chamber electrolysis cell, as expected. This result demonstrates the potential for producing 100% pure  $\text{H}_2$  through electrolysis of formic acid. Additionally, the analysis showed that hydrogen production is achievable at a relatively low voltage of 2 V and a moderate temperature of  $50^\circ\text{C}$ . Although  $\text{H}_2$  was produced at the cathode chamber, CO was formed at the anode instead of the expected  $\text{CO}_2$ . This is likely due to several factors. The high applied potential favored the formation of CO over  $\text{CO}_2$ , as CO requires less energy to form [101, 102].

**Table 1.** Comparative overview of hydrogen production rates in FA and similar electrolysis studies

Electrolysis raw material	Electrolyte	Electrode Type	Applied Voltage (V)/ current density ( $\text{mA}/\text{cm}^2$ )	Hydrogen Production Rate	Ref.
3 M FA	2.5 M NaOH	Pt (anode-cathode)	8 $\text{mA}/\text{cm}^2$	53 $\mu\text{mol}/\text{h}$	[20]
Methanol-water solution	Polymer electrolyte membrane	Pt (anode) $\text{IrO}_2$ (cathode)	160 $\text{mA}/\text{cm}^2$	30 $\text{mL}/\text{min}$	[100]
Glycerol-water solution	Polymer electrolyte membrane	20% Pt on Ru-Ir oxide (anode) Pt (cathode)	10 $\text{A}/\text{m}^2$	10 $\text{m}^3 \text{ day}^{-1} \text{ m}^{-3}$	[98]
0.4 M glycerol	0.04 M $\text{H}_2\text{SO}_4$ Polymer electrolyte membrane	Zn pair (anode-cathode)	2 V	0.2 $\text{mL}/\text{min}$	[99]
Coal-water slurry	0.004 M $\text{H}_2\text{SO}_4$ Polymer electrolyte membrane	Zn pair (anode-cathode)	2 V	0.3 $\text{mL}/\text{min}$	[73]

before being filtered, washed, and heated to  $900^\circ\text{C}$  to obtain  $\text{Zn}_2\text{P}_2\text{O}_7$  for weighing.

The analysis results indicate a total mass loss of around 10% from the electrodes after the 4-hour long-term performance test.

### 3.2.4. Determination of hydrogen generation and gas analysis

For gas analysis, 2 M formic acid and 0.004 M  $\text{H}_2\text{SO}_4$  were placed in the anode chamber, while the cathode chamber contained 0.004 M  $\text{H}_2\text{SO}_4$ . The hydrogen evolution rate for formic acid with Zn/Pt electrodes was then measured with a mass flow meter (Cole-Parmer) with single-digit precision. Hydrogen production occurred at a rate of about  $0.4 \text{ mL} \cdot \text{min}^{-1}$  when a constant voltage of 2 V was applied. These findings align with those observed in comparable research, suggesting that higher hydrogen production rates are achievable [73, 98, 99]. These experimental results were further evaluated by comparing them with those reported in similar studies in the literature. A summary of hydrogen production rates under various conditions from related works is presented in Table 1, providing a broader context for assessing the performance of the present system.

A gas chromatography (GC) system with a thermal conductivity detector (TCD) was used to analyze the gas products formed during these experiments. The analysis was performed with the SRI Instruments brand and SRI 310C model, utilizing a 6" silica gel column. In the experiment conducted for gas analysis, it was observed

Additionally, the acidic environment, the electrode material, and the temperature conditions promoted intermediate reactions, leading to CO formation [103-105]. These factors caused the reaction pathway at the anode to shift under the given conditions, resulting in the formation of CO instead of  $\text{CO}_2$ .

Faradaic efficiency was calculated for the experiment. Under a constant potential of 2 V, at room temperature, and over a duration of 3.5 hours, a constant current density of  $1.63 \text{ mA}/\text{cm}^2$  was achieved. Under these conditions, the Faradaic efficiency was calculated to be 92%.

## 4. CONCLUSIONS

This study presents an energy-efficient electrochemical method for hydrogen production via formic acid electrolysis using two distinct electrode configurations. In the first electrolysis cell, a Zn electrode pair was found to achieve four times the current density compared to a commercial Pd/Pt electrode pair. In the second electrolysis cell, where Zn was used as the anode and a more stable Pt electrode was employed at the cathode, the Zn anode electrode exhibited 33% higher current density compared to the Pd catalyst, which is commonly preferred as an anode catalyst in electrolysis processes. By utilizing formic acid as both the proton source and anodic reactant, the process resulted in a significant reduction in the required operational voltage-achieving hydrogen generation at only 2 V and a moderate

temperature of 50°C. These conditions were found to be substantially milder than those required in conventional water electrolysis systems, marking a notable advancement in the field of low-energy hydrogen production.

The system demonstrated a current density of 1.63 mA·cm<sup>-2</sup> and a hydrogen production rate of 0.4 mL·min<sup>-1</sup>, with a sustained Faradaic efficiency of 92% over 4 hours of continuous operation. These performance metrics, which were found to be consistent with values reported in the literature, validate the stability of the Zn/Pt-based electrochemical setup. Notably, the use of zinc, a low-cost and earth-abundant material, was shown to provide a promising alternative to noble metal electrodes, thereby enhancing both the economic and environmental feasibility of the process.

A notable aspect of this study is the utilization of formic acid as an anodic reactant, which has been shown to play a significant role in reducing the overall cell voltage required for hydrogen evolution. This is largely attributed to the relatively low oxidation potential of formic acid compared to water, which results in a lower energy threshold for the electrochemical reaction. The results obtained support the practical applicability of this approach in low-temperature and low-voltage formic acid-based electrolysis systems. This strategy offers a complementary alternative to conventional water electrolysis, particularly in scenarios where mild operating conditions or alternative feedstocks -such as biomass- derived formic acid- are preferred.

Despite a 10% mass loss from the Zn/Pt electrodes due to dissolution of zinc ions and reduction in active surface area, the overall stability of the system was maintained. These findings indicate that the Zn/Pt electrode system, particularly with the inclusion of zinc as a relatively low-cost material, offers a practical approach for hydrogen production from formic acid under low-voltage conditions. Moreover, as the European Green Deal and global sustainability initiatives increasingly emphasize the transition to low-carbon technologies, the development of such alternative, energy-efficient hydrogen production methods becomes even more crucial. In this context, formic acid electrolysis - especially when the feedstock is derived from biomass or industrial waste- offers a promising pathway to reduce energy consumption and carbon emissions. Hence, the insights provided by this study contribute not only to the advancement of electrochemical hydrogen technologies but also to broader climate goals by supporting cleaner and more sustainable energy solutions.

## ACKNOWLEDGEMENTS

We would like to express our heartfelt thanks to Esat Kitaplıoğlu and Kübra Opsar for their valuable contributions and support throughout this work.

## DECLARATION OF ETHICAL STANDARDS

The authors of this article declare that the materials and methods used in this study do not require ethical committee permission and/or legal-special permission.

## AUTHORS' CONTRIBUTIONS

**Özgü YÖRÜK:** Conceptualization, Methodology, Formal analysis, Investigation, Writing - Original Draft, Visualization.

**Duygu UYSAL:** Conceptualization, Methodology, Validation, Writing - Review & Editing, Supervision.

**Özkan Murat DOĞAN:** Conceptualization, Methodology, Validation, Writing - Review & Editing, Supervision.

## CONFLICT OF INTEREST

There is no conflict of interest in this study.

## REFERENCES

- [1] Megia, P. J., Vizcaíno, A. J., Calles, J. A., Carrero, A., "Hydrogen production technologies: from fossil fuels toward renewable sources. A mini review", *Energy & Fuels*, 35(20): 16403-16415, (2021).
- [2] Tashie-Lewis, B. C., Nnabuife, S. G., "Hydrogen production, distribution, storage and power conversion in a hydrogen economy-a technology review", *Chemical Engineering Journal Advances*, 8, 100172, (2021).
- [3] Gielen, D., Taibi, E., Miranda, R. Hydrogen: A reviewable energy perspective: Report prepared for the 2nd hydrogen energy ministerial meeting in tokyo, japan, (2019).
- [4] Büyük, P., Eryaşar, A., "Energy and exergy analysis of green hydrogen production". *Politeknik Dergisi*, 461-468, (2025).
- [5] Öztan, H., Çapoğlu, İ. K., Uysal, D., Doğan, Ö., "A parametric study to optimize the temperature of hazelnut and walnut shell gasification for hydrogen and methane production", *Bioresource Technology Reports*, 23, 101581, (2023).
- [6] Yao, D., Liu, C., Zhang, Y., Wang, S., Nie, Y., Qiao, M., Zhu, D., "Modulating Selectivity and Stability of the Direct Seawater Electrolysis for Sustainable Green Hydrogen Production", *Materials Today Catalysis*, 100089, (2025).
- [7] Franco, A., Giovannini, C., "Recent and future advances in water electrolysis for green hydrogen generation: Critical analysis and perspectives", *Sustainability*, 15(24), 16917, (2023).
- [8] Dash, S., Singh, A., Jose, S., Elangovan, D., Surapraraju, S. K., Natarajan, S. K., "Advances in green hydrogen production through alkaline water electrolysis: A comprehensive review", *International Journal of Hydrogen Energy*, 83, 614-629, (2024).
- [9] Anwar, S., Khan, F., Zhang, Y., Djire, A., "Recent development in electrocatalysts for hydrogen production through water electrolysis", *International Journal of Hydrogen Energy*, 46(63), 32284-32317, (2021).

- [10] Emam, A. S., Hamdan, M. O., Abu-Nabah, B. A., Elnajjar, E., "A review on recent trends, challenges, and innovations in alkaline water electrolysis", *International Journal of Hydrogen Energy*, 64, 599-625, (2024).
- [11] Arshad, F., Haq, T. u., Hussain, I., Sher, F., "Recent advances in electrocatalysts toward alcohol-assisted, energy-saving hydrogen production", *ACS Applied Energy Materials*, 4(9), 8685-8701, (2021).
- [12] Bambagioni, V., Bevilacqua, M., Bianchini, C., Filippi, J., Lavacchi, A., Marchionni, A., Vizza, F., Shen, P. K., "Self-sustainable production of hydrogen, chemicals, and energy from renewable alcohols by electrocatalysis", *ChemSusChem*, 3(7), 851-855, (2010).
- [13] Ju, H., Giddey, S., Badwal, S. P., "The role of nanosized SnO<sub>2</sub> in Pt-based electrocatalysts for hydrogen production in methanol assisted water electrolysis", *Electrochimica Acta*, 229, 39-47, (2017).
- [14] Cárdenas-Acero, A., Álvarez-Romero, C., Daza, C., Álvarez, A., Baquero, E. A., "Exploring heterogeneous Ru-based catalysts: CO<sub>2</sub> hydrogenation towards formic acid, formaldehyde, and methanol", *Discover Catalysis*, 1(1), 4, (2024).
- [15] Chen, X., Liu, Y., Wu, J., "Sustainable production of formic acid from biomass and carbon dioxide", *Molecular Catalysis*, 483, 110716, (2020).
- [16] Preuster, P., Albert, J., "Biogenic formic acid as a green hydrogen carrier", *Energy Technology*, 6(3), 501-509, (2018).
- [17] Bulushev, D. A., Ross, J. R., "Towards sustainable production of formic acid", *ChemSusChem*, 11(5), 821-836, (2018).
- [18] Kainth, S., Sharma, P., Pandey, O. P., "Green sorbents from agricultural wastes: A review of sustainable adsorption materials", *Applied Surface Science Advances*, 19, 100562, (2024).
- [19] Hafeez, S., Harkou, E., Spanou, A., Al-Salem, S. M., Villa, A., Dimitratos, N., Manos, G., Constantinou, A., "Review on recent progress and reactor set-ups for hydrogen production from formic acid decomposition", *Materials Today Chemistry*, 26, 101120, (2022).
- [20] Guo, W., Li, L., Li, L., Tian, S., Liu, S., Wu, Y., "Hydrogen production via electrolysis of aqueous formic acid solutions", *International Journal of Hydrogen Energy*, 36(16), 9415-9419, (2011).
- [21] Li, Z., Xu, Q., "Metal-nanoparticle-catalyzed hydrogen generation from formic acid", *Accounts of Chemical Research*, 50(6), 1449-1458, (2017).
- [22] Sordakis, K., Tang, C., Vogt, L. K., Junge, H., Dyson, P. J., Beller, M., Laurenczy, G., "Homogeneous catalysis for sustainable hydrogen storage in formic acid and alcohols", *Chemical reviews*, 118(2), 372-433, (2018).
- [23] Lv, C., Lou, P., Shi, C., Wang, R., Fu, Y., Gao, L., Wang, S., Li, Y., Zhang, C., "Efficient hydrogen production via sunlight-driven thermal formic acid decomposition over a porous film of molybdenum carbide", *Journal of Materials Chemistry A*, 9(39), 22481-22488, (2021).
- [24] Younas, M., Rezakazemi, M., Arbab, M. S., Shah, J., Rehman, W. U., "Green hydrogen storage and delivery: Utilizing highly active homogeneous and heterogeneous catalysts for formic acid dehydrogenation", *International Journal of Hydrogen Energy*, 47(22), 11694-11724, (2022).
- [25] Tazikeh, S., Davoudi, A., Zendejboudi, S., Saady, N. M. C., Albayati, T. M., "Predicting hydrogen production from formic acid dehydrogenation using smart connectionist models", *International Journal of Hydrogen Energy*, 109, 574-590, (2025).
- [26] Wen, H., Liu, Y., Liu, S., Peng, Z., Wu, X., Yuan, H., Jiang, J., Li, B., "Heterogeneous catalysis in production and utilization of formic acid for renewable energy", *Small*, 20(18), 2305405, (2024).
- [27] Grasemann, M., Laurenczy, G., "Formic acid as a hydrogen source—recent developments and future trends" *Energy & Environmental Science*, 5(8), 8171-8181, (2012).
- [28] Al-Nayili, A., Majdi, H. S., Albayati, T. M., Saady, N. M. C., "Formic acid dehydrogenation using noble-metal nanoheterogeneous catalysts: Towards sustainable hydrogen-based energy", *Catalysts*, 12(3), 324, (2022).
- [29] Asefa, T., Koh, K., Yoon, C. W., "CO<sub>2</sub>-mediated H<sub>2</sub> storage-release with nanostructured catalysts: recent progresses, challenges, and perspectives", *Advanced Energy Materials*, 9(30), 1901158, (2019).
- [30] Chaparro-Garnica, J. A., Navlani-García, M., Salinas-Torres, D., Morallón, E., Cazorla-Amorós, D., "H<sub>2</sub> Production from Formic Acid Using Highly Stable Carbon-Supported Pd-Based Catalysts Derived from Soft-Biomass Residues: Effect of Heat Treatment and Functionalization of the Carbon Support", *Materials*, 14(21), 6506, (2021).
- [31] Navlani-García, M., Salinas-Torres, D., Cazorla-Amorós, D., "Hydrogen production from formic acid attained by bimetallic heterogeneous PdAg catalytic systems", *Energies*, 12(21), 4027, (2019).
- [32] Boddien, A., Loges, B., Junge, H., Gärtner, F., Noyes, J. R., Beller, M., "Continuous hydrogen generation from formic acid: highly active and stable ruthenium catalysts", *Advanced Synthesis & Catalysis*, 351(14-15), 2517-2520, (2009).
- [33] Czaun, M., Goepfert, A., Kothandaraman, J., May, R. B., Haiges, R., Prakash, G. S., Olah, G. A., "Formic acid as a hydrogen storage medium: ruthenium-catalyzed generation of hydrogen from formic acid in emulsions", *ACS catalysis*, 4(1), 311-320, (2014).
- [34] Strauss, S., Whitmire, K., Shriver, D., "Rhodium (I) catalyzed decomposition of formic acid", *Journal of Organometallic Chemistry*, 174(3), C59-C62, (1979).
- [35] Hermosilla, P., Urriolabeitia, A., Iglesias, M., Polo, V., Casado, M. A., "Efficient solventless dehydrogenation of formic acid by a CNC-based rhodium catalyst", *Inorganic Chemistry Frontiers*, 9(17), 4538-4547, (2022).
- [36] Boddien, A., Loges, B., Gärtner, F., Torborg, C., Fumino, K., Junge, H., Ludwig, R., Beller, M., "Iron-catalyzed hydrogen production from formic acid", *Journal of the American Chemical Society*, 132(26), 8924-8934, (2010).
- [37] Zell, T., Butschke, B., Ben-David, Y., Milstein, D., "Efficient hydrogen liberation from formic acid catalyzed by a well-defined iron pincer complex under mild conditions", *Chemistry—A European Journal*, 19(25), 8068-8072, (2013).
- [38] Bavykina, A., Goesten, M., Kapteijn, F., Makkee, M., Gascon, J., "Efficient production of hydrogen from

- formic acid using a Covalent Triazine Framework supported molecular catalyst", *ChemSusChem*, 8(5), 809-812, (2015).
- [39] Czaun, M., Kothandaraman, J., Goepfert, A., Yang, B., Greenberg, S., May, R. B., Olah, G. A., Prakash, G. S., "Iridium-catalyzed continuous hydrogen generation from formic acid and its subsequent utilization in a fuel cell: toward a carbon neutral chemical energy storage", *ACS catalysis*, 6(11), 7475-7484, (2016).
- [40] Russo, D., Calabrese, M., Marotta, R., Andrezzi, R., Di Benedetto, A., "Thermodynamics of the cyclic formate/bicarbonate interconversion for hydrogen storage", *International Journal of Hydrogen Energy*, 47(73), 31370-31380, (2022).
- [41] Rodriguez-Reinoso, F., "The role of carbon materials in heterogeneous catalysis", *Carbon*, 36(3), 159-175, (1998).
- [42] Lam, E., Luong, J. H., "Carbon materials as catalyst supports and catalysts in the transformation of biomass to fuels and chemicals", *ACS catalysis*, 4(10), 3393-3410, (2014).
- [43] Enthaler, S., von Langermann, J., Schmidt, T., "Carbon dioxide and formic acid-the couple for environmental-friendly hydrogen storage", *Energy & Environmental Science*, 3(9), 1207-1217, (2010).
- [44] Li, Y., Yao, M.-S., He, Y., Du, S., "Recent Advances of Electrocatalysts and Electrodes for Direct Formic Acid Fuel Cells: from Nano to Meter Scale Challenges", *Nano-Micro Letters*, 17(1), 148, (2025).
- [45] Singh, A. K., Singh, S., Kumar, A., "Hydrogen energy future with formic acid: a renewable chemical hydrogen storage system", *Catalysis Science & Technology*, 6(1), 12-40, (2016).
- [46] Tang, W., Zhang, L., Qiu, T., Tan, H., Wang, Y., Liu, W., Li, Y., "Efficient conversion of biomass to formic acid coupled with low energy consumption hydrogen production from water electrolysis", *Angewandte Chemie International Edition*, 62(30), e202305843, (2023).
- [47] Kiliç, E. Ö., Koparal, A. S., Ögütveren, Ü. B., "Hydrogen production by electrochemical decomposition of formic acid via solid polymer electrolyte", *Fuel Processing Technology*, 90(1), 158-163, (2009).
- [48] Ren, J.-T., Chen, L., Wang, H.-Y., Tian, W.-W., Yuan, Z.-Y., "Water electrolysis for hydrogen production: from hybrid systems to self-powered/catalyzed devices", *Energy & Environmental Science*, 17(1), 49-113, (2024).
- [49] Dutta, I., Chatterjee, S., Cheng, H., Parsapur, R. K., Liu, Z., Li, Z., Ye, E., Kawanami, H., Low, J. S. C., Lai, Z., "Formic acid to power towards low-carbon economy", *Advanced Energy Materials*, 12(15), 2103799, (2022).
- [50] Lu, X., Leung, D. Y., Wang, H., Leung, M. K., Xuan, J., "Electrochemical reduction of carbon dioxide to formic acid", *ChemElectroChem*, 1(5), 836-849, (2014).
- [51] Ramdin, M., Morrison, A. R., De Groen, M., Van Haperen, R., De Kler, R., Irtem, E., Laitinen, A. T., Van Den Broeke, L. J., Breugelmans, T., Trusler, J. M., "High-pressure electrochemical reduction of CO<sub>2</sub> to formic acid/formate: effect of pH on the downstream separation process and economics", *Industrial & Engineering Chemistry Research*, 58(51), 22718-22740, (2019).
- [52] Orlić, M., Hochenauer, C., Nagpal, R., Subotić, V., "Electrochemical reduction of CO<sub>2</sub>: A roadmap to formic and acetic acid synthesis for efficient hydrogen storage", *Energy Conversion and Management*, 314, 118601, (2024).
- [53] Ewis, D., Arsalan, M., Khaled, M., Pant, D., Ba-Abbad, M. M., Amhamed, A., El-Naas, M. H., "Electrochemical reduction of CO<sub>2</sub> into formate/formic acid: A review of cell design and operation", *Separation and Purification Technology*, 316, 123811, (2023).
- [54] Tasgin, B., İlbaş, M., "Pressure analysis investigation of PEM electrolyzer cell used for green hydrogen production", *Journal of Polytechnic-Politeknik Dergisi*, 26(4), 1533-1541, (2023).
- [55] Zhigalenok, Y., Abdimomyn, S., Levi, M., Shpigel, N., Ryabicheva, M., Lepikhin, M., Galeyeva, A., Malchik, F., "Water activity: the key to unlocking high-voltage aqueous electrolytes", *Journal of Materials Chemistry A*, 12(48), 33855-33869, (2024).
- [56] Kroll, F., Schörner, M., Schmidt, M., Kohler, F. T., Albert, J., Schühle, P., "Hydrogen production from wet biomass via a formic acid route under mild conditions", *International Journal of Hydrogen Energy*, 62, 959-968, (2024).
- [57] Boddula, R., Lee, Y.-Y., Masimukku, S., Chang-Chien, G.-P., Pothu, R., Srivastava, R. K., Sarangi, P. K., Selvaraj, M., Basumatary, S., Al-Qahtani, N., "Sustainable hydrogen production: Solar-powered biomass conversion explored through (Photo) electrochemical advancements", *Process Safety and Environmental Protection*, (2024).
- [58] Achour, M., Álvarez-Hernández, D., Ruiz-López, E., Megías-Sayago, C., Ammari, F., Ivanova, S., Centeno, M. A., "Formic acid as renewable reagent and product in biomass upgrading", *Tetrahedron Green Chem*, 2, 100020, (2023).
- [59] Saravanan, A., Vo, D.-V. N., Jeevanantham, S., Bhuvaneshwari, V., Narayanan, V. A., Yaashikaa, P., Swetha, S., Reshma, B., "A comprehensive review on different approaches for CO<sub>2</sub> utilization and conversion pathways", *Chemical Engineering Science*, 236, 116515, (2021).
- [60] Wang, Z., Li, H., Dong, T., Geng, Y., Tian, X., Chang, R., Lai, J., Feng, S., Wang, L., "Efficient acidic CO<sub>2</sub> electroreduction to formic acid by modulating electrode structure at industrial-level current", *Chemical Engineering Journal*, 489, 151238, (2024).
- [61] Fernández-Caso, K., Diaz-Sainz, G., Alvarez-Guerra, M., Irabien, A., "Electroreduction of CO<sub>2</sub>: advances in the continuous production of formic acid and formate", *ACS Energy Letters*, 8(4), 1992-2024, (2023).
- [62] Wang, S., Lu, A., Zhong, C.-J., "Hydrogen production from water electrolysis: role of catalysts", *Nano Convergence*, 8(1), 4, (2021).
- [63] Goren, A. Y., Temiz, M., Erdemir, D., Dincer, I., "The role of effective catalysts for hydrogen production: A performance evaluation", *Energy*, 315, 134257, (2025).
- [64] Tumiwa, J. R., Mizik, T., "Advancing nickel-based catalysts for enhanced hydrogen production: Innovations in electrolysis and catalyst design", *International Journal of Hydrogen Energy*, 109, 961-978, (2025).

- [65] Vidal-Barreiro, I., Sánchez, P., de Lucas-Consuegra, A., Romero, A., "A New Doped Graphene-Based Catalyst for Hydrogen Evolution Reaction Under Low-Electrolyte Concentration and Biomass-Rich Environments", *Energy & Fuels*, (2025).
- [66] Folkman, S. J., González-Cobos, J., Giancola, S., Sánchez-Molina, I., Galán-Mascarós, J. R., "Benchmarking catalysts for formic acid/formate electrooxidation", *Molecules*, 26(16), 4756, (2021).
- [67] Chen, A., Ostrom, C., "Palladium-based nanomaterials: synthesis and electrochemical applications", *Chemical Reviews*, 115(21), 11999-12044, (2015).
- [68] Rego de Vasconcelos, B., Lavoie, J.-M., "Recent advances in power-to-X technology for the production of fuels and chemicals", *Frontiers in chemistry*, 7, 392, (2019).
- [69] Yasin, M. C., Johar, M., Gupta, A., Shahgaldi, S., "A comprehensive review of the material innovations and corrosion mitigation strategies for PEMWE bipolar plates", *International Journal of Hydrogen Energy*, 88, 726-747, (2024).
- [70] Nnabuife, S. G., Hamzat, A. K., Whidborne, J., Kuang, B., Jenkins, K. W., "Integration of renewable energy sources in tandem with electrolysis: A technology review for green hydrogen production", *International Journal of Hydrogen Energy*, (2024).
- [71] Proietto, F., Rinicella, R., Galia, A., Scialdone, O., "Electrochemical conversion of CO<sub>2</sub> to formic acid using a Sn based cathode: Combined effect of temperature and pressure", *Journal of CO<sub>2</sub> Utilization*, 67, 102338, (2023).
- [72] Vos, R. E., Kolmeijer, K. E., Jacobs, T. S., van der Stam, W., Weckhuysen, B. M., Koper, M. T., "How temperature affects the selectivity of the electrochemical CO<sub>2</sub> reduction on copper", *ACS catalysis*, 13(12), 8080-8091, (2023).
- [73] Yörük, Ö., Uysal, D., Doğan, Ö. M., "Carbon-assisted hydrogen production via electrolysis at intermediate temperatures: Impact of mineral composition, functional groups, and membrane effects on current density", *Fuel*, 380, 133268, (2025).
- [74] Qiao, H., Han, M., Ouyang, S., Zheng, Z., Ouyang, J., "An integrated lignocellulose biorefinery process: two-step sequential treatment with formic acid for efficiently producing ethanol and furfural from corn cobs", *Renewable Energy*, 191, 775-784, (2022).
- [75] Li, Z., Xu, Y., Li, R., Jia, M., Wang, Q., Chen, Y., Cai, R., Han, Z., "Impact of the water evaporation on the heat and moisture transfer in a high-temperature underground roadway", *Case Studies in Thermal Engineering*, 28, 101551, (2021).
- [76] Yıldız, M. G., Yörük, Ö., Uysal, D., Doğan, Ö. M., "Investigation of Hydrogen Production via Black Water Electrolysis", *Journal of Polytechnic*, 28(2), 585-594, (2025).
- [77] Yagizatli, Y., Ar, I., "Novel fluoroboric acid additive for blend membrane to be used in PEM fuel cell, characterization studies, and performance test", *Journal of Polymers and the Environment*, 32(8), 3569-3590, (2024).
- [78] Tan, H., Zhao, S., Ali, S. E., Zheng, S., Alanazi, A. K., Wang, R., Zhang, H., Abo-Dief, H. M., Xu, B. B., Algadi, H., "Perfluorosulfonic acid proton exchange membrane with double proton site side chain for high-performance fuel cells at low humidity", *Journal of Materials Science & Technology*, 166, 155-163, (2023).
- [79] Ito, H., Maeda, T., Nakano, A., Takenaka, H., "Properties of Nafion membranes under PEM water electrolysis conditions", *International Journal of Hydrogen Energy*, 36(17), 10527-10540, (2011).
- [80] Kusoglu, A., Savagatrup, S., Clark, K. T., Weber, A. Z., "Role of Mechanical Factors in Controlling the Structure-Function Relationship of PFSA Ionomers", *Macromolecules*, 45(18), 7467-7476, (2012).
- [81] Ma, M., Shen, L., Zhao, Z., Guo, P., Liu, J., Xu, B., Zhang, Z., Zhang, Y., Zhao, L., Wang, Z., "Activation methods and underlying performance boosting mechanisms within fuel cell catalyst layer", *EScience*, 100254, (2024).
- [82] Xu, Z., Qi, Z., He, C., Kaufman, A., "Combined activation methods for proton-exchange membrane fuel cells", *Journal of Power Sources*, 156(2), 315-320, (2006).
- [83] Lufitano, E., Simari, C., Di Vona, M. L., Nicotera, I., Narducci, R., "How the morphology of nafion-based membranes affects proton transport", *Polymers*, 13(3), 359, (2021).
- [84] Yagizatli, Y., Ulas, B., Sahin, A., Ar, I., "Preparation and Characterization of SPEEK-PVA Blend Membrane Additives with Colloidal Silica for Proton Exchange Membrane Fuel Cell", *Journal of Polymers and the Environment*, 32(9), 4699-4715, (2024).
- [85] Kuwertz, R., Kirstein, C., Turek, T., Kunz, U., "Influence of acid pretreatment on ionic conductivity of Nafion® membranes", *Journal of Membrane Science*, 500, 225-235, (2016).
- [86] Kinumoto, T., Inaba, M., Nakayama, Y., Ogata, K., Umabayashi, R., Tasaka, A., Iriyama, Y., Abe, T., Ogumi, Z., "Durability of perfluorinated ionomer membrane against hydrogen peroxide", *Journal of Power Sources*, 158(2), 1222-1228, (2006).
- [87] Tang, H., Peikang, S., Wang, F., Pan, M., "A degradation study of Nafion proton exchange membrane of PEM fuel cells", *Journal of Power Sources*, 170(1), 85-92, (2007).
- [88] Kortlever, R., Balemans, C., Kwon, Y., Koper, M. T., "Electrochemical CO<sub>2</sub> reduction to formic acid on a Pd-based formic acid oxidation catalyst", *Catalysis Today*, 244, 58-62, (2015).
- [89] Yörük, Ö., Yıldız, M. G., Uysal, D., Doğan, Ö. M., Uysal, B. Z., "Experimental investigation for novel electrode materials of coal-assisted electrochemical in-situ hydrogen generation: Parametric studies using single-chamber cell", *International Journal of Hydrogen Energy*, 48(11), 4173-4181, (2023).
- [90] Bodard, A., Chen, Z., ELJarray, O., Zhang, G., "Green Hydrogen Production by Low-Temperature Membrane-Engineered Water Electrolyzers, and Regenerative Fuel Cells", *Small Methods*, 8(12), 2400574, (2024).
- [91] Charisiou, N. D., Siakavelas, G. I., Papageridis, K. N., Motta, D., Dimitratos, N., Sebastian, V., Polychronopoulou, K., Goula, M. A., "The effect of noble metal (M: Ir, Pt, Pd) on M/Ce<sub>2</sub>O<sub>3</sub>-γ-Al<sub>2</sub>O<sub>3</sub> catalysts for hydrogen production via the steam reforming of glycerol", *Catalysts*, 10(7), 790, (2020).

- [92] Yan, H., Li, S., Zhong, J., Li, B., "An electrochemical perspective of aqueous zinc metal anode", *Nano-Micro Letters*, 16(1), 15, (2024).
- [93] Chen, S., Ouyang, K., Liu, Y., Qin, H., Cui, M., Liu, A., Wang, Y., Zhang, K., Huang, Y., "Strong Metal-Support Interaction to Invert Hydrogen Evolution Overpotential of Cu Coating for High-Coulombic-Efficiency Stable Zn Anode in Aqueous Zn-Ion Batteries", *Advanced Materials*, 2417775, (2025).
- [94] Wang, Y., Jia, S., Wu, J., Wang, X., Bai, Y., "Two-Step Water Splitting for Hydrogen Production Based on Zinc Deposition and Dissolution", *Renewables*, 2(6), 414-420, (2024).
- [95] Qiu, D., Li, B., Zhao, C., Dang, J., Chen, G., Qiu, H., Miao, H., "A review on zinc electrodes in alkaline electrolyte: Current challenges and optimization strategies", *Energy Storage Materials*, 61, 102903, (2023).
- [96] Helliwell, M., Helliwell, J., Kaucic, V., Zabukovec Logar, N., Teat, S., Warren, J., Dodson, E., "Determination of zinc incorporation in the Zn-substituted gallophosphate ZnULM-5 by multiple wavelength anomalous dispersion techniques", *Structural Science*, 6(3), 345-357, (2010).
- [97] Hu, R.-p., Yu, Y.-h., WU, L., Li, K., Liao, H., Qian, Z., "Preparation of high purity zinc phosphate by precipitation transformation method", *Mod. Chem. Ind.*, 30(11), 48-51, (2010).
- [98] Marshall, A., Haverkamp, R., "Production of hydrogen by the electrochemical reforming of glycerol-water solutions in a PEM electrolysis cell", *International Journal of Hydrogen Energy*, 33(17), 4649-4654, (2008).
- [99] Yıldız, M. G., Yörük, Ö., Uysal, D., Doğan, Ö. M., Uysal, B. Z., "Parametric study on electrochemical reforming of glycerol for hydrogen production", *International Journal of Hydrogen Energy*, 47(95), 40196-40203, (2022).
- [100] Sanchez, C., Espinos, F. J., Barjola, A., Escorihuela, J., Compañ, V., "Hydrogen production from methanol-water solution and pure water electrolysis using nanocomposite perfluorinated sulfocationic membranes modified by polyaniline", *Polymers*, 14(21), 4500, (2022).
- [101] Liang, S., Huang, L., Gao, Y., Wang, Q., Liu, B., "Electrochemical reduction of CO<sub>2</sub> to CO over transition metal/N-doped carbon catalysts: the active sites and reaction mechanism", *Advanced Science*, 8(24), 2102886, (2021).
- [102] Larrazábal, G. O., Martín, A. J., Mitchell, S., Hauert, R., Pérez-Ramírez, J., "Enhanced reduction of CO<sub>2</sub> to CO over Cu-In electrocatalysts: catalyst evolution is the key", *ACS catalysis*, 6(9), 6265-6274.
- [103] Zou, X., Gu, J., "Strategies for efficient CO<sub>2</sub> electroreduction in acidic conditions", *Chinese Journal of Catalysis*, 52, 14-31, (2023).
- [104] Li, F.-Z., Qin, H.-G., Zhang, H.-L., Yue, X., Fu, L.-K., Xu, B., Lin, M., Gu, J., "Another role of CO-formation catalyst in acidic tandem CO<sub>2</sub> electroreduction: Local pH modulator", *Joule*, 8(6), 1772-1789, (2024).
- [105] Vass, Á., Kormányos, A., Kószó, Z., Endrodi, B., Janáky, C., "Anode catalysts in CO<sub>2</sub> electrolysis: challenges and untapped opportunities", *ACS catalysis*, 12(2), 1037-1051, (2022).