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Getting the Most of Your Catalyst: How Process Parameters and Pulse Procedures Affect the Performance of eCO₂R

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ABSTRACT

Electrochemical pathways that convert CO₂ into multi-carbon (C₂₊) products could mitigate greenhouse gas emissions while supplying chemical building blocks. Realizing this potential requires scalable process designs and optimized operating strategies, including dynamic modes such as pulsed current. Here, we systematically investigate the effects of current density, electrolyte temperature, CO₂ excess rate, and pulsed operation on C₂₊ production in a commercially available flow cell equipped with gas diffusion electrodes (GDEs) and industrially relevant materials. High current densities up to 400 mA cm⁻² significantly increased the Faradaic efficiency toward C₂₊ products. Lower electrolyte temperature (20 °C) enhanced C₂₊ production compared to 40 °C, likely due to greater CO₂ solubility and CO adsorption, which promote CO dimerization. A reduced CO₂ excess rate ($\lambda = 2$) further favored C₂₊ formation, potentially by decreasing CO₂ adsorption in favor of CO surface coverage. Contrary to prior reports in H-type cells, pulsed current operation did not improve C₂₊ production in the GDE-equipped flow cell, suggesting that enhanced mass transport minimizes pulsing benefits observed in diffusion-limited systems. This study identifies low temperature, reduced CO₂ excess, and statically applied high current densities as key parameters for enhancing C₂₊ formation under scalable conditions.

1 | Introduction

With an increasing concentration of the harmful greenhouse gas carbon dioxide (CO₂) in the atmosphere, the detrimental effects of climate change are becoming increasingly perceptible. To mitigate further climate change, drastic measures must be taken to limit global warming [1]. An often-proposed technology to close the carbon cycle is electrochemical CO₂ reduction (eCO₂R). During eCO₂R, CO₂ is reduced to value-added chemicals in conjunction with renewable electrical energy. Thus, the demand for fossil resources to produce platform chemicals is decreased [2]. Often proposed products of eCO₂R are C₁ molecules such as carbon monoxide (CO) [3–5], formic acid (HCOOH) [6–8], or methane (CH₄) [9, 10]. Beyond C₁-molecules, a multitude of studies focus

on the production of C₂₊ products such as ethylene (C₂H₄) [11–13], ethanol (C₂H₅OH) [14, 15], or products with longer carbon chains [16, 17]. Among all catalyst materials, copper catalysts are the only materials that catalyze the reaction from CO₂ to C₂₊ products [18]. However, eCO₂R with copper catalysts suffers from low selectivity for individual products as not only C₂₊ products are formed but also a variety of C₁ byproducts evolve [19, 20]. However, recent studies show promising results in flow cells with regard to C₂₊ production by optimizing the gas diffusion electrode (GDE) or modifying the utilized catalyst [21–23]. Despite these advances, C₂₊ selectivity in industrially relevant flow-cell configurations remains highly sensitive to multiple interdependent operating parameters, such as electrolyte composition, gas flow rate, electrode architecture, and pulsing protocols.

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Recent literature often focuses on catalyst design and the synthesis of novel materials to steer the selectivity of eCO₂R toward C₂₊ products. With novel catalyst designs, remarkable results were achieved in terms of Faradaic efficiency (FE) toward C₂₊ products. For example, Li et al. observed an FE of 72% toward ethylene by functionalizing the catalyst surface with organic molecules that stabilize reaction intermediates and therefore increase the C₂₊-formation [24]. Ma et al. report a C₂₊-FE of 80% using fluorine-modified copper as a catalyst. Fluorine has been reported to increase water activation, CO adsorption, and CO hydrogenation to CHO [25]. Bian et al. report a hierarchically structured Ag-Cu-NC tandem catalysis electrode that promotes efficient *CO generation, spillover, and C–C coupling, enabling highly selective C₂₊ production with FEs up to 87.5% at industrially relevant current densities [26]. As the amount of catalyst materials described in the literature steadily increases, the scalability of highly specialized materials remains to be proven because most studies on catalyst performance are conducted in H-type cells or with low geometric electrode areas.

Beyond catalyst design, the operating environment of the catalyst plays a critical role in shaping both the catalytic microenvironment and the resulting macroscopic performance. This environment is influenced by process parameters such as applied current density, temperature, CO₂ excess (λ), and pulsed operation, as illustrated in Figure 1. While many studies have investigated the effect of individual process parameters [27–34], a comprehensive strategy for optimizing the electrochemical flow reactor by combining multiple parameters is largely missing from the literature.

For instance, Hori et al. observed that increasing the temperature shifts product selectivity from CH₄ to C₂H₄ [27]. Furthermore, Vos et al. recently identified two distinct temperature regimes in eCO₂R, with C₂₊ products dominating up to 48 °C, while C₁ products become prevalent at higher temperatures [28]. Similarly, a reduced CO₂ supply under constant current conditions has been linked to increased C₂₊ formation. This enhancement is attributed to higher local pH and increased *CO surface coverage [29–31]. With respect to current density, several studies have shown that elevated current densities lead to higher FEs for C₂₊ products

[35–37]. Lv et al. demonstrated that increasing the cathode potential enhances C₂₊ selectivity [35]. Bui et al. attributed this to the rise in local pH at the catalyst surface at high potentials [36], while Goodpaster et al. explained the improved dimerization of CO by a higher degree of CO adsorption on the copper surface under alkaline conditions [37]. Pulsed operation has also shown potential for improving selectivity by dynamically altering the catalyst surface and the local electrolyte composition [32–40]. While most studies on potentiostatically pulsed CO₂ electrolysis showed positive effects in terms of C₂₊ formation [32, 33, 39, 40], increased C₂₊ production with galvanostatic pulses was only observed with a specific current profile that resembled the current response to a potential pulse [38]. Furthermore, studies on potentiostatically pulsed eCO₂R have been conducted predominantly in systems with limited mass transport, in which current reduction enabled CO₂ enrichment at the interface between the cathode and the electrolyte [32, 33, 39, 40].

Although these findings provide valuable insight, most of them are based on experiments using H-type cells at relatively low current densities. These setups suffer from inherently limited CO₂ supply and high mass transport resistance, making them unsuitable for evaluating industrial-scale feasibility. Therefore, further research is needed to investigate the combined influence of process parameters under conditions that reflect real-world application.

This study addresses this gap by systematically evaluating the effects of applied current density, temperature, CO₂ excess, and pulsed operation on eCO₂R performance in a commercially available electrochemical flow reactor. We hypothesize that tuning process parameters in a GDE-equipped flow reactor can selectively enhance C₂₊ product formation by modulating the local catalytic environment. We use CuO as a readily available catalyst and operate the system with a GDE of 25 cm² geometric area. Initially, we examine how temperature and CO₂ excess influence product selectivity. Based on these findings, we subsequently studied the impact of various pulsing protocols. Industrially relevant current densities are applied throughout. To our knowledge, only a few studies have explored pulsed eCO₂R with copper catalysts under

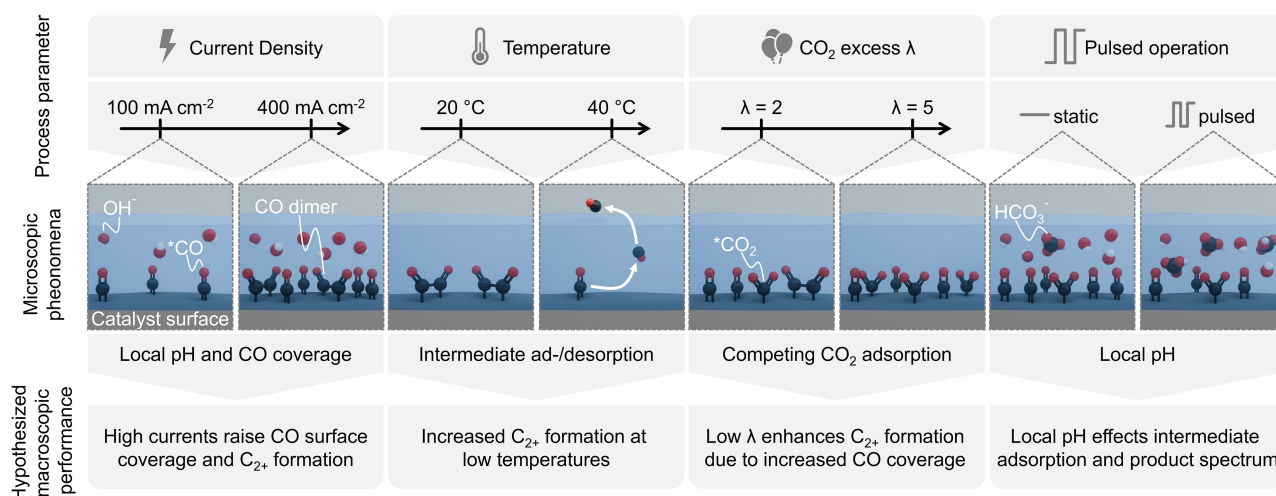


FIGURE 1 | Conceptual hypothesis: dynamic modulation of the catalytic microenvironment via process parameters such as current density, temperature, CO₂ excess rate, and current pulsing influences C₂₊ product selectivity in eCO₂R.

such conditions [41, 42]. We hypothesize that tuning process parameters such as current density, temperature, CO₂ excess rate, and pulsed operation can be used to engineer the catalytic microenvironment in a scalable flow reactor, thereby enhancing selectivity for C₂₊ products during eCO₂R. Unlike previous mechanistic studies conducted under laboratory conditions, this work elucidates how scalable process variables jointly determine product selectivity in industrially relevant GDE systems.

In this work, the electrochemical reactor contains a liquid catholyte and therefore differs from catholyte-free zero-gap CO₂ electrolyzers; the investigated parameters are directly relevant to practical gaseous CO₂ electrolysis. Temperature and CO₂ excess influence CO₂ availability, CO residence time, intermediate coverage, and C–C coupling tendencies. Therefore, the findings from this work may be qualitatively transferable across GDE-based reactor concepts. However, the quantitative optimum values identified here should not be directly transferred to zero-gap systems, where ion transport, water management, membrane–electrode contact, carbonate crossover, salt precipitation, and local pH profiles can differ substantially [43].

2 | Experimental

2.1 | Setup and Analytics

In all experiments, the commercially available Flex-E-Cell flow cell reactor (FXC Engineering GmbH, Germany) was used. Figure 2a shows an exploded view of the flow cell reactor used in this work. The reactor was operated in a one-sided zero-gap setup with the anode directly in contact with a F-14 100 cation exchange membrane (FUMATECH BWT GmbH, Germany). Between the membrane and the cathode, a Santoprene flow field with a 3D-printed spacer was used to establish the catholyte compartment with a gap width of 3 mm. The cathode and anode were electrically contacted by metal flow fields made of stainless steel and titanium, respectively. Between the metal flow fields and the Flex-E-Cell frame, 0.5 mm Santoprene gaskets were installed. All other sealings inside the reactor were made of polytetrafluoroethylene (PTFE). A photo of the fully assembled reactor is shown in Figure S1 in the Supporting Information. For the cathode, a Freudenberg H23 C6 gas diffusion layer (GDL) was coated with a catalytic ink consisting of CuO nanoparticles with a size of 40 nm (IoLiTec Ionic Liquids Technologies GmbH, Germany), 5 wt.-% Nafion solution (QuinTech, Germany) and 2-propanol. After 30 min of sonification, the catalytic ink was coated onto the GDL using automated ultrasonic spray coating (PRISM Ultracoat 400, Ultrasonic Systems, Inc., USA). The anode was produced by manually spray coating a titanium mesh (QuinTech, Germany) with catalyst ink consisting of IrO₂ particles (Sigma–Aldrich, USA), 5 wt.-% Nafion solution and 2-propanol. The anode and cathode had a geometric surface area of 5 cm × 5 cm. For both electrodes, 2 mg cm^{−2} catalyst loading was applied. More detailed recipes for both catalytic ink recipes and spray coating procedures are given in section 1.2 of the Supporting Information.

Throughout the experiments, the CO₂ feed was controlled by a mass flow controller (Alicat Scientific, Inc., USA) and humidified in a bubble column. The contribution of water introduced

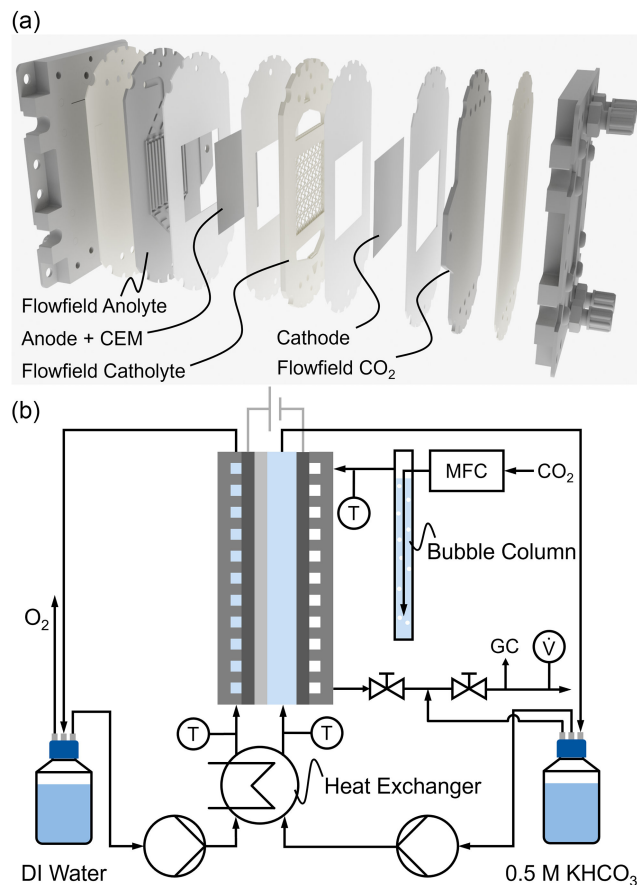


FIGURE 2 | Representation of the reactor and components used in this work. (a) Exploded view of the cell design with the cell frame, flow fields for anolyte, catholyte, and CO₂, cathode and anode membrane electrode assembly. (b) Experimental setup with pumps, heat exchanger, CO₂ humidification stage, and sensor placement.

by humidified CO₂ was negligible compared to the total electrolyte volume (400 mL). Therefore, bulk pH variations from humidification were insignificant. An excess pressure of 400 mbar was regulated at the outlet of the cell by two manual back pressure regulators (BPRs) (Swagelok, Germany). The second BPR pressurized the gas phase and the catholyte to an excess pressure of 350 mbar. With the first BPR, a differential pressure of 50 mbar was regulated from the gas compartment to the catholyte. The catholyte and anolyte were cycled through the system using gear pumps (GATHER Industrie GmbH, Germany). An in-house-designed heat exchanger was implemented in the electrolyte cycles to control the electrolyte bulk temperature. Heating/cooling water was supplied by a CORIO CD-900F thermostat (Julabo GmbH, Germany).

The gas evolving on the cathode side in the catholyte was mixed with the product gas coming from the backside of the GDE between the two BPRs. The volumetric flow rate of the gas mixture was measured with a bubble flow meter, and its composition was analyzed by gas chromatography (GC). A GC (Agilent 8860) was equipped with a PoraBond U column (25 m length) and two ShinCarbon packed columns (1 m length and 0.3 m length). For the detection of the products, the system was equipped with two thermal conductivity detectors. Corresponding to gas samples, liquid samples were taken from the catholyte. The

product concentration in the liquid samples was then determined by high-performance liquid chromatography (HPLC). For HPLC (Agilent 1100), a packed organic acid resin column (250 mm length, 8 mm diameter, 10 μ m particle size) was used, equipped with a pre-column. For component detection, a refractive index detector (RID) and a diode array detector (DAD) were used. In all experiments, the current was supplied by a Biologic SP-150e potentiostat supported by a Biologic 20 V/20 A Essential booster.

2.2 | Experimental Procedures

The experiments were conducted in static or pulsed operation. To identify the ideal process conditions for pulsed operation, we first conducted static experiments. For static operation, current densities of 100, 200, 300, and 400 mA cm⁻² were applied to the electrochemical flow reactor. In pulsed operation, two different profiles were employed as depicted in Figure 3. The nominal current (j_h) was altered with a reduced current density (j_l), which was either 25% of the nominal current, or the current was switched off completely. The time periods in which high or low currents are applied are referred to as t_h or t_l , respectively. Figure 3 schematically shows the applied square wave of the current density. The investigated pulse durations (t_h/t_l) were 25 s/5 s, 20 s/10 s, and 1 s/1 s and were chosen to allow comparison with the recent literature [32, 33]. If not stated otherwise, the experiment duration was at least 3 h for all experiments. GC and HPLC samples were taken every 23 min. The plotted FE values are averages over one experiment. Error bars show the standard deviation over these time points. They therefore reflect temporal variations during one experiment, not the scatter of independent replicates. Independent repetitions of selected operating points confirmed the observed trends in FE and product distribution. For pulsed electrolysis, Faradaic efficiencies were calculated using the time-averaged current density during pulsed operation. A surge flask was implemented downstream of the cathode to homogenize the gas mixture prior to GC sampling. The CO₂ flow rate was controlled by a mass flow controller and maintained constant ($\lambda = 2$, 400 mA cm⁻² equivalent) throughout the pulse cycles.

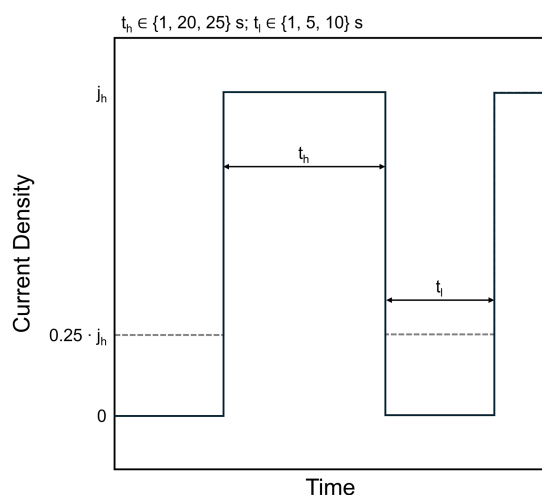


FIGURE 3 | Schematic representation of the square wave pattern used to apply the current density in pulsed experiments with the high current density j_h , the low current density j_l , and the time intervals t_h and t_l .

The volumetric flow rate of CO₂ was adjusted with respect to the current density and the CO₂-excess rate λ . λ describes the ratio of CO₂ fed to the reactor to CO₂ that can theoretically be converted at a given current density. Two λ -values were assessed ($\lambda = 2 \vee 5$) with respect to the complete conversion of CO₂ to CO. The volumetric flow rate was then calculated as follows:

$$\dot{V}_{\text{STP}} = \frac{\lambda \cdot j \cdot A_{\text{geo}} \cdot T \cdot R}{p \cdot F \cdot z} \quad (1)$$

Thereby, T and p are temperature and pressure with standard conditions assumed ($T = 298.15$ K, $p = 1.013$ bar). R is the universal gas constant ($R = 8.314$ J mol⁻¹ K⁻¹), and F is the Faraday constant ($F = 96,485$ C mol⁻¹). j represents the applied current density, and A_{geo} is the geometric surface area of the cathode. As a complete conversion of CO₂ to CO was assumed for the calculation of λ , z equals 2. A table with all volumetric flow rates to their respective current densities is given in Table S3 in the Supporting Information.

In all experiments, an aqueous 0.5 M KHCO₃ solution was used as catholyte. On the anode side of the reactor, deionized water was used as the electrolyte. A volume of 400 mL of each electrolyte was provided at the start of the experiment. Both were recirculated at a flow rate of 120 mL min⁻¹. Before entering the cell, the anolyte and catholyte passed through the heat exchanger and were tempered to either 20 °C or 40 °C. The electrolyte bulk temperature was kept constant over the course of the experiment.

3 | Results and Discussion

In the discussion, *CO coverage, competitive adsorption, and local pH are used to interpret the observed product trends. These effects are discussed based on the literature. They were not directly measured in the present study unless stated otherwise.

3.1 | Static Current Experiments

3.1.1 | Influence of Current Density

In the literature, elevated current densities have been shown to enhance the formation of C₂₊ products in eCO₂R [35–37]. Lv et al. [35] observed that higher cathode potentials lead to increased C₂₊ selectivity. This effect has been attributed to a rise in local pH near the catalyst at high current densities [36], which promotes CO adsorption and facilitates *CO dimerization, as described by Goodpaster et al. [37]. To identify the ideal current density for C₂₊ production in the reactor used in this work, several experiments were carried out at different current densities. Figure 4a shows the influence of the current density on the FE. The experiments were carried out at an electrolyte bulk temperature of 40 °C and at $\lambda = 5$.

Figure 4a shows that the FE for H₂ decreases with increasing current density. We assume that this is due to less H adsorption at the catalyst sites and a more alkaline pH in proximity to the catalyst. Alongside the decrease in HER, the FE for the products of eCO₂R increases. Minor deviations of the total FE above 100% arise from combined analytical uncertainties in

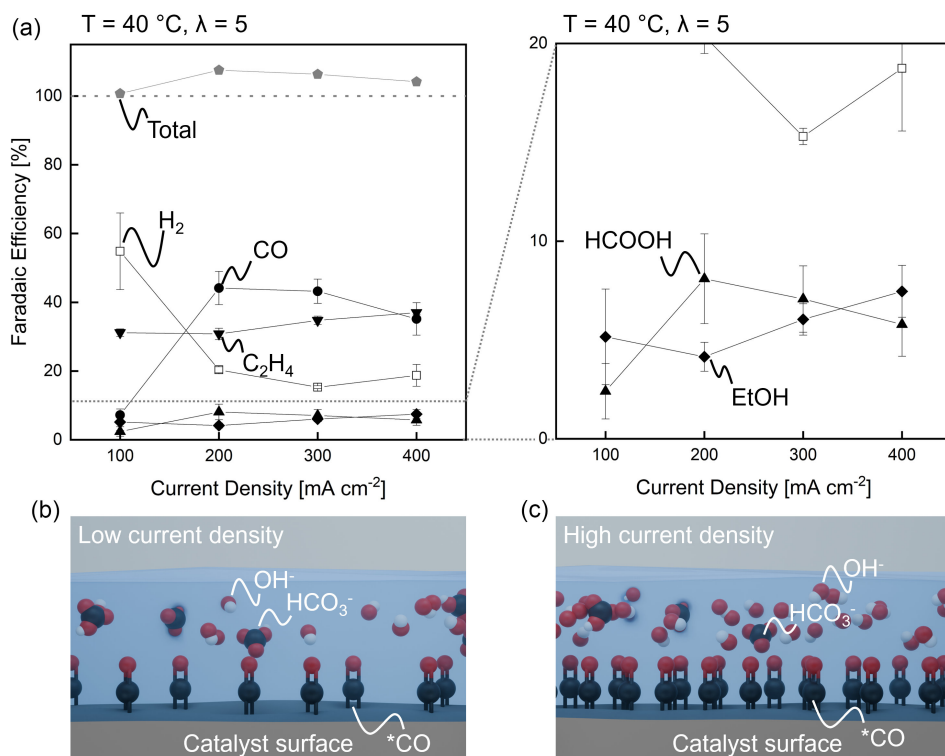


FIGURE 4 | Influence of the current density on the performance of eCO₂R. (a) Faradaic efficiencies plotted over the current density for all products observed in this work (H₂, CO, HCOOH, C₂H₄, and EtOH) as well as the total FE. (b) Illustration of the *CO coverage at the catalyst surface with adsorbed *CO and HCO₃⁻ and OH⁻ ions for a low current density. (c) Illustration of the *CO coverage with HCO₃⁻ and OH⁻ ions at a high current density. The error bars indicate the temporal deviation of the FE over the course of 3 h.

multiphase product quantification. The FE calculation depends on several independently measured quantities, including gas flow rate, pressure, temperature, gas-phase product composition, and liquid-phase product concentration. The accumulation of these individual uncertainties can lead to total FEs slightly above 100%. In all experiments, the total FE remained below 110%, which is within the expected error range for multiphase product analysis. For 100 mA cm⁻², the FE for C₂H₄ is at 31% while the FE for CO is below 10%. This indicates that most of the reaction intermediate CO further reacts to C₂₊ products. This is enabled either by subsequent reactions in the adsorbed state or a high residence time of desorbed CO in the reactor and further reaction at different catalyst sites due to low applied gas flow rates at 100 mA cm⁻² (see Table S3). With a further rise in current density, the FE for C₂H₄ increases from 31% at 100 mA cm⁻² to 37% at 400 mA cm⁻². We reason that this is due to a more alkaline pH at the GDE and thus beneficial *CO-adsorption conditions at the catalyst surface. This phenomenon is underlined by Figure 4b,c. At low current densities, the local concentration of OH⁻ ions and therefore the pH is lower compared to high current densities. Increasing the current density is expected to enhance interfacial OH⁻ generation, leading to more alkaline local conditions that can favor *CO adsorption and C–C coupling [37]. The trend of the EtOH FE (C₂H₅OH) is in line with the trend for C₂H₄. For CO, the FE increases from approximately 7% to approximately 44% when the current density increases from 100 to 200 mA cm⁻². If the current density is further increased, the FE for CO decreases again to 35% at 400 mA cm⁻². We argue for this behavior with enhanced eCO₂R activity at elevated current densities. An increased pH at the GDE catholyte interface

at increased current densities shifts the selectivity toward C₂₊ products. The trend for FE for HCOOH compares with the trend for CO. When the current density is increased from 100 to 200 mA cm⁻², an increase in FE from 2.4% to 8% is observed. With an increase of the current density to 400 mA cm⁻², the FE for HCOOH decreases again. In general, investigations on the impact of current density showed that high current densities are beneficial for the formation of C₂₊ products. At a temperature of 40 °C and at λ = 5, the highest accumulated FE for C₂₊ products was observed at 400 mA cm⁻² with approximately 44%. Results for the whole set of investigated process parameters (40 °C and λ = 2; 20 °C and λ = 5; 20 °C and λ = 2) are given in Figures S2–S4 and reveal the same trend of increasing C₂₊ production at increased current densities. Although an increase in local pH and CO adsorption is a plausible mechanism for enhanced C₂₊ selectivity, other factors such as local water activity or changes in double-layer structure can also influence product distribution.

The local pH was not directly measured in this study. Therefore, absolute interfacial pH values cannot be assigned to the investigated operating conditions. However, substantial local alkalization is expected in bicarbonate-fed GDE systems. During cathodic CO₂ reduction and HER, OH⁻ is generated at the catalyst–electrolyte interface, while local pH changes are buffered by the bicarbonate/carbonate equilibrium. Operando pH mapping on Cu GDEs has shown that the local pH can increase from near-neutral values to above pH 10, even at considerably lower current densities than those applied here [44]. Accordingly, the observed increase in C₂₊ selectivity with current density is consistent with an increasingly alkaline catalytic microenvironment.

3.1.2 | Temperature Influence

To elaborate on the effects of temperature on C_{2+} -formation, experiments were carried out with varying electrolyte bulk temperature. Previous studies have already pointed out the change in product spectra depending on temperature in H-type cells [27, 28]. Lu et al. observed a decreasing FE for C_{2+} products in a zero-gap flow cell when the temperature was increased [45]. To our knowledge, this is the first study elucidating temperature effects in a one-sided zero-gap flow cell.

In Figure 5a, the accumulated FE for all C_{2+} products considered in this work (C_2H_4 , EtOH) and H_2 obtained in experiments carried out with an electrolyte bulk temperature of either 20 °C or 40 °C is presented. For each current density, the CO_2 excess rate was 5. Figure 5a shows that an electrolyte bulk temperature of 20 °C results in a higher FE for C_{2+} products compared to 40 °C, independent of the current density. The difference is most pronounced at 200 and 300 $mA\ cm^{-2}$ with approximately 15 percentage points higher FE for C_{2+} products. We hypothesize that this effect is due to the advantageous adsorption conditions for CO at reduced temperatures [46, 47]. This phenomenon is underlined by Figure 5b. Ethanol was detected predominantly in the liquid phase, indicating negligible volatilization losses at 40 °C. Differences in FE trends for C_2H_4 and C_2H_5OH can be attributed to distinct activation barriers of their formation pathways [27, 28].

The FE for C_1 products is higher at 40 °C compared to 20 °C at all investigated current densities. The maximum difference is observed at 200 and 300 $mA\ cm^{-2}$. The higher C_{2+} FE at 20 °C is consistent with reduced CO desorption and increased *CO

residence time at the catalyst surface. This can increase the probability of *CO dimerization and thereby promote C_{2+} formation [47]. Although CO_2 solubility decreases at higher temperatures, increased diffusion coefficients may partly offset this effect, leading to complex selectivity behavior. The overall trend suggests that solubility and *CO stabilization dominate over diffusional enhancement at elevated temperatures. This effect is represented by Figure 5c,d. At $T = 20\ ^\circ C$, desorption of the crucial intermediate CO is mitigated. Therefore, the *CO coverage at the catalyst surface increases, and CO dimerization is more likely. With an increase in temperature, CO desorption becomes enhanced, which decreases the FE for C_{2+} products due to less pronounced CO dimerization. Furthermore, CO_2 solubility in the aqueous electrolyte increases at lower temperatures, leading to higher concentrations of CO_2 at the catalyst surface. It has to be noted that the temperature directly at the catalyst–electrolyte interface deviates from the electrolyte bulk temperature. In addition to a more pronounced C_{2+} formation, the activity of the HER is decreased at 20 °C. An increase in HER activity has already been observed in the literature at elevated temperatures and will not be further discussed in this work [28]. As the results of this section reveal 20 °C superior temperature for C_{2+} production, this temperature is set for all future experiments.

3.1.3 | Influence of CO_2 -excess factor λ

To further investigate the influence of the local CO_2 concentration in the catalyst layer, experiments with different CO_2 excess rates λ were carried out. Tan et al. [29]. found that decreasing the local CO_2 concentration favors the formation of C_{2+} compounds by improving the ratio of adsorbed *CO,

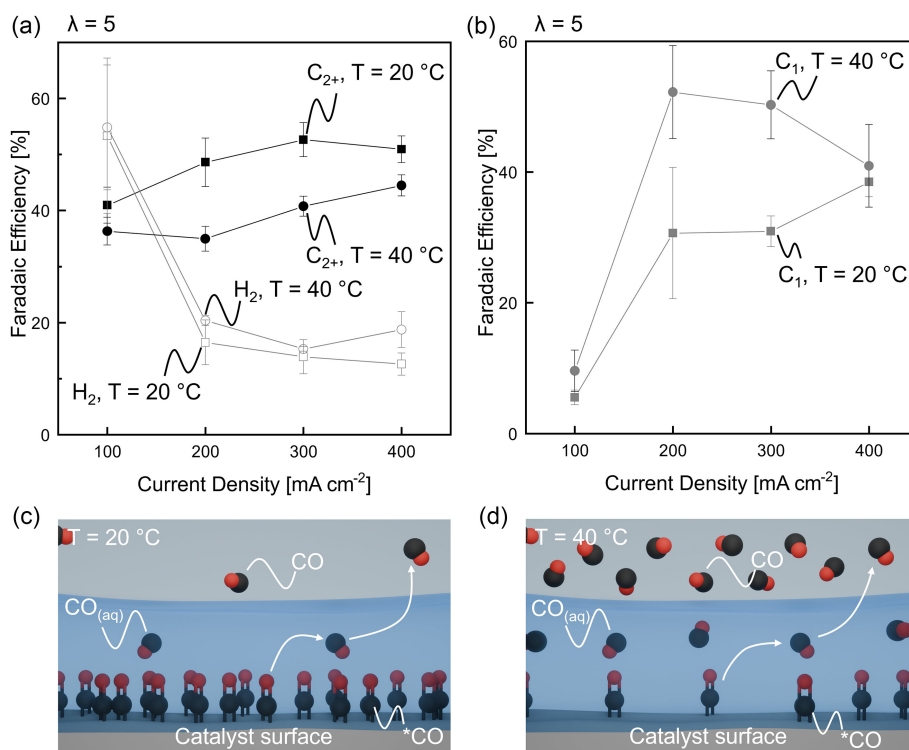


FIGURE 5 | Temperature influence on eCO_2R . (a) Comparison of the accumulated FE for C_{2+} products and H_2 at 20 °C and 40 °C at a constant CO_2 excess rate of $\lambda = 5$. (b) Accumulated FE for C_1 products at 20 °C and 40 °C and $\lambda = 5$. (c) Illustration of the *CO coverage and desorption at the catalyst surface at 20 °C. (d) Illustration of the *CO coverage and desorption at the catalyst surface at 40 °C. The error bars indicate the temporal deviation over 3 h.

CO₂, and H species. Furthermore, recent studies show that an increase in CO concentration in the rear sections of the reactor improves C₂₊ formation [48]. Figure 6a illustrates the impact of the CO₂ excess rate on the formation of C₂₊ products as well as on the activity of HER. As in previous experiments, current densities of 100 to 400 mA cm⁻² were applied. All experiments were carried out at an electrolyte bulk temperature of 20 °C, as this temperature was shown to be beneficial for C₂₊ production in previous experiments.

Figure 6a indicates that a low CO₂ excess ($\lambda=2$) is beneficial for C₂₊ formation for all applied current densities except 100 mA cm⁻². At $\lambda=5$, the accumulated C₂₊ FE increases from 40% at 100 mA cm⁻² to 51% at 400 mA cm⁻². At $\lambda=2$, the FE for C₂₊ products increases from 32% at 100 mA cm⁻² to 61% at 400 mA cm⁻². We assume with reference to the literature that an elevated C₂₊ formation is due to improved CO adsorption at the catalyst caused by lower CO₂ availability, and thus less competitive adsorption at the adsorption sites [29]. Figure 6b further shows that increasing the CO₂ excess factor from $\lambda=2$ to $\lambda=5$ also increases the FE for C₁ products. For $\lambda=2$, the FE for C₁ products increases from 4% at 100 mA cm⁻² to 18% at 400 mA cm⁻². While the FE for C₁ products is comparable for $\lambda=2$ and $\lambda=5$ at 100 mA cm⁻², at 400 mA cm⁻² the FE for C₁ products is 38% at $\lambda=5$. We hypothesize that, caused by competitive adsorption at the catalyst surface at $\lambda=5$, CO desorbs, therefore increasing the FE for C₁ products and decreasing the FE for C₂₊ products. Furthermore, the adsorption rate of CO₂ is independent of the applied current density. However,

a high current density enhances the conversion of CO to C₂₊ products, therefore increasing C₂₊ FE. While in situ Raman measurements could directly confirm *CO surface coverage, these techniques are not compatible with the employed GDE configuration. Nevertheless, our results are consistent with previous reports showing that reduced CO₂ excess increases local *CO coverage and promotes C–C coupling by minimizing competitive CO₂ adsorption [29, 48]. The effect of changing CO adsorption is schematically represented by Figure 6c,d. At $\lambda=2$, the lower CO₂ feed is expected to reduce competitive CO₂ adsorption and create conditions that favor CO-derived surface intermediates, which is consistent with enhanced C₂₊ formation. At $\lambda=5$, increased local CO₂ availability is expected to intensify CO₂/OH⁻ neutralization and bicarbonate formation, which can lower the local pH and reduce conditions favorable for CO adsorption. Therefore, fewer C₂₊ compounds are produced [49]. In addition to a change in the CO desorption behavior, the desorbed CO remains longer in the reactor due to the low volumetric flow rates at $\lambda=2$. This effect is consistent with the literature, where a longer residence time of CO in the reactor led to an increase in the electrochemical reduction of CO to the C₂₊ products [48]. Compared to $\lambda=5$, experiments with $\lambda=2$ resulted in increased H₂ formation. This is due to a decreased CO₂ availability at the catalyst surface [50]. However, the increase in C₂₊ formation compensates for the enhanced HER activity. Results from experiments with $T=40$ °C are given in the Supporting Information. Although reduced CO₂ flow ($\lambda=2$) improves CO residence time and C₂₊ selectivity, it may also enhance HER, requiring a trade-off between selectivity and efficiency. To further support the hypotheses established

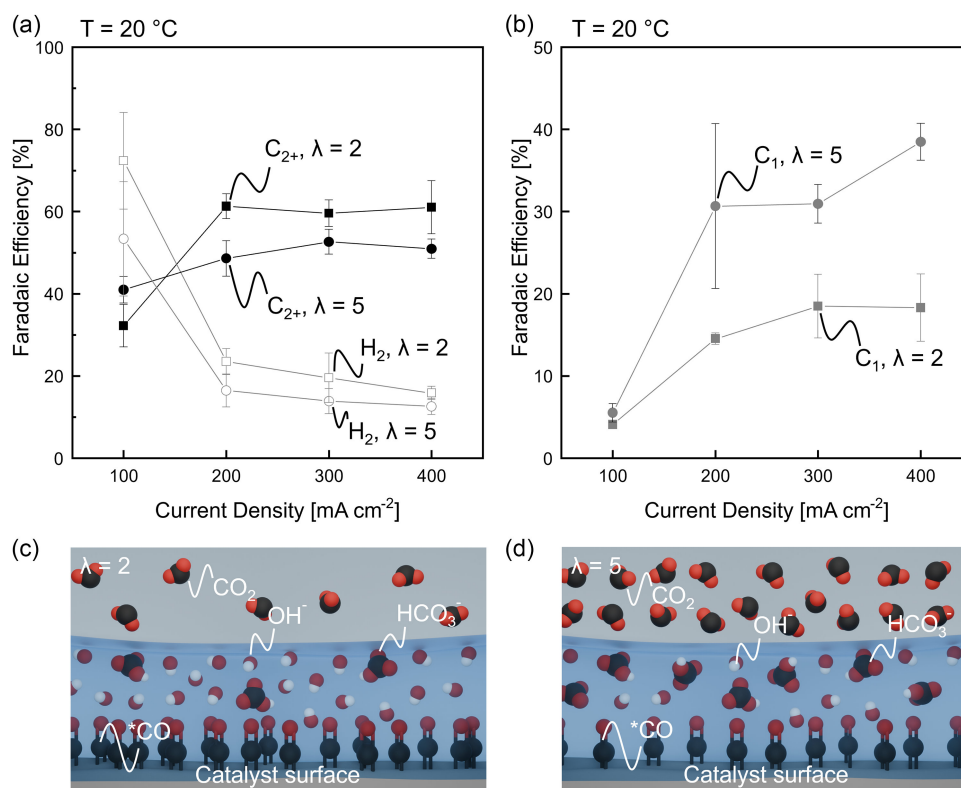


FIGURE 6 | Influence of the CO₂ excess rate. (a) FEs for C₂₊ products and H₂ at current densities from 100 to 400 mA cm⁻² at $\lambda=2$ and $\lambda=5$ and $T=20$ °C. (b) Accumulated FEs for all C₁ products at current densities from 100 to 400 mA cm⁻² at $\lambda=2$ and $\lambda=5$ and $T=20$ °C. (c) Illustration of high *CO coverage at the catalyst surface at $\lambda=2$. (d) Illustration of lower *CO coverage at the catalyst surface at $\lambda=5$. The error bars indicate the temporal deviation of the FE over the course of 3 h.

for static experiments, the flow of CO₂, CO₂ conversion, carbon balance, and Reynolds number in the gas chamber are specified for all static experiments in sections 1.5 to 1.8 of the Supporting Information.

3.2 | Pulsed Current Experiments

As $\lambda=2$ at 20 °C and a current density of 400 mA cm⁻² have been shown to be beneficial for static eCO₂R, these conditions were chosen for pulsed electrolysis experiments. As pulsed eCO₂R yielded already remarkable results for C₂₊ enhancement in the literature on full-metal electrodes in H-type cells [32, 33, 51–53], this study aims to transfer these findings to flow cells equipped with GDEs.

Figure 7a presents a comparison of static eCO₂R and pulsed experiments. Throughout pulsed experiments, the current density was reduced to 25% of the current density applied in the static experiment. FEs for the pulsed experiments were calculated with the average applied current density over time. Figure 7a shows that pulsing did not significantly affect the outcome of the experiment. Although pulsing reduces the HER activity for a nominal current density of 300 mA cm⁻², all FEs measured at the nominal current density 400 mA cm⁻² are in an equal range. In contrast to results from the literature, phenomena in H-type cells with full metal electrodes are not applicable in a flow cell equipped with GDEs. We hypothesize that enhanced mass transfer with GDEs compensates for the CO₂ mass transport limitation often observed in H-type cells. Thus, the mass transport of CO₂ into the boundary layer of the GDE does not depend on the current reduction. As the overall transferred charge is not equal in the compared experiments presented in Figure 7a further experiments were carried out with an identical transferred charge in the static and pulsed experiments. Thereby, the pulse intervals were shortened to investigate whether higher frequency pulsing can enhance the CO₂ mass transport.

Figure 7b shows the results of a static eCO₂R reference experiment at 100 mA cm⁻² compared with a pulsed current experiment with $j_h=200$ mA cm⁻² and $j_l=0$ mA cm⁻² ($t_h=t_l=1$ s). Compared to the static experiment, the HER activity decreases significantly in the pulsed experiment, while the FE of the C₁ and C₂₊ products increases. A possible cause for this behavior might be a more alkaline local pH in the catalytic microenvironment. Increasing the current density in the current-on phase also increases the pH due to the increased release of OH⁻ ions. Thus, the local pH increases, and more favorable conditions for eCO₂R are present. With an increase in the current density of 200 mA cm⁻², or 400 mA cm⁻² during t_h and 0 mA cm⁻² during t_l , similar results have been observed. It is noticeable that, compared to lower current densities, the FE for C₂₊ products slightly decreases. Together with a decrease in C₂₊ formation, there is a strong increase in C₁ FE, indicating that intermediates such as *CO desorb from the catalyst in the current-off phase. Thus, these intermediates cannot be further reduced to C₂₊ products. This effect might be due to CO₂ stripping of *CO from the catalyst surface or due to adsorbed CO₂ that prevents the dimerization of adsorbed *CO molecules.

To further underline that current pulsing does not yield higher FEs for C₂₊ products with GDEs, experiments with different pulsing parameters were performed. Figure 8 represents the results obtained from these experiments.

For all experiments performed, the overall FE for C₂₊ products was approximately 60%, which indicates that regardless of the pulsing parameters, the FE for C₂₊ products is not enhanced by current pulsing with GDEs. In contrast to the constant FE for C₂₊ products, the FE for C₁ products increases with a decrease in the average current density. The increase in C₁ product formation suggests that current pulsing with GDEs may promote intermediate desorption or reduce intermediate retention in the catalyst layer. Thus, intermediates cannot further react with C₂₊ species. Furthermore, current pulsing reduces HER activity. We hypothesize that this is caused by an enhanced CO₂ availability at

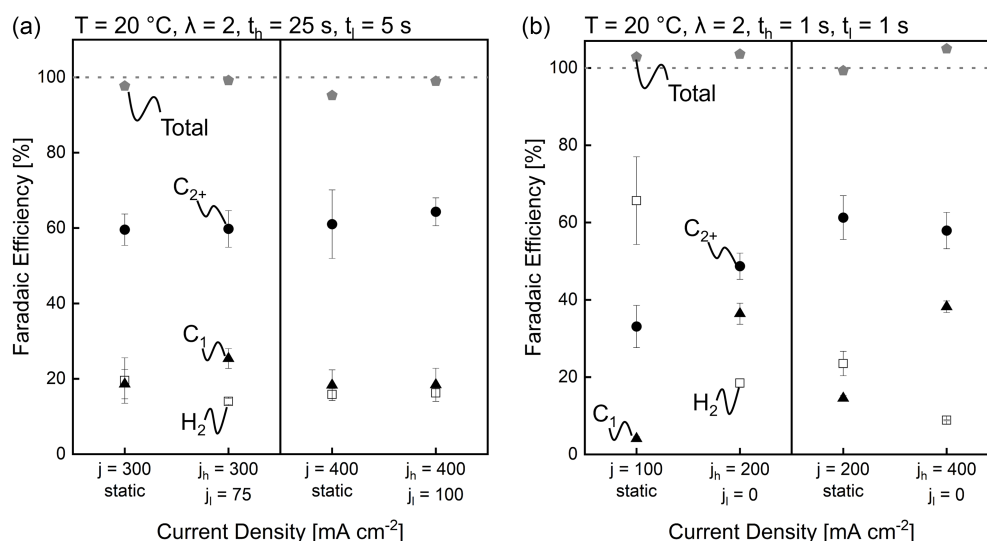


FIGURE 7 | Influence of current pulsing on the FEs of eCO₂R. (a) Comparison of static and pulsed experiments at 20 °C and $\lambda=2$ where j_h was equal to the current density applied in the static experiment. j_l was set to 25% of j_h . In pulsed experiments, the time periods for j_h were set to 25 s and for j_l to 5 s. (b) Experiments conducted at the same average current density at 20 °C and $\lambda=2$. j_l was always set to 0 mA cm⁻². A symmetric pulse profile with $t_h=t_l=1$ s was applied. The error bars indicate the temporal deviation of the FE over the course of 3 h.

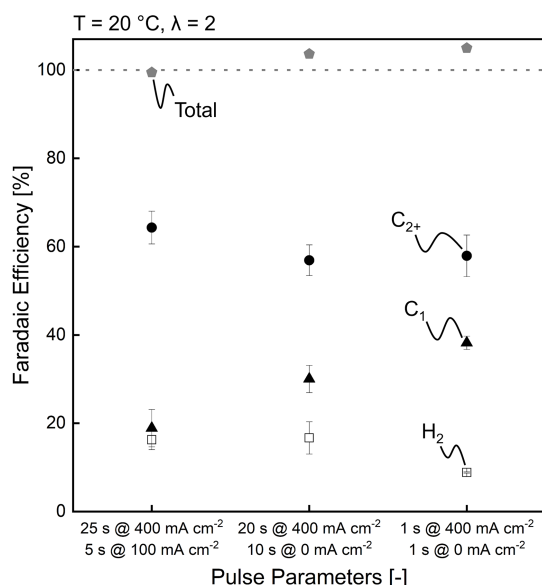


FIGURE 8 | Influence of pulse parameters on FEs obtained at $j_h = 400 \text{ mA cm}^{-2}$ and $j_l = 0.25 j_h$ or $j_l = 0 \text{ mA cm}^{-2}$. The error bars indicate the temporal deviation of the FE over the course of 3 h.

the cathode, as well as a strongly alkaline local pH due to the high applied current densities in the current-on phase. These effects are in accordance with recent literature where similar trends were observed when current pulses were applied to the system [38]. While current pulsing in this setup does not enhance C_{2+} formation, it may still prove beneficial under different conditions, for example, with alternative catalyst structures, modified flow field geometries, or tailored pulse profiles designed to retain intermediates more effectively. Thus, the lack of benefit from pulsed operation observed here refers specifically to C_{2+} formation and C–C coupling under the investigated galvanostatic pulse protocols, whereas pulsing still affects the overall product distribution by suppressing HER in selected experiments and increasing C_1 product formation.

4 | Conclusion

This study systematically investigated how key process parameters, namely current density, temperature, CO_2 excess rate, and pulsed operation, collectively influence the catalytic microenvironment and macroscopic product distribution in electrochemical CO_2 reduction (e CO_2R). By employing a commercially available flow cell with GDEs and scalable catalyst materials, we created a relevant platform for the holistic engineering of e CO_2R systems.

Our results show that increasing the current density up to 400 mA cm^{-2} enhances C_{2+} formation. Based on literature-supported mechanistic interpretation, this trend is consistent with increased interfacial alkalinity, more favorable CO adsorption, and promoted C–C coupling. Lowering the electrolyte bulk temperature to 20°C further favors C_{2+} formation by enhancing CO_2 solubility and reducing CO desorption, both of which increase the probability of CO dimerization. A reduced CO_2 excess rate ($\lambda = 2$) enhances the local CO concentration and suppresses competitive CO_2 adsorption, which also supports C_{2+} production. Together, these findings illustrate that engineering

the catalytic microenvironment through an integrated control of process parameters is essential to steer selectivity.

Pulsed current operation, although previously shown to improve C_{2+} selectivity in H-type cells, did not further enhance C_{2+} formation under the investigated GDE flow-cell conditions. The improved mass transport characteristics of GDEs likely compensate for the limitations that pulsing is intended to address. In fact, pulsing was observed to not only reduce hydrogen evolution reaction (HER) activity but also promote the desorption of intermediates, which may suppress further conversion to multicarbon products.

Overall, this work underscores the importance of holistically optimizing reactor design and process conditions to tailor the local catalytic environment for efficient CO_2 -to- C_{2+} conversion. This simultaneous evaluation of multiple process parameters under high-current, flow cell operation provides mechanistic insight directly applicable to industrial electrolyzers. Our findings bridge the gap between isolated parameter studies and scalable reactor engineering and offer a roadmap for future research on sustainable CO_2 utilization. The trends identified here should therefore be regarded as qualitative guidance for GDE-based CO_2 electrolyzers, whereas direct quantitative transfer to MEA or zero-gap systems requires additional consideration of ion transport, water management, carbonate crossover, salt precipitation, and local pH gradients. Further studies on dynamic reactor operation and real-time control of the microenvironment may unlock new possibilities for optimizing selectivity and stability in industrially relevant systems.

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Conflicts of Interest

The authors declare no conflicts of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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Supporting Information

Additional supporting information can be found online in the Supporting Information section.