

Organic Electrosynthesis in CO₂-eXpanded Electrolytes: Enabling Selective Acetophenone Carboxylation to Atrolactic Acid

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Cite This: <https://doi.org/10.1021/acssuschemeng.1c03073>

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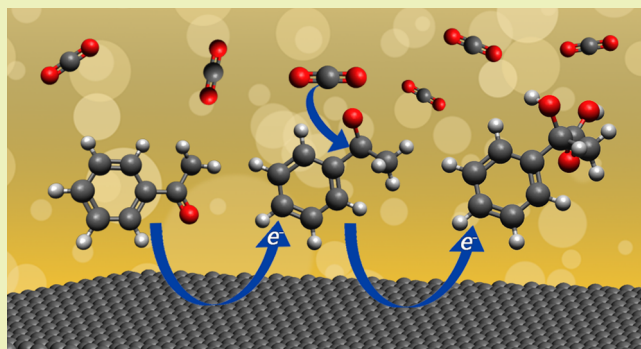
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Supporting Information

ABSTRACT: Electrochemical carboxylation is an organic electro-synthesis technique where CO₂ is coupled with one or more organic molecules to form carboxylic acids. Here, we show that process intensification and selectivity enhancements are simultaneously achieved by performing electrochemical carboxylation in CO₂-eXpanded electrolytes (CXE)—a class of media that accommodates multimolar concentrations of CO₂ in organic solvents at modest pressures. We observed that electrochemical carboxylation of acetophenone does not occur at ca. 1 atm (0.2 MPa) CO₂ headspace pressure. Instead, acetophenone hydrogenation was dominant, producing the undesired 1-phenylethanol as the major product. However, in the CXE media (at 1.4–4.2 MPa CO₂ headspace pressure), (±)-atrolactic acid was the major product with a maximum faradaic efficiency of 72% observed at 2.8 MPa. Achieving the pressure-tunable carboxylation results from the high liquid-phase CO₂ concentrations afforded by the CXE media. At CO₂ pressures exceeding 2.8 MPa, we observed a lower rate of carboxylation, which is attributed to the decreased electrolyte polarity at progressively greater liquid-phase CO₂ concentrations present at higher pressures.

KEYWORDS: Sustainable chemistry, CO₂ utilization, Electrochemistry, Electrocatalysis, C–C coupling



INTRODUCTION

New and sustainable carbon dioxide (CO₂) reaction pathways are needed to leverage CO₂ as a carbon feedstock. CO₂ conversion is challenging because it is both (1) thermodynamically uphill, requiring an external input of free energy, and (2) kinetically limited, resulting in the need to overcome large activation energies.¹ While several chemocatalytic methods have been reported for converting CO₂ into value-added products,^{2,3} electrochemical CO₂ conversion holds promise because it could be powered with renewable wind and solar energy sources. A grand challenge in electrochemical CO₂ conversion is synthesizing high-carbon content products through carbon–carbon coupling. Copper electrocatalysts have long been known to couple CO₂ with itself to produce a number of C₂ (i.e., two-carbon) products in aqueous media.^{4–6} It has been suggested that C–C coupling occurs uniquely on Cu because the CO adsorption energy is at an optimum level that enables the surface to be covered by adsorbed CO. This suppresses the hydrogen evolution reaction and promotes the formation of C₂ products through dimerization of the adsorbed CO radical intermediate.^{7–10} However, because the C–C coupling occurs through CO dimerization, the selectivity and efficiency toward any one product is typically low.¹ Moreover, in aqueous media at

ambient pressures, the overall rates are limited by the low solubility of CO₂ in water.¹¹

Recently, we demonstrated that organic solvent-based CO₂-eXpanded electrolytes (CXEs) can dissolve multimolar amounts of liquid CO₂ at moderate pressures while retaining sufficient supporting electrolyte concentrations to facilitate electrochemistry.^{12–14} We refer to these as CO₂-eXpanded electrolytes because the liquid-phase volume expands with increasing CO₂ pressure (from 1.4–5.5 MPa) due to the dissolution of CO₂ (Supporting Information, Figure S1). In previous work, we observed (1) an order-of-magnitude enhancement of the catalytic current for CO₂ reduction to CO on heterogeneous catalysts (polycrystalline gold and copper),^{12,13} (2) a significant enhancement of the catalytic rate for homogeneous (Re(CO)₃(bpy)Cl (bpy = 2,2'-bipyridyl)) catalysts,¹⁴ and (3) a maximum in the electrocatalytic current at intermediate CO₂ pressures of ~3 MPa.

Received: May 7, 2021

Revised: July 7, 2021



In this work, we demonstrate that the favorable properties of CXEs enhance the rate and selectivity of high-carbon content products via electrochemical carboxylation reaction pathways. Electrochemical carboxylation is an alternative approach to produce high-carbon-content carboxylic acids via the electrochemical coupling of CO₂ with organic compounds. Organic electrosynthesis has become a promising method to produce a wide variety of chemicals with high atom economy.¹⁵ Previous studies on electrochemical carboxylation¹⁶ have explored coupling CO₂ with alcohols,¹⁷ alkenes,^{18,19} aldehydes,²⁰ epoxides,^{21,22} organic halides,^{23–26} and a few other organic compounds.^{27,28} However, elevated liquid-phase CO₂ concentrations have not, to the best of our knowledge, been reported for enhancing electrosynthetic carboxylation, offering an opportunity to explore CXEs for this challenging transformation.

RESULTS AND DISCUSSION

As a model reaction, we demonstrate that CXEs enhance electrochemical carboxylation of acetophenone, selectively producing (±)-atrolactic acid (**1**) over either 1-phenylethanol (**2**) or 2,3-diphenyl-2,3-butanediol (**3**). The electrochemical carboxylation of acetophenone is of interest in the production of nonsteroidal anti-inflammatory (NSAID) pharmaceuticals such as Ibuprofen and Naproxen (Figure 1b). The Monsanto

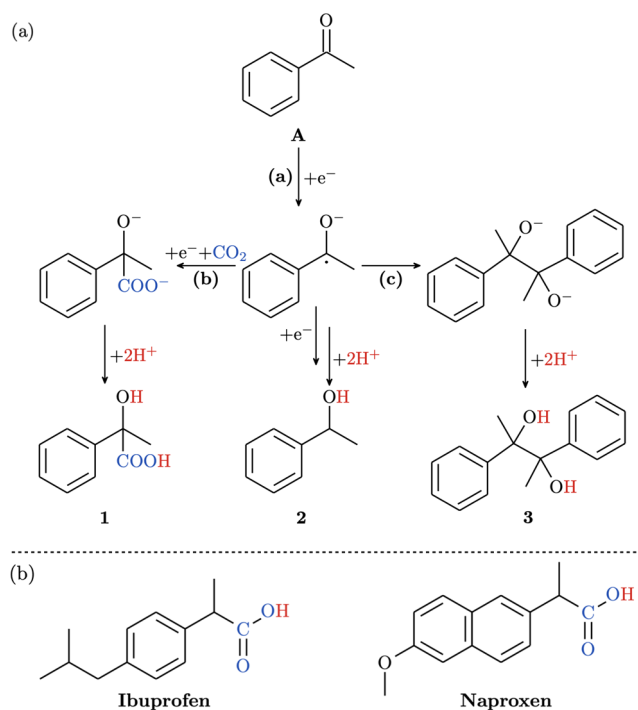


Figure 1. (a) Proposed mechanism for the electrocarboxylation of acetophenone resulting in the formation of atrolactic acid (**1**), 1-phenylethanol (**2**), and 2,3-diphenylbutane-2,3-diol (**3**). (b) Chemical structures for Ibuprofen and Naproxen, demonstrating similarities with atrolactic acid.

Corporation and others^{29–39} had been interested in the electrochemical carboxylation of acetophenone to produce atrolactic acid (**1**); however, controlling the reaction to produce the desired carboxylic acid product **1** with high rates and selectivities (i.e., without formation of the alcohol **2** or dimer **3**) has been a challenge.^{29,39}

To assess the electrochemical behavior of acetophenone carboxylation in the CXE media, cyclic voltammetry experiments were performed in tetrabutylammonium hexafluorophosphate-supported acetonitrile under 0.2 MPa Ar and CO₂ headspace pressures of 0.2, 1.4, 2.8, 4.2, and 5.5 MPa with a glassy carbon working electrode and a Mg sacrificial counter electrode (details provided in Supporting Information, Section 1). The sacrificial Mg/Mg²⁺ counter oxidation reaction (Supporting Information, Figure S2) was chosen to charge balance the acetophenone reduction without oxidizing the electrolyte. In each panel of Figure 2, the voltammetry response of acetophenone reduction (blue voltammogram) is compared to a blank (red voltammogram) at identical headspace pressures with no acetophenone present.

During the electrochemical conversion, we anticipate that acetophenone can undergo a one-electron transfer reduction to form a ketyl radical anion (Figure 1a, reaction (a)). This ketyl anion can either react with CO₂ to form a carboxylate anion (Figure 1a, reaction (b)), dimerize (Figure 1a, reaction (c)), or undergo H⁺/H• transfer to form an alcohol (Figure 1a, (2)). When CO₂ is absent from the system (Figure 2a), we observed a voltammetric wave with a peak current of 36.3 mA cm⁻² consistent with a two-electron reduction where the first step is rate determining (Supporting Information, Section 2).⁴⁰ When CO₂ is added to the system (Figure 2b), we observed an increase in the peak current of the voltammetric wave to 63.4 mA cm⁻². This increase is consistent with a two-electron reduction where the second electron-transfer step is rate determining suggesting a change in the reaction pathway (Supporting Information, Section 3). The absence of an oxidation event on the return sweep is consistent an electrochemical reduction followed by a homogeneous chemical reaction (e.g., EC, EEC, or ECE) where the kinetics of the homogeneous chemical reaction are fast and the product is not redox active.^{40,41}

A unique feature of the CXE media is the ability to pressure-tune the liquid-phase CO₂ concentration enabling us to study its effect on the electrochemical carboxylation of acetophenone. Under CXE conditions, when acetophenone is absent (Figure 2c–f, red voltammograms), we do not observe significant current flow above background levels at the potentials investigated. This demonstrates that acetophenone reduction does not compete with direct CO₂ reduction on glassy carbon in the CXE, even though CO₂ is present in high liquid-phase concentrations.

As the headspace CO₂ pressures increase beyond ambient conditions, we observed a near identical peak current of ca. 63 mA cm⁻² in the voltammograms. We also observed a slight shift of the peak potential to more negative potentials, with the largest shift occurring at pressures exceeding 2.8 MPa. This indicates that the electron-transfer kinetics slow as the CXE medium becomes more nonpolar, attributed to the high liquid-phase CO₂ concentrations. In fact, at 5.5 MPa CO₂ pressure, the acetophenone reduction wave is not present at the potentials investigated. The observed effect for acetophenone carboxylation appears to be similar to what we observed during electrochemical CO₂ reduction to CO in the CXE media.¹²

To quantify the liquid-phase CO₂ concentration effect on acetophenone carboxylation, bulk electrolysis experiments were performed under both standard and CXE conditions with the results summarized in Table 1 (bulk electrolysis chronoamperograms shown in Supporting Information). After the bulk electrolysis experiments, hydrochloric acid was added

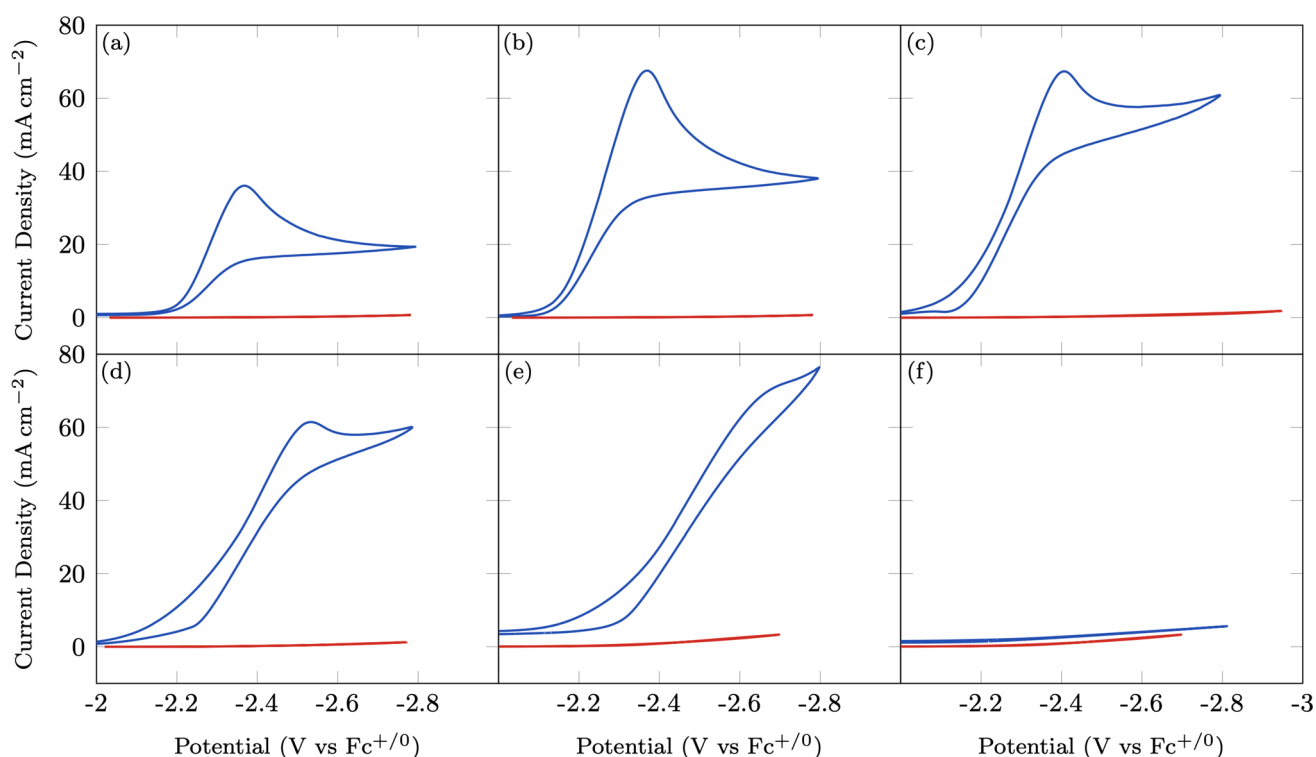


Figure 2. Cyclic voltammetry of acetophenone reduction (blue) under both standard and CXE conditions compared to blank electrolytes (red) at various headspace pressures: (a) 0.2 MPa Ar, (b) 0.2 MPa CO₂, (c) 1.4 MPa CO₂, (d) 2.8 MPa CO₂, (e) 4.2 MPa CO₂, and (f) 5.5 MPa CO₂. Working electrode: 1 mm diameter glassy carbon. Counter electrode: Mg metal sacrificial anode. Reference electrode: Cu quasi-reference electrode. Scan rate: 50 mV s⁻¹.

Table 1. Bulk Electrolysis Data for Electrocarboxylation of Acetophenone to (±)-Atrolactic in CXEs for 12 h at −2.6 V vs Fc/Fc⁺ on a Glassy Carbon Electrode^a

CO ₂ pressure (MPa)	Liquid-phase CO ₂ (M)	Charged passed (C)	(±)-Atrolactic acid ^b (mmol)	Rate ^c (mmol h ⁻¹ cm ⁻²)	Faradaic efficiency ^d (%)
0	—	39.6	—	—	—
0.2	0.1	54.2	—	—	—
1.4	1.7	48.3	0.11 ± 0.01	1.19 ± 0.09	44.9 ± 1.2
2.8	4.4	46.9	0.18 ± 0.01	1.86 ± 0.14	72.0 ± 1.9
4.2	8.5	21.7	0.07 ± 0.01	0.73 ± 0.01	60.7 ± 1.6
5.5	14.0	2.3	—	—	—

^a(±)-Atrolactic acid concentration determined from peak integration of ¹H-NMR spectrum. Error analysis from triplicate measurements at 2.8 MPa CO₂ pressure. "—" denotes atrolactic acid was not detected. ^bCalculated by quantitative ¹H NMR using 1,3,5-trimethoxybenzene as an internal standard. ^cCalculated from the number of moles of (±)-atrolactic acid, bulk electrolysis time, and area of the electrode. ^dFaradaic efficiency based on moles of product per mole of electron passed assuming two e⁻ are required.

in excess to protonate the liquid-phase products and make them visible via ¹H NMR. Figure 3 shows the ¹H NMR spectra obtained after 12 h bulk electrolysis experiments under 2.8 MPa CO₂, 0.2 MPa CO₂, and 0.2 MPa Ar. These are compared to ¹H NMR spectra measured for purchased standards of **1**, **2**, and **3**. Additional ¹H NMR spectra from the other CO₂ pressures tested are shown in the Supporting Information.

Under 0.2 MPa Ar, the major observed product is alcohol **2**. The resonance peaks present at 7.35 ppm are characteristic of the 1-phenylethanol standard (Figure 3, 2). When Ar is replaced with 0.2 MPa of CO₂, 1-phenylethanol (**2**) remains the major product observed. Clearly, the multiplet at 7.35 ppm is present in both 0.2 MPa Ar (Figure 3, A) and in 0.2 MPa CO₂ (Figure 3, B). However, at higher CO₂ pressures, we observed a change in selectivity toward (±)-atrolactic acid (**1**). Evidence of this shift in selectivity is represented by different resonance peaks emerging between 7.38 and 7.45 ppm

accompanied by a shift in resonance lined between 7.3 and 7.35 ppm (Figure 3, C). Additionally, the characteristic resonance of 1-phenylethanol at 7.35 ppm is diminished in the 2.8 MPa sample.

The rate of (±)-atrolactic acid production was determined via quantification of the ¹H NMR signal using a 1,3,5-trimethoxybenzene internal standard. Interestingly, we observed a maximum in both production rate and faradaic efficiency at 2.8 MPa CO₂ headspace pressure (1.9 mmol h⁻¹ cm⁻² and 72%, respectively). At headspace pressures exceeding 4.2 MPa, we observed an attenuation in the (±)-atrolactic acid production rate (Figure 4). Similar to our previous studies on electrochemical CO₂ reduction,^{12–14} we attribute the decrease in rate to a decrease in the polarity of the electrolyte as the liquid-phase CO₂ concentrations approach that of pure liquid CO₂. Gas chromatography analysis of the headspace after bulk electrolysis showed only trace gas-phase products (e.g., H₂ or

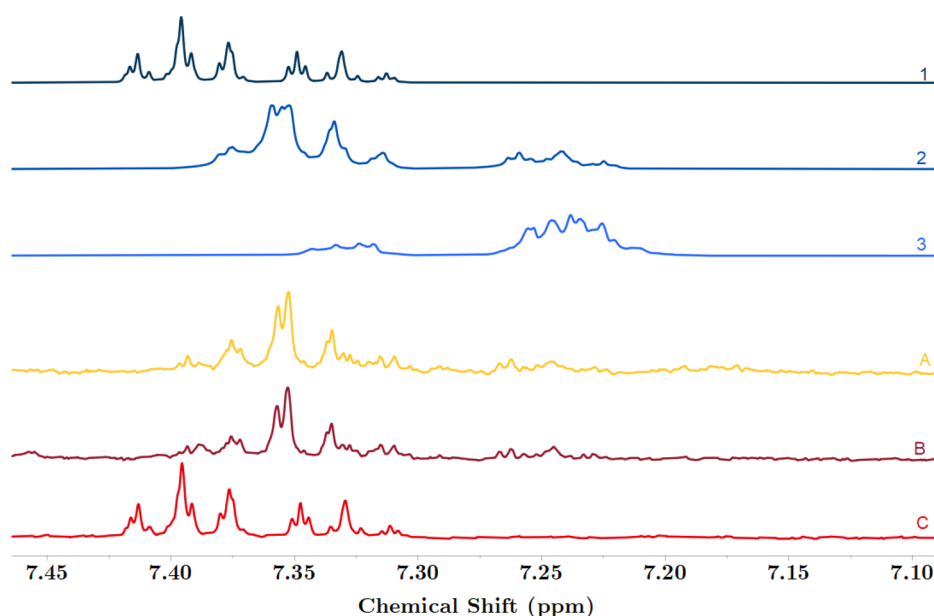


Figure 3. ^1H NMR results after 12 h bulk electrolysis under different reaction conditions at -2.6 V vs Fc/Fc^+ : (1) $(\pm)$ -atrolactic acid standard, (2) 1-phenylethanol standard, (3) 2,3-diphenylbutane-2,3-diol standard, (A) 0.2 MPa argon pressure, (B) 0.2 MPa CO_2 pressure, and (C) 2.8 MPa CO_2 pressure.

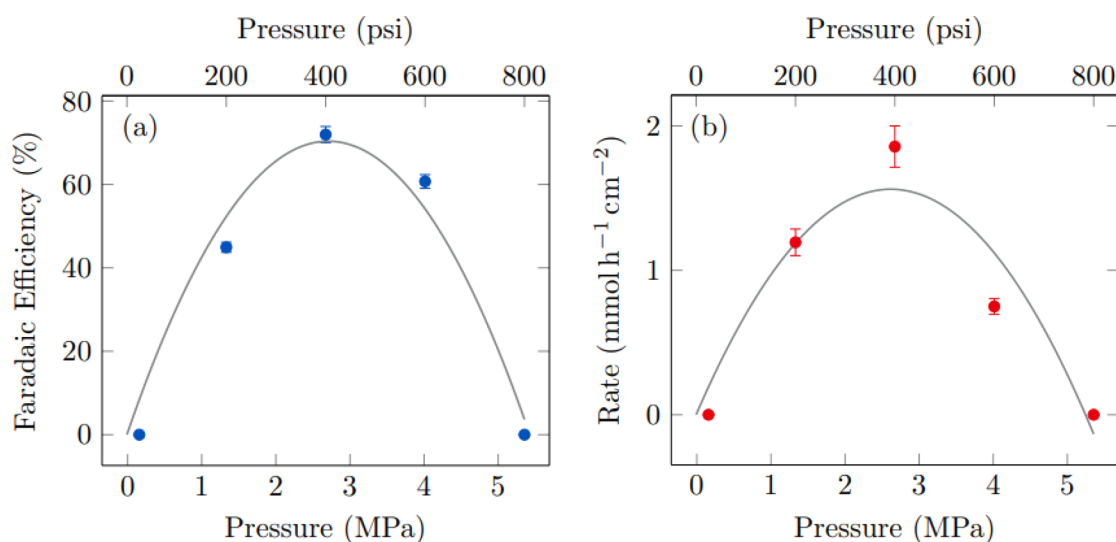


Figure 4. Faradaic efficiency (a) and rate of reaction (b) for electrocarboxylation of acetophenone to atrolactic acid as a function of pressure for 12 h bulk electrolysis experiments.

CO), revealing total faradaic efficiencies that are less than unity (Supporting Information Table S1). Interestingly, we also observed similar faradaic efficiencies for CO_2 reduction to CO in our previous work using the same reactor setup (74% on Au^{13} and 70% with $\text{Re}(\text{CO})_3(\text{bpy})\text{Cl}^{14}$). This was attributed to the use of a single compartment electrochemical cell, which may allow some reduced species formed at the working electrode to be potentially oxidized at the counter electrode (or vice versa) resulting in lower faradaic yields.

Under Ar -saturated conditions, the measured and expected product is **2**, which corresponds to a two-electron/two-proton reduction product. At present, the exact mechanistic route in the aprotic media is still ambiguous. It is possible that a dianion is formed via a two-electron reduction that is stabilized by Mg^{2+} formed on the sacrificial anode. Alternatively, proton transfer could occur from trace water, the supporting

electrolyte, or other organic molecules after the first electron step. Under standard CO_2 conditions (0.2 MPa CO_2 headspace pressure, Figure 2b), the increase in the peak current in voltammetry experiments compared to Ar -saturated conditions suggests a possible change in the reaction pathway. However, the desired product **1** was not observed as the major product in bulk electrolysis experiments for 0.2 MPa CO_2 . Under near atmospheric CO_2 pressures, the ratio of the number of moles of CO_2 in the reactor compared to the number of electrons passed during the bulk electrolysis experiment is ca. 3:1. In contrast, the CO_2 -to- e^- ratio is ca. 170:1 under CXE conditions at a headspace pressure of 2.8 MPa. This demonstrates that the high liquid-phase CO_2 concentrations afforded in the CXE media are necessary to sustain electrochemical carboxylation of acetophenone to $(\pm)$ -atrolactic acid over the 12 h bulk electrolysis experiment.

CONCLUSION

This experimental study clearly demonstrates that process intensification and selectivity enhancements in electrochemical carboxylation can be achieved in CXE media. Interestingly, the optimum liquid phase CO₂ concentration (ca. 4.5 M), with respect to rate of reaction, is identical for both electrochemical carboxylation and electrochemical CO₂ reduction to CO in acetonitrile-based CXE media. This gives credence to the hypothesis that the polarity of the electrolyte decreases at higher liquid-phase CO₂ concentrations beyond an optimum pressure. Fortunately, the optimum pressure is relatively modest favoring the practical viability of CXE-based electrochemical carboxylations.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acssuschemeng.1c03073>.

Detailed description of experimental methods and equipment, additional cyclic voltammetry analysis, additional ¹H NMR spectra, additional chronoamperograms, and CO₂ expansion data (PDF)

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<https://pubs.acs.org/doi/10.1021/acssuschemeng.1c03073>

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was supported by the U.S. National Science Foundation through Award CBET-1605524. M. A. Stalcup and C. K. Nilles were also supported by a the U.S. National Science Foundation Research Traineeship (NRT) grant through Award DGE-1922649. The team would also like to acknowledge helpful discussion with Prof. R.V. Chaudhari.

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