Quantitative Analysis of Formate Production from Plasma-Assisted Electrochemical Reduction of CO₂ on Pd-Based Catalysts

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Abstract: The escalating levels of atmospheric CO₂, primarily attributed to human activities, underscore the urgent need for innovative solutions to mitigate environmental challenges. This study delves into the electrochemical reduction of CO₂ as a promising avenue for sustainable carbon capture and utilization. Focused on the formation of formate (HCOO⁻/HCOOH), a high-value product, the research explores the integration of nonthermal plasma (NTP) with electrochemical processes—an approach rarely studied in existing literature. A comprehensive investigation involves varying parameters such as plasma discharging voltage, carrier gas, discharging mode, electrolysis voltage, polarity, and plasma type. The electrochemical tests employ a 10 wt.% Pd/C catalyst, and formate production is quantitatively analyzed using NMR. Results reveal that NTP significantly enhances CO₂ reduction, with key factors influencing formate yield elucidated. The study reveals the complexity of CO₂ electrochemical reduction, providing novel insights into the synergistic effects of NTP. These findings contribute to advancing sustainable technologies for CO₂ utilization, paving the way for more efficient and environmentally friendly processes in the pursuit of a carbon-neutral future.

Keywords: formate; electrochemical CO₂ reduction; plasma; Pd catalyst

1. Introduction

CO₂ stands as a notorious greenhouse gas, and human activities, primarily the combustion of fossil fuels, have led to a significant and alarming increase in atmospheric CO₂ concentration over recent decades [1]. To address this environmental challenge, the electrochemical reduction of CO₂ merges as a promising approach for converting CO₂ into valuable products, such as CH₄ [2], C₂H₄ [3], CO [4], HCOO⁻/HCOOH [5], and CH₃OH [6]. Among all those products, HCOO⁻/HCOOH is particularly favored due to its relatively high market price, despite its current low production volume [7].

The electrochemical reduction of CO₂ presents a versatile and sustainable solution to the escalating environmental challenges associated with rising CO₂ levels. Over the past decades, the electrochemical reduction of CO₂ into HCOO⁻/HCOOH with water as the hydrogen source has been extensively investigated by numerous researchers. Early studies of CO₂RR mainly focused on bulk transition and polycrystalline metal-based catalysts, e.g., Pd, Pb, In, Sn, etc. Notably, Pd and Pd-based nanostructures were identified for their efficiency in enhancing formate formation [8]. For instance, Hori et al. reported the use of Pd foil in 0.1 M KHCO₃ for electrochemical reduction of CO₂ into formate [9] and achieved a Faradaic efficiency of formate (FE_formate) formation of 2.8%. Subsequent studies explored catalyst variations, including decorated or supported Pd nanoparticles. Zhao et al. employed Pd nanoparticles decorated on polyaniline-covered MWNPs surfaces (Pd-PANI/CNT) as catalysts for formate production from CO₂RR [10]. An overall 83% of FE_formate was reported in their study. Min et al. used Pd/C as the catalyst for synthesizing formate in 0.5 M KHCO₃ electrolyte and showed that the Pd nanoparticles loaded...
on a carbon-supported electrode demonstrated a great potential for high-mass activities (50–80 mA HCO$_2^-$) [11]. By switching to Pd-metal-based nanoparticles (Pd NPs), Gao et al. discovered the pathway of CO$_2$RR to formate on the active phase ($\alpha+\beta$ PdH$_x$ PdH$_x$) of Pd NPs and the FE$_\text{formate}$ was as high as 90% [12]. Those prior studies suggest that the electrochemical reduction of CO$_2$ into formate is considerably complicated, involving many factors that are dependent on the catalyst type and structure, composition, catalyst deactivation, reversible evolution of active phases induced by the applied potential, electrolyte type, etc. All these complexities arise from the high inertness of CO$_2$ and highly sensitive CO$_2$RR intermediates. However, in the open literature, the studies integrating electrochemical processes and nonthermal plasma in electrochemical CO$_2$RR are rare.

The impact of nonthermal plasma discharge on electrochemical active surface area and hydrogen adsorption/desorption on Pd catalysts has been investigated in our previous study [13]. In this paper, we systematically studied the use of nonthermal plasma to assist electrochemical reduction of CO$_2$ towards formate. Specifically, constant-voltage electrochemical CO$_2$RR tests were conducted, and the produced formate was precisely quantified using NMR. Subsequently, different experimental conditions, including plasma discharging voltage, plasma carrier gas, plasma discharging mode, electrolysis voltage, plasma polarity, and plasma type were explored, and the produced formate was correlated to the test conditions to establish a complete knowledge base of nonthermal plasma-assisted electrochemical CO$_2$RR. Those results provide a novel insight into the key factors and mechanism in NTP-assisted electrochemical CO$_2$RR.

2. Materials and Methods

2.1. Materials

The 10 wt.% Pd/C (palladium 10% on carbon, surface area: 1000 m$^2$/g) was procured from Alfa Aesar Inc. (Haverhill, MA, USA). The 5 wt.% Nafion solution, IPA (99.5%), D$_2$O (99.9 atom % D), dimethyl sulfoxide (99.9%), and KHCO$_3$ (99.7%) were all sourced from Sigma-Aldrich Inc. (St. Louis, MO, USA). The carbon dioxide was obtained from Airgas (Radnor, PA, USA).

2.2. Preparation of Pd/C Electrodes

To prepare a high-quality working electrode (WE), the glassy-carbon electrode (GCE) was polished using Alpha Alumina (CH Instrument, Inc., Bee Cave, TX, USA) powder with particle sizes of 1.0 µm, 0.3 µm, and 0.05 µm in a sequential manner. After each polishing step, the electrode was thoroughly washed with deionized (DI) water. Subsequently, the electrode was sonicated in a mixed solution of DI water and isopropanol for 3 min. For investigating the catalyst’s effect on formate formation, the catalyst ink was prepared by mixing 20 mg Pd/C (palladium 10% on carbon) in 8 mL DI water, followed by sonication for 15 min. Then, 2 mL IPA (99.5%, Sigma-Aldrich St. Louis, MO, USA) was added to the mixture, and sonication continued for an additional 15 min. A 5 µL catalyst ink was pipetted onto the GCE (3 mm diameter with an electrode area of 7.07 mm$^2$). Subsequently, 10 µL of Nafion solution (5 wt%, Sigma-Aldrich St. Louis, MO, USA) was dripped onto the GCE after the catalyst was fully dried. The electrode was then transferred to an oven and cured for 30 min at 80 °C.

2.3. Electrochemical Measurements and Product Analysis

All electrochemical experiments were conducted in an H-shaped cell using a Versa 3 Potentiostat (Princeton Applied Research, Nashville, TN, USA). The experimental setup is illustrated in Figure 1. To prevent the transport of chemical species produced by the Pt mesh into the left chamber, a Nafion membrane was employed to partition the H-shaped cell into two parts. In the left chamber (refer to Figure 2), a stainless-steel capillary tube (Varian, Inc., Palo Alto, CA, USA) with an inner diameter of 180 µm was suspended approximately 2 mm above the surface of an aqueous electrolyte. The 3-electrode electrochemical system comprised a working electrode (WE) and a reference electrode (RE) placed in the left
chamber, while the counter electrode (CE) was placed in the right chamber. To minimize the resistance, the WE and RE were positioned as close as possible, considering the critical role of electrolyte internal resistance in CO$_2$RR.

Figure 1. Schematic illustration of the experimental setup. Plasma is formed by a stainless-steel capillary suspended ~2 mm above the surface of an aqueous electrolyte under a negative bias between 1250 and 2500 V relative to a submerged Pt electrode.

Figure 2. The experimental setup of the plasma-assisted electrochemical system. The reactor is an H-cell with two compartments separated by a Nafion membrane. The working electrode, i.e., a glassy carbon electrode coated with Pd catalysts, is submerged in an aqueous electrolyte, above which a micro plasma jet is ignited. The ignited plasma jet is shown in the inset.

For electrochemical tests without plasma discharge, the experiments were conducted following the standard electrochemical procedure. In electrochemical tests involving direct
current (DC) plasma, the plasma jet was connected to the negative pole of a high-voltage supply (PS325 2500 V; 25 W, Stanford Research Systems, Sunnyvale, CA, USA), relative to a submerged Pt electrode in the other chamber. The plasma was ignited at 2.5 kV, with a 274 kΩ ballast resistor limiting the plasma current. The left chamber’s headspace was filled with Ar gas through the capillary tube at a flow rate of 30 sccm. Switching the polarity of the DC plasma involved connecting the capillary tube to the positive pole of the DC power supply, making the plasma jet the anode, and the Pt electrode connected to the negative pole as the cathode. For alternative current (AC)-driven nonthermal plasma electrochemical tests, the setup mirrored the DC-driven plasma, except the plasma jet was ignited by a high-voltage, high-frequency power supply (PVM/DDR plasma drive GME PM89 CLASS 2.5, Information Unlimited, Amherst, NH, USA) at 2.5 kV to achieve an AC plasma.

Before all electrochemical tests, CO$_2$ was sparged into a 0.5 M KHCO$_3$ solution for 30 min to achieve CO$_2$-saturated electrolyte. Subsequently, cyclic voltammetry (CV) and chronocoulometry tests were performed under various operating conditions (detailed in Tables 1–3). In the CV tests, the potential was scanned at 20 mV/s between $-1.1$ and 1 V vs. Ag/AgCl. The chronocoulometry tests were conducted at constant voltage of $-0.92$ V.

### Table 1. The experiments conducted using Pd, 10% on carbon catalyst.

<table>
<thead>
<tr>
<th>Plasma Off</th>
<th>Plasma Discharging Voltage</th>
<th>Plasma Operating Gas</th>
<th>Plasma Discharging Mode</th>
<th>Electrolysis Voltage</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1.5 kV</td>
<td>2.5 kV</td>
<td>Ar</td>
<td>CO$_2$</td>
</tr>
<tr>
<td>PdC1</td>
<td>×</td>
<td>×</td>
<td>×</td>
<td>×</td>
</tr>
<tr>
<td>PdC2</td>
<td>×</td>
<td>×</td>
<td>×</td>
<td>×</td>
</tr>
<tr>
<td>PdC3</td>
<td>×</td>
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<td>×</td>
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<tr>
<td>PdC4</td>
<td>×</td>
<td>×</td>
<td>×</td>
<td>×</td>
</tr>
<tr>
<td>PdC5</td>
<td>×</td>
<td>×</td>
<td>×</td>
<td>×</td>
</tr>
<tr>
<td>PdC6</td>
<td>×</td>
<td>×</td>
<td>×</td>
<td>×</td>
</tr>
<tr>
<td>PdC7</td>
<td>×</td>
<td>×</td>
<td>×</td>
<td>×</td>
</tr>
</tbody>
</table>

×: applicable test condition. a: “SIM” is an abbreviation for “simultaneously”. It indicates that electrochemical experiments are conducted at the same time as plasma discharge. b: “SEP” is an abbreviation for “separately”. It indicates that the plasma discharge is conducted first, followed by electrochemical experiments.

### Table 2. Experimental conditions for different plasma types.

<table>
<thead>
<tr>
<th>Without Plasma</th>
<th>AC Plasma</th>
<th>DC Plasma</th>
</tr>
</thead>
<tbody>
<tr>
<td>PdC1</td>
<td>Pd/C</td>
<td>Pd/C</td>
</tr>
<tr>
<td>PdC8</td>
<td>2.5 kV</td>
<td>2.5 kV</td>
</tr>
<tr>
<td>PdC3</td>
<td>Ar</td>
<td>Ar</td>
</tr>
<tr>
<td>Catalyst</td>
<td>N/A</td>
<td>Simultaneously</td>
</tr>
<tr>
<td>Plasma discharging voltage</td>
<td>N/A</td>
<td>Plasma jet</td>
</tr>
<tr>
<td>Plasma carrier gas</td>
<td>N/A</td>
<td>Plasma jet</td>
</tr>
<tr>
<td>Plasma discharging mode</td>
<td>N/A</td>
<td>Pt mesh</td>
</tr>
<tr>
<td>Anode</td>
<td>N/A</td>
<td>Pt mesh</td>
</tr>
<tr>
<td>Cathode</td>
<td>N/A</td>
<td>AC</td>
</tr>
<tr>
<td>Current type</td>
<td>N/A</td>
<td>DC</td>
</tr>
</tbody>
</table>

Note: The condition “Without plasma” indicates that the electrochemical tests are conducted when the plasma is turned off. This is the control experiment, in which conventional electrochemical CO$_2$ reduction takes place. AC (alternative current) plasma and DC (direct current) plasma refer to the conditions when the electrochemical tests are performed under an AC plasma and a DC plasma, respectively. When either DC or AC plasma are utilized, the electrochemical tests are conducted simultaneously (at the same time) with plasma discharging. N/A means that the information is not available.
Table 3. The experimental conditions for different plasma voltage polarity conditions.

<table>
<thead>
<tr>
<th></th>
<th>Without Plasma</th>
<th>Plasma as Anode</th>
<th>Plasma as Cathode</th>
</tr>
</thead>
<tbody>
<tr>
<td>Catalyst</td>
<td>Pd/C</td>
<td>Pd/C</td>
<td>Pd/C</td>
</tr>
<tr>
<td>Plasma discharging voltage</td>
<td>N/A</td>
<td>2.5 kV</td>
<td>2.5 kV</td>
</tr>
<tr>
<td>Plasma carrier gas</td>
<td>N/A</td>
<td></td>
<td>Ar</td>
</tr>
<tr>
<td>Plasma discharging mode</td>
<td>N/A</td>
<td>Simultaneously</td>
<td>Simultaneously</td>
</tr>
<tr>
<td>Anode</td>
<td>N/A</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cathode</td>
<td>N/A</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Current type</td>
<td>N/A</td>
<td>DC</td>
<td>DC</td>
</tr>
</tbody>
</table>

Note: Without plasma means that electrochemical tests are conducted when the plasma is turned off. Plasma as anode denotes the test conditions when the electrochemical tests are performed with the plasma jet as the anode, and Plasma as cathode represents that the plasma jet is the cathode during electrochemical tests. Either plasma as the anode or as the cathode can be achieved by switching the polarity of the DC voltage generated by the high-voltage generator. N/A means that the information is not available. This happens when the plasma is turned off. Simultaneously means when the electrochemical tests are conducted at the same time as plasma discharging.

2.4. Quantitative Analysis of Formate

To quantify formate yield, chronoamperometry tests were conducted in a CO$_2$-saturated 0.5 M KHCO$_3$ electrolyte, with the applied voltage varying as indicated in Table 1. The tests lasted for 1 h. Following the tests, the electrolyte was collected and subjected to NMR analysis. In our prior work [14], we reported 1H-NMR spectra of the electrolyte. The NMR analysis was performed using a JEOL (Tokyo, Japan) 400 MHz spectrometer. The electrolyte was mixed with 100 µL of D$_2$O (99.9 atom % D, Sigma Aldrich, St. Louis, MO, USA) and 0.03 µL of dimethyl sulfoxide (99.9%, Sigma Aldrich, St. Louis, MO, USA). D$_2$O served for frequency locking, and DMSO acted as an internal reference and quantification standard. A distinctive peak of formate at the chemical shift of 8.2 ppm was observed, indicating formate as the primary CO$_2$RR product [11,12]. The obtained 1H-NMR spectra resemble those reported in the literature but lack other byproducts like phenols, suggesting potentially high selectivity toward formate in our electrochemical CO$_2$RR experiments.

We are interested in exploring conditions that could produce the most amount of formate. Thus, a precisely quantitative analysis of formate formation using NMR is essential. A calibration curve of formate concentration vs. formate peak intensity in the NMR spectra deserves to be established. To create such a curve, a series of standard formate solutions (0.010 mol/L, 0.017 mol/L, 0.037 mol/L, 0.071 mol/L, 0.086 mol/L, 0.111 mol/L, and 0.130 mol/L) were prepared, and then NMR analysis was performed. The intensity of the characteristic peak of formate at the chemical shift of 8.2 ppm was utilized to construct a calibration curve. After the calibration curve was established, a series of well-controlled chronoamperometry experiments were conducted. In those experiments, four factors, including plasma discharging voltage, plasma operating gas, and plasma discharging mode, were systematically varied, as shown in Tables 1–3.

2.5. Faradic Efficiency and Production Rate Calculation

To further quantify the influence of NTP on the formate formation at different testing conditions, the Faradic efficiency ($FE$) was calculated using the following equation:

$$FE_{\text{formate}} = \frac{n \times n_{\text{formate}} \times \frac{F}{\int_0^t I \, dt}}{100\%}$$

where $FE_{\text{formate}}$ is the faradic efficiency, $n$ is the number of the transferred electrons when CO$_2$ is converted to formate and in this study $n = 2$, $n_{\text{formate}}$ is the amount (in moles) of the produced formate, $F$ is the Faraday’s constant, which is 96,485 C mole$^{-1}$, $I$ is the electrochemical current, and $t$ is the electrolysis time (s). The production rate ($R$) can be calculated from Equation (2):
\[ R = \frac{n_{\text{formate}}}{t} \]  

where the \( R \) is the production rate (moles/h); \( t \) is the time of electrolysis experiment.

3. Results and Discussions

Our previous studies indicate that the effectiveness of plasma in assisting CO\(_2\)RR is involved with multiple parameters (e.g., plasma discharging voltage, carrier gas, plasma discharging mode, etc.) \[13,14\]. To study the impact of those parameters, we conducted a series of comprehensive experiments in Tables 1–3. Those experiments were all performed in an H-shaped reactor (shown in Figures 1 and 2).

3.1. Impact of Plasma on CO\(_2\)RR

To investigate the impact of plasma discharge on electrochemical CO\(_2\)RR, cyclic voltammetry (CV) was performed in a 0.5 M KHCO\(_3\) solution under three different conditions: without saturated CO\(_2\) and plasma, with saturated CO\(_2\) and no plasma, and with saturated CO\(_2\) and plasma. Figure 3 presents the CV curves from \(-1.1\) V to 1.0 V vs. Ag/AgCl. In the absence of CO\(_2\) and plasma discharge, only the reduction peak corresponding to hydrogen evolution was observed (grey solid line in Figure 3). Upon purging CO\(_2\) into the electrolyte for 30 min, an additional reduction peak at \(-0.92\) V emerged, indicating the CO\(_2\) reduction reaction (red and pink lines in Figure 3). However, this reduction peak appeared to shrink with increasing CV cycles, as shown in four consecutive CV scans. Two oxidation peaks at \(-0.51\) V and 0 V appeared, possibly due to the oxidation of CO\(_2\)RR intermediates.

![Cyclic voltammetry test results using Pd, 10 wt% on carbon catalyst. The experiments were conducted in a 0.5 M KHCO\(_3\) solution with and without the presence of saturated CO\(_2\) and DC plasma discharge.](image)

To assess the impact of plasma on CO\(_2\)RR, the nonthermal plasma was ignited above the aqueous electrolyte immediately after the previous CV tests. Upon turning on the plasma discharge, we observed a drastic expansion of the cyclic voltammograms, i.e., the oxidation and reductions peaks augment in the direction, as indicated by the arrows shown in Figure 3. Particularly, the CO\(_2\)RR peak at \(-0.92\) V was greatly enhanced, suggesting that nonthermal plasma discharge facilitates electrochemical CO\(_2\)RR. It is widely acknowledged that CO formation is inevitable during CO\(_2\)RR \[11,12\]. The formed CO, which is bonded
to the surface of the catalyst, blocks the active catalytic sites and diminishes the activity, resulting in low CO$_2$RR performance, as demonstrated by the attenuated reduction peak at $-0.92$ V in the presence of CO$_2$ but without plasma discharge. As discussed in the previous and a wealth of studies, such as reference [15], nonthermal plasma discharge above an aqueous solution produces H$_2$O$_2$. In our discovery, the formed H$_2$O$_2$ by the nonthermal plasma discharge appears to be beneficial for electrochemical CO$_2$RR, possibly owing to CO oxidation from the catalyst surface by the plasma-generated H$_2$O$_2$, therefore leading to more active catalytic sites for CO$_2$RR. The capability of the nonthermal plasma discharge on the adsorbate removal and catalyst activation is corroborated by the nearly 2× enhancement in CO$_2$ reduction current at $-0.92$ V. Recognizing that a voltage of $-0.92$ V is favorable for CO$_2$ reduction, subsequent experiments used this specific electrolysis voltage. The electrolysis voltage refers to the applied voltage in the electrochemical CO$_2$RR tests. Comparison of the produced formate concentrations from a series of experiments using the 10 wt% Pd/C catalyst at electrolysis voltage $-0.92$ V is illustrated in Figure 4. The bar graph illustrates the formic acid concentration (measured in millimoles per liter, mM) under different test conditions. These conditions vary based on the plasma conditions, plasma operating gas, and discharge mode, which are labeled from PdC1 to PdC9 (as shown in Table 1). The electrolysis voltage used in these tests is $-0.92$ V. PdC1, in which electrochemical nitrogen reduction occurs, serving as the control in the experiments. PdC2, when both electrochemical reduction and plasma discharge were conducted simultaneously, results in the highest formic concentration. As we move from PdC2 to PdC9, the bars sequentially decrease in height, suggesting a reduction in formic acid concentration. This graph provides insights into how the formic acid concentration varies with different electrolysis conditions and will be discussed in further context.

![Comparison of the produced formate concentrations from a series of experiments listed in Tables 1–3. The concentration was determined using the characteristic peak of formate located at the chemical shift of 8.2 ppm in NMR spectra and the calibration curve.](image)

3.2. Impact of Plasma Discharging Voltage

It is reported that plasma discharging voltage is critical to obtain energetic electrons at different energy levels [16] in a nonthermal plasma jet. Those energetic electrons are
vital to generate hydrated electrons upon entering the liquid, producing hydroxyl radicals and H$_2$O$_2$ [17] that is responsible for removing the adsorbed CO from the Pd catalyst surface. The comparison of plasma discharging voltage effect on the formate production is illustrated in Figure 5. Compared to other cases, the CO$_2$RR experiment in the absence of plasma (i.e., PdC1) yields the lowest formate concentration, suggesting that the CO$_2$ reduction by electrochemical process without plasma discharge is ineffective.

![Figure 5](image.png)

Figure 5. The effect of plasma discharging voltage on the produced formate concentrations from a series of experiments listed in Table 1 under different plasma discharging mode: (a) SIM and (b) SEP.

When the plasma operates at 1.5 kV (PdC6 and PdC7), it yields a higher formate production than the condition without plasma (PdC1, in the absence of plasma discharge). In addition, with an increase in plasma discharging voltage to 2.5 kV (PdC3 and PdC4), the concentration of formate production surpasses that observed at 1.5 kV (PdC6 and PdC7). This difference is attributed to the elevated plasma discharging voltage, leading to a greater generation of high-energy electrons within the electrochemical system. These electrons play a crucial role in the production of hydroxyl radicals and H$_2$O$_2$, which could facilitate reactivation of the catalyst [13] and contribute to enhanced formate production. Furthermore, a comparison between Figure 5a,b at identical plasma discharge voltages reveals that when electrochemical CO$_2$RR and plasma discharge occur simultaneously (SIM), CO$_2$ reduction to formate is enhanced compared to when they occur separately (SEP, i.e., in sequence). This observation strongly implies a synergistic effect between plasma discharge and electrochemical CO$_2$RR, a phenomenon that will be further explored in subsequent investigations.

3.3. Impact of Plasma Carrier Gas

Plasma carrier gas is employed to generate the plasma discharge. In this study, high DC voltages (2.5 kV and 1.5 kV) were applied beyond the dielectric limit of the operating
gas, inducing electrical breakdown. During this stage, the gas undergoes a transition from insulator to conductor as it becomes increasingly ionized. Various gases are used in plasma science, including Ar, He, Ne, H2, N2, etc. In this work, two operating gases (Ar or CO2) were investigated. CO2 served as both the carrier gas and the source of CO2 to compensate for its loss in the electrolyte during electrochemical CO2RR. Additionally, when used as the carrier gas, CO2 may undergo vibrational excitation by the plasma, potentially leading to enhanced electrochemical CO2RR by reducing the activation barrier.

Figure 6 illustrates the comparison of formate production using different plasma carrier gases (CO2 and Ar). In comparison to both CO2 and Ar as the plasma carrier gas, the formate concentration produced under nonplasma conditions (PdC1, in the absence of plasma discharge) is the lowest. When the plasma was activated with Ar as the carrier gas (PdC3), the produced formic concentration was higher than that of the nonplasma condition. Furthermore, upon switching the carrier gas to CO2 (PdC2), the Pd/C catalysts produced at least 36% more formate than their counterparts when Ar was used as the carrier gas at −0.92 V (Figure 6a). Similarly, when the electrochemical tests were conducted after plasma discharging (also referred to as “SEP” in Table 1), the concentration of formate produced with CO2 as the carrier gas (PdC4) remained higher than with Ar as the carrier gas (PdC5) (Figure 6b). The observed enhancement using CO2 as the carrier gas might diminish due to the less-negative voltage (resulting in less electrochemical driving force for CO2RR) and unoptimized electrochemical conditions. Nevertheless, CO2 molecules in the carrier gas are easily activated under nonthermal plasma discharging conditions. Additionally, plasma could facilitate the transport of CO2 molecules in the liquid electrolyte, making them largely available at the Pd catalysts.

Figure 6. The effect of plasma carrier gas on the produced formate concentrations from a series of experiments listed in Table 1 under different plasma discharging mode: (a) SIM and (b) SEP.
3.4. Impact of Plasma Discharging Mode

This study investigates two different plasma discharging modes: simultaneous (SIM) plasma discharging and separate (SEP) plasma discharging. In SIM plasma discharging, plasma discharging occurs simultaneously with the electrochemical tests, while SEP plasma discharging involves conducting plasma discharging first, followed by the electrochemical tests. Figure 7 compares the formate concentrations using Pd/C using different plasma supply gases (CO₂ and Ar). When the plasma supply gas was CO₂ (Figure 7a), the concentration of formate produced by SIM plasma (PdC2) was higher than SEP plasma (PdC4). If the plasma was turned off (PdC1), the produced formate concentration was the lowest, as seen in Figure 7a. A similar pattern was observed when Ar was used as the plasma supply gas (Figure 7b), where SIM plasma (PdC3) resulted in the highest formate production, followed by SEP plasma (PdC5) and, finally, the condition without plasma discharging (PdC1).

![Figure 7](image)

**Figure 7.** The effect of plasma discharging mode (2.5 kV) on the produced formate concentrations from a series of experiments listed in Table 1 using different plasma carrier gas: (a) CO₂ and (b) Ar. Three different plasma discharge modes are studied: SEP, SIM, and without plasma, i.e., with the absence of plasma discharge.

Whether at high (2.5 kV) or low (1.5 kV) plasma discharging voltage, SIM plasma is more effective in producing formate compared to SEP plasma. This is attributed to the reactive species generated by plasma. Reactive species produced by nonthermal plasma are short-lived and tend to react with water or other molecules in the electrolyte. During SIM plasma discharging, reactive species are continually produced, promoting the formation of H₂O₂ and assisting CO₂RR. Switching to SEP plasma discharging, reactive species also facilitate the formation of large amounts of H₂O₂. By the time SEP plasma discharging...
finishes, the H$_2$O$_2$ concentration reaches a plateau. However, after SEP plasma discharge, H$_2$O$_2$ is gradually consumed by the electrochemical test, and no more H$_2$O$_2$ is supplied to the electrolyte to promote CO$_2$RR. The Pd/C catalyst’s active surface is likely blocked by the byproduct (mainly CO) of CO$_2$RR, leading to catalyst deactivation. As more CO is produced from electrochemical tests, the catalyst’s activity keeps declining, resulting in a lower formate concentration.

3.5. Impact of Plasma Type

Typically, nonthermal direct current (DC) plasma is characterized by low voltage and high current density. Conversely, high-frequency alternative current (AC) plasma is produced by an AC power supply with rapidly changing polarity. To investigate the impact of plasma type on electrochemical formate production, CV and chronoamperometry tests were conducted under three conditions: with a DC plasma, an AC plasma, or no plasma. The condition without plasma represents the conventional electrochemical CO$_2$RR, where the plasma is deactivated during electrochemical tests. In contrast, the AC and DC plasmas are generated using high AC and DC voltages, respectively. The specific experimental conditions are detailed in Table 2.

Figure 8 presents a comparison of CV curves under three different plasma conditions: without plasma discharging (dash curve), AC plasma discharging, and DC plasma discharging. In comparison to the condition without plasma (red dash curve) and DC plasma (blue dotted curve), both the reduction and oxidation peaks in the CV curves diminish after turning on the AC plasma. Specifically, the current of the reduction peak at $-1.0$ V reduces by 3.4 times upon activating the AC plasma, indicating the suppression of the electrochemical behavior of the Pd electrode in the aqueous electrolyte. Conversely, for the oxidation peak at $-0.5$ V, the current intensity without plasma is 4.05 times higher than that with AC plasma. In contrast, immediately after turning on the DC plasma, the CV curve experiences a significant enhancement. The current intensity for the reduction peak at $-1.0$ V is 4.43 times higher with the presence of DC plasma compared to AC plasma. Similarly, the oxidation peak at $-0.5$ V is 10.34 times stronger than that with AC plasma. When comparing the three plasma conditions, it is notable that the CV curves with AC plasma are not smooth, displaying high-frequency current fluctuations with changing electrolysis voltage. This behavior is attributed to the intrinsic nature of AC plasma, which periodically reverses direction and continuously changes its amplitude over time. Consequently, the AC voltage affects the stability of plasma discharging above the electrolyte, influencing the smoothness of the CV curves.

Figure 9 depicts a comparison of chronoamperometry tests conducted at $-0.92$ V vs. Ag/AgCl under different plasma conditions, including without plasma, AC plasma, and DC plasma. Consistent with the CV results, the electrochemical CO$_2$RR under $-0.92$ V with AC plasma exhibits a significantly smaller current. Upon activating the AC plasma, the electrochemical CO$_2$RR current decreases sharply by 10 times, dropping from $-0.1$ mA to around $-0.01$ mA. In contrast, the electrochemical CO$_2$RR current in the presence of DC plasma gradually declines from $-0.16$ mA to around $-0.025$ mA. These findings suggest that the electrochemical CO$_2$ reduction performance benefits from DC plasma discharge, while AC plasma appears to have a negative impact, possibly arising from diminished electrochemical active surface area evidenced from Figure 8.

Following the electrochemical test, the electrolyte was collected for NMR analysis, and the formate concentration was calculated. Figure 10 illustrates the formate concentrations in the electrolyte after the electrochemical CO$_2$RR tests under three conditions: without plasma discharge, with high-frequency AC plasma, and with DC plasma. The results clearly show that DC plasma generated the highest amount of formate, with a concentration of 0.133 mM. In contrast, the formate concentration produced by AC plasma is only 0.025 mM, which is 5.32 times less than that of DC plasma. Surprisingly, compared to the test without plasma discharging, the formate concentration produced with AC plasma is even smaller, by $-0.003$ mM. These results further validate the observation that plasma conditions
significantly impact electrochemical performance, with nonthermal DC plasma proving the most effective among the three conditions.

![CV curves comparison](image1.png)

**Figure 8.** The comparison of CV curves for plasma electrochemical CO$_2$RR at three different conditions (PdC1, PdC3, and PdC8): AC plasma, DC plasma, and in the absence of plasma. A 2.5 kV discharging voltage, simultaneously discharging mode, Ar gas, and Pd/C, were used in the experiments.

![Chronoamperometry test results](image2.png)

**Figure 9.** The chronoamperometry test results for plasma electrochemical CO$_2$RR at three different plasma conditions (PdC1, PdC3, and PdC8): AC plasma, DC plasma, and in the absence of plasma. A 2.5 kV discharging voltage, simultaneously discharging mode, Ar gas, Pd/C, and $-0.92$ V vs. Ag/AgCl electrolysis voltage, were used in the experiments.
In the context of AC plasma liquid interaction, the gas temperature can reach higher levels than in DC plasma [18]. Despite being labeled nonthermal, the AC plasma used in this work still exhibits temperature elevation [19]. The accumulated heat in the reactor could lead to electrolyte evaporation, evident by fog and condensation observed on the reactor wall after a few minutes of AC plasma discharging. Additionally, it is reported that formate and H$_2$O$_2$ are prone to decomposition at high temperatures [20,21]. Thus, employing AC plasma in assisting electrochemical CO$_2$RR may lead to the decomposition of formate and H$_2$O$_2$, hindering catalyst activities and resulting in lower formate formation through AC plasma.

### 3.6. Impact of Switching Plasma Polarity

Numerous published studies highlight the significance of intrinsic electrical properties of plasma, such as current type (DC or AC) and polarity (plasma jet as the anode or cathode), in influencing both charged and chemical species generation [22,23]. Specifically, the difference between AC and DC plasma lies in their generation mechanisms. DC plasma operates by ionizing a carrier gas between two electrodes with a sufficiently high potential, leading to electron acceleration from the cathode towards the liquid electrolyte and ionized species from the anode towards the electrolyte. In contrast, AC plasma requires an AC power source, and the directions of electrons and ionized species switch at a high frequency (usually in the RF range of 10–14 MHz). To explore the impact of switching plasma polarity, comprehensive experiments were conducted under different conditions, as outlined in Table 3.
Figure 11 presents CV curves obtained under various conditions, including electrochemical CO$_2$RR in the absence of plasma discharge (PdC1), DC plasma as the anode (PdC9), or as the cathode (PdC3). A comparison of CV curves with different plasma voltage polarities reveals that the CO$_2$ reduction peak ($-1.0$ V vs. Ag/AgCl) becomes barely noticeable when the nonthermal anode plasma jet is used alongside electrochemical CO$_2$RR, indicating significant suppression of CO$_2$RR activity. Upon switching plasma polarity (i.e., the plasma jet becomes the cathode), CO$_2$RR peaks reappear. On the other hand, hydrogen evolution ($-1.1$ to $-0.75$ V vs. Ag/AgCl) with plasma as the anode is notably enhanced and the maximum current intensity is around 11 times higher than that with plasma as the cathode. However, this enhancement in hydrogen evolution unavoidably undermines the rate and efficiency of CO$_2$ reduction.

![CV curves comparison](image)

Figure 11. The comparison of CV curves for plasma electrochemical CO$_2$RR at three different conditions (PdC1, PdC3, and PdC9). A 2.5 kV discharging voltage, simultaneously discharging mode, Ar gas, and Pd/C, were used in the experiments.

Figure 12 compares chronoamperometry tests for three different voltage polarities (without plasma, plasma as anode, and plasma as cathode). It is evident that when the nonthermal plasma jet serves as the anode, the current obtained is significantly higher than values achieved without plasma or with plasma as the cathode. The maximum current obtained when plasma serves as the anode is almost 75 times higher than when it serves as the cathode. Additionally, the electrolytes after chronoamperometry tests were collected and analyzed. Figure 13 illustrates the comparison of formate concentrations under three different plasma voltage polarity conditions. The plasma cathode (PdC3) produces the highest formate concentration, followed by the test in the absence of plasma discharge, and then the plasma anode. Compared to the nonthermal plasma serving as the anode, the formate concentration produced when it serves as the cathode is 7.9 times higher. Even in the absence of plasma discharging, the concentration of formate produced from electrochemical CO$_2$RR is still higher, providing further evidence that the plasma anode is not conducive to electrochemical CO$_2$RR. All the above test results consistently indicate that the plasma anode is not favorable for electrochemical CO$_2$RR.
3.7. Faradic Efficiency and Production Rate

The production rates and faradic efficiency ($\text{FE}_{\text{formate}}$) of the tests are detailed in Table 4. The highest $\text{FE}_{\text{formate}}$, reaching 23.52%, was observed in the test utilizing high plasma voltage at 2.5 kV, CO$_2$ as the carrier gas, 10 wt% Pd on carbon catalyst, and SEP mode (PdC4). The elevated plasma discharging facilitated the generation of more energy-reactive species, promoting CO$_2$RR and enhancing $\text{FE}_{\text{formate}}$. While some plasma-generated reactive species are short-lived and prone to decomposition or reactions with other compounds or molecules [16], long-lived H$_2$O$_2$ from nonthermal plasma discharge fosters CO$_2$RR. Surprisingly, the highest formate concentration was achieved under the condition of high plasma voltage at 2.5 kV, CO$_2$ as the carrier gas, 10 wt% Pd on carbon

![Figure 12](image1.png)

Figure 12. Chronoamperometry test results for plasma electrochemical CO$_2$RR at three different conditions (PdC1, PdC3, and PdC9). A 2.5 kV discharging voltage, Ar gas as the plasma supply gas, Pd/C, and $-0.92$ V vs. Ag/AgCl electrolysis voltage were used in the experiments.

![Figure 13](image2.png)

Figure 13. The effect of switching plasma polarity on the produced formate concentrations from a series of experiments listed in Table 3.
catalyst, and SIM mode (PdC2). This suggests that a higher formate concentration does not necessarily equate to a higher formate faradic efficiency.

### Table 4. Faradic efficiency and production rate of formate at different conditions for Pd, on 10% carbon catalyst.

<table>
<thead>
<tr>
<th>Experiment Conditions</th>
<th>FE_{formate}</th>
<th>Production Rate (mole/h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PdC1</td>
<td>2.87%</td>
<td>7.034 × 10^{-9}</td>
</tr>
<tr>
<td>PdC2</td>
<td>4.87%</td>
<td>1.697 × 10^{-8}</td>
</tr>
<tr>
<td>PdC3</td>
<td>8.10%</td>
<td>2.975 × 10^{-8}</td>
</tr>
<tr>
<td>PdC4</td>
<td>23.52%</td>
<td>3.925 × 10^{-8}</td>
</tr>
<tr>
<td>PdC5</td>
<td>17.60%</td>
<td>5.571 × 10^{-8}</td>
</tr>
<tr>
<td>PdC6</td>
<td>11.21%</td>
<td>6.389 × 10^{-8}</td>
</tr>
<tr>
<td>PdC7</td>
<td>8.60%</td>
<td>1.443 × 10^{-8}</td>
</tr>
<tr>
<td>PdC8</td>
<td>7.88%</td>
<td>1.300 × 10^{-8}</td>
</tr>
<tr>
<td>PdC9</td>
<td>0.016%</td>
<td>8.195 × 10^{-9}</td>
</tr>
</tbody>
</table>

The FE_{formate} under three different plasma voltage polarity conditions (PdC1, PdC3, and PdC9) is also presented in Table 4. Under the SIM mode, the maximum FE_{formate} is achieved when the nonthermal plasma serves as the cathode (PdC3) and can reach as high as 8.1%. In contrast, the FE_{formate} is less than 1% when the nonthermal plasma jet serves as the anode (PdC9). As indicated in Equation (1), the calculation of FE_{formate} involves several parameters, including the number of transferred electrons when CO\textsubscript{2} is converted to formate and the amount of produced formate, among others. Figures 11 and 12 suggest that substantial parasitic reactions, such as hydrogen evolution or oxygen reduction, occur when the nonthermal plasma jet serves as the anode. However, when comparing electrochemical CO\textsubscript{2}RR tests with or without the presence of the plasma cathode, the concentration of formate produced when the nonthermal plasma serves as the anode is barely notable (Table 4, PdC9). Even with plenty of electrons flowing through the electrochemical system, the majority of them contribute to massive hydrogen evolution or oxygen reduction. Additionally, electrochemical CO\textsubscript{2}RR does produce formate. Regarding the formate production rate, when the nonthermal jet serves as the anode (Table 4, PdC3), electrochemical CO\textsubscript{2}RR produces 8.12 times more formate than when using plasma as the anode.

The obtained faradaic efficiencies in Table 4 are slightly lower than reported values in the literature, which typically range from 35% to 90% when electrochemical CO\textsubscript{2} reduction is conducted at high pressure [24] or using a two-compartment flow cell [25]. The obtained formate production rates are also lower. However, under similar experimental setup, the highest FE achieved in Table 4 (FE = 23.52%) surpasses values obtained at 1 atm CO\textsubscript{2} pressure (FE = 3.52%) and even at 9 atm (FE = 20.8%) reported in reference [26].

The power consumption of our plasma electrochemical system is significantly higher (2~3 times larger) compared to that of electrochemical CO\textsubscript{2}RR, primarily attributed to the added energy demand from plasma discharge. Nonetheless, exploring modifications such as adjusting electrode geometry or exploring the use of AC plasma instead of the DC plasma utilized in this study holds promise for integrating the system with renewable energy sources. This is particularly noteworthy as the costs associated with renewable energy are consistently decreasing. With further exploration and optimization, the approach presented here could become a potentially promising technology for green, economical CO\textsubscript{2} production.

### 4. Conclusions

In conclusion, this study investigates the intricate effect of nonthermal plasma (NTP)-assisted electrochemical reduction of CO\textsubscript{2}, focusing on the production of formate (HCOO\textsuperscript{-} / HCOOH) as a valuable end product. The research systematically explores various factors influencing NTP-assisted electrochemical CO\textsubscript{2} reduction, including plasma discharging
voltage, carrier gas, discharging mode, polarity, and plasma type. Experimental results demonstrate that NTP discharge significantly enhances formate production compared to conventional electrochemical processes. The impact of parameters such as voltage, carrier gas, and discharging mode is thoroughly investigated, providing valuable insights into optimizing conditions for efficient formate synthesis. Moreover, the study elucidates the advantage of nonthermal DC plasma over AC plasma, emphasizing its positive influence on electrochemical CO₂ reduction. The investigation into switching plasma polarity reveals that the plasma cathode significantly outperforms the plasma anode in terms of formate production. Faradic efficiency and production rate calculations underscore the effectiveness of NTP in promoting CO₂ reduction, with notable achievements in certain experimental conditions. The findings contribute valuable knowledge to the emerging field of NTP-assisted electrochemical CO₂ reduction, paving the way for sustainable solutions to mitigate rising CO₂ levels and address environmental concerns.

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References


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