

The pH and Potential Dependence of Pb-Catalyzed Electrochemical CO₂ Reduction to Methyl Formate in a Dual Methanol/Water Electrolyte

Dillon T. Hofsommer,^a Ying Liang,^{b, c} Sandesh S. Uttarwar,^c Manu Gautam,^c Sahar Pishgar,^c Saumya Gulati,^c Craig A. Grapperhaus,^{a,*} and Joshua M. Spurgeon^{c,*}

[a] Dr. D. Hofsommer, Prof. C. Grapperhaus
Department of Chemistry
University of Louisville
2320 South Brook Street, Louisville, Kentucky 40292, USA.
E-mail: craig.grapperhaus@louisville.edu

[b] Dr. Y. Liang
School of Chemistry and Chemical Engineering
Guangdong Pharmaceutical University
Guangzhou, Guangdong 510006, China.

[c] Dr. Y. Liang, S.S. Uttarwar, Dr. M. Gautam, Dr. S. Pishgar, S. Gulati, Dr. J.M. Spurgeon
Conn Center for Renewable Energy Research
University of Louisville
Louisville, Kentucky 40292, USA.
Email: joshua.spurgeon@louisville.edu

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Abstract: The conversion of waste CO₂ to value-added chemicals through electrochemical reduction is a promising technology for mitigating climate change while simultaneously providing economic opportunities. The use of non-aqueous solvents like methanol allows for higher CO₂ availability and novel products. In this work, the electrochemistry of CO₂ reduction in acidic methanol catholyte at a Pb working electrode was investigated while using a separate aqueous anolyte to promote a sustainable water oxidation half-reaction. The selectivity among methyl formate (a product unique to reduction of CO₂ in methanol), formic acid, and formate was critically dependent on the catholyte pH, with higher pH conditions leading to formate and low pH favoring methyl formate. The potential dependence of the product distribution in acidic catholyte was also investigated, with a faradaic efficiency for methyl formate as high as 75% measured at -2.0 V vs Ag/AgCl.

Introduction

Electrochemical reduction of CO₂ provides an attractive route to produce valuable fuels and chemicals that can simultaneously lower greenhouse gas emissions when powered by renewable electricity.^[1] While recent technological advances have shown the feasibility of industrial CO₂ electroreduction,^[2] many challenges remain to improve this technology and expand the list of economically viable products. The vast majority of electrochemical CO₂ reduction research has been conducted in aqueous media under neutral to alkaline conditions, leading to commonly reported products including carbon monoxide, formic acid, methane, methanol, ethylene, acetic acid, and ethanol.^[3] In comparison, nonaqueous media for CO₂ reduction has been underexplored but represents a possible avenue to yield new products and improved operating conditions.

Methanol, for instance, is an attractive solvent for the reduction of CO₂ which benefits from significantly increased CO₂ solubility compared to water (~ 160 mM in CH₃OH compared to 38 mM in H₂O at 20 °C and 1 atm CO₂ partial pressure)^[4] while maintaining water-like reactivity endemic to a polar protic solvent. The high solubility of CO₂ in methanol is even exploited industrially in the removal of CO₂ from feed gas streams by the Rectisol process.^[5] Several other conventional CO₂ capture technologies require basic conditions, e.g. strong alkali or amines,^[6] which chemically modify the CO₂ into bicarbonates, carbonates, or carbamates that are more difficult to reduce than free CO₂. Although dissolved CO₂ in alkaline methanol produces an unreactive methyl carbonate species, neutral to acidic methanol is able to dissolve high quantities of chemically reactive CO₂. Despite methanol's promise for high solubility CO₂ reduction, there have been limited literature reports using methanol solvent for electrochemical CO₂ conversion.^[7] In general, reduction of CO₂ in methanol on metal cathodes has shown qualitatively similar selectivity to related aqueous systems but with higher selectivity towards formic acid and lower selectivity towards hydrogen.^[8]

Several reports of electrochemical reduction^[8b, 9] and homogeneous hydrogenation^[10] of CO₂ in methanol have demonstrated the synthesis of a novel C2 product, methyl formate (HCOOCH₃), largely replacing selectivity to formic acid (HCOOH), the more common product in aqueous media. Isotopic labeling studies indicate that methyl formate in these examples arises through the esterification of CO₂-derived formic acid and the methanol solvent.^[9a] Thus, in addition to increased CO₂ solubility, a nonaqueous solvent such as methanol opens a route to introduce an intermediate species into the electrochemical CO₂ reduction process to drive the reaction selectivity to value-added products that are not favored in aqueous systems. Although the conditions required to form methyl formate were not fully

RESEARCH ARTICLE

elucidated, in these previous cases it was generally formed under high pressure (40 atm^[11]) CO₂ while Brønsted or Lewis acid catalysts were required at lower pressures.^[10b] One advantage of methyl formate as an electrolysis product is that it is highly volatile (boiling point of 32 °C at 1 atm), so it is more easily purified by distillation than the more common formyl products, formic acid or formate. Industrially, methyl formate is typically produced through base-catalyzed methanol carbonylation and is used as a precursor to manufacture formamides.^[12] Other applications include the production of methyl carbamates^[13] or hydrocarbons,^[14] and as a component in quick-dry finishes and polyurethane foams. Despite several promising markets for this chemical, exploration into the electrochemical synthesis of methyl formate has been quite limited.

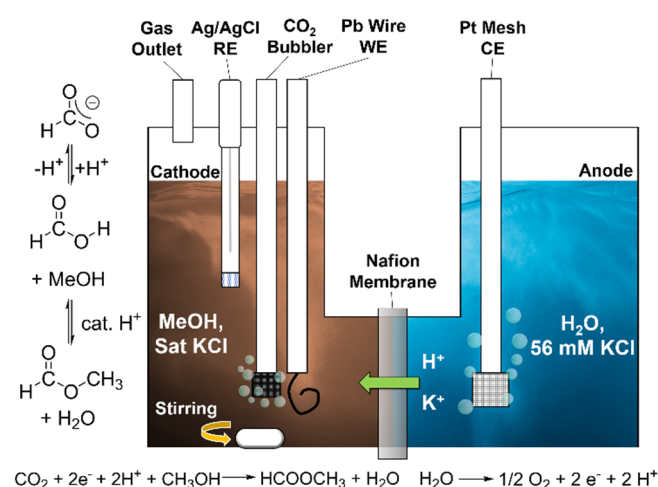


Figure 1. Schematic of the electrochemical H-cell used for CO₂ reduction experiments, with a Pb wire working electrode (WE), Ag/AgCl reference electrode (RE), and Pt mesh counter electrode (CE).

Herein, the key electrolysis parameters of pH and applied potential were investigated for their effects on the reduction of CO₂ in methanol. H-cell experiments such as depicted in Figure 1 are reported to determine the feasibility of CO₂ electroreduction in methanol with three key parameters changed from previous studies in methanol: (1) operation of the electrolyzer at lower (1 atm) CO₂ pressure, (2) the use of an aqueous anolyte to promote a sustainable half-reaction (water oxidation) and avoid anodic methanol degradation that can produce spurious methyl formate,^[9a, 9b, 15] and (3) the use of acidic catholyte. A Pb metal cathode, which is known to suppress hydrogen evolution in acidic media^[16] and promote formic acid production in water and analogous methyl formate in methanol, was chosen to drive selectivity toward methyl formate.^[3a, 8b] Because a sustainable and scalable process is desired for the value-added conversion of waste CO₂ to methyl formate, decomposition of the methanol electrolyte at the anode should be minimized. A dual electrolyte approach was therefore developed with methanol catholyte and aqueous anolyte to promote water oxidation at the anode.

Results and Discussion

Dual Methanol/Water Electrolyte System. There are five main products of electrochemical CO₂ reduction in methanol on Pb:

hydrogen, carbon monoxide, methyl formate, formic acid, and the formate anion. The three non-gaseous products can be readily distinguished by ¹H NMR spectroscopy as shown in Figure 2. In the detection matrix employed, methyl formate appears as two singlets at 8.00 and 3.60 (3H) ppm, and formate (in basic media) is a singlet at ~8.42 ppm while formic acid (in acidic media) is a singlet at ~7.99 ppm. In neutral or mildly acidic media, formic acid is partially ionized. Because HCOOH and HCOO⁻ rapidly interconvert on the NMR timescale, a mixture of formic acid and formate appears as one singlet with a chemical shift equal to the weighted average between the two extreme values of chemical shift (see SI for sample calculations).^[17] The use of NMR spectroscopy thus allows the clear distinction between the three liquid products of CO₂ reduction.

Methanol in the absence of water can be oxidized at a Pt anode to produce methyl formate.^[18] In control experiments using methanol bubbled with Ar for both the catholyte and anolyte, methyl formate was detected in the anode compartment due to methanol oxidation pathways. Despite the absence of CO₂ bubbling, a much smaller amount of methyl formate was detected in the cathode compartment attributed to membrane crossover from the anode. Therefore, a dual electrolyte system with methanol catholyte and aqueous anolyte was pursued in order to avoid complications in the product quantification due to methyl formate crossover from the anode. Further, the use of aqueous anolyte increases the sustainability of the overall process by minimizing decomposition of methanol by oxidation. With an aqueous anolyte, methanol that crosses the membrane from the catholyte can still be oxidized at the anode, however low methanol concentrations have been shown to lead to full oxidation to CO₂ as the primary oxidation product.^[19] Notably, a number of previous electrochemical CO₂ reduction studies in methanol were conducted with both the cathode and anode immersed in the methanol without a separator, making the reported methyl formate values difficult to deconvolute between the CO₂ reduction and methanol oxidation pathways.^[8b, 9a]

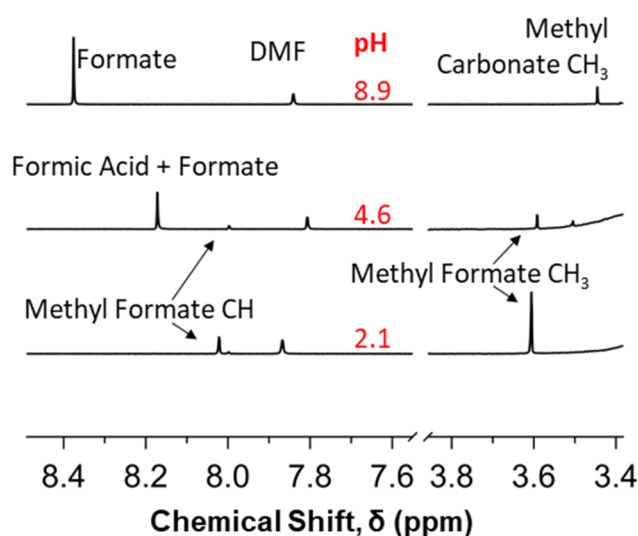


Figure 2. ¹H NMR spectra for formic acid dissolved in methanol and adjusted to different pH values.

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To show that an aqueous anode does not interfere with CO₂ reduction in methanol, preliminary experiments were conducted and compared with previously reported conditions using methanol as both catholyte and anolyte.^[20] CO₂-saturated solutions of 0.3 M KOH in methanol or water were used as the catholyte and anolyte, respectively. The Pb wire working electrode was held at -1.8 V or -2.0 V vs Ag/AgCl for two hours. At -1.8 V, hydrogen and formate were each produced at ~ 50% faradaic efficiency (FE), which was close to the 60% FE for “formic acid” reported previously in methanol only.^[20] At -2.0 V, the formate selectivity in the dual methanol/water system increased to 90% FE compared to 80% FE reported in an all methanol system. The consistency of the results between these preliminary experiments and published results indicated that substituting water for methanol as the solvent in the anolyte did not significantly disrupt the high faradaic efficiency for the electrochemical conversion of CO₂ to formate in methanol catholyte. Although high selectivity for CO₂ reduction products was attained in these preliminary measurements, nearly all the liquid product was present as HCOO⁻ due to the alkaline conditions in 0.3 M KOH in methanol. To promote in-situ methyl formate production, conditions were shifted to investigate electrolysis in neutral or acidic electrolytes.

The current density versus potential (*J-E*) behavior for a Pb cathode was measured in pH ~1.5 methanol saturated with KCl (~56 mM) as supporting electrolyte under Ar or CO₂ bubbling with a corresponding aqueous 3 mM HCl, 56 mM KCl in water anolyte. For Pb in methanol at low pH under Ar, the *J-E* behavior yielded low current density (smaller than -2 mA cm⁻²) at potentials more positive than ~ -1.8 V vs Ag/AgCl (Figure 3). Comparing the performance under Ar between Pb and a Pt wire working electrode, the significantly more cathodic onset potential for Pb indicates that hydrogen evolution is strongly suppressed on a Pb cathode even under acidic conditions. Under active CO₂ bubbling, a plateau in the current density was observed between -1.4 to -1.75 V vs Ag/AgCl, followed by an exponential increase in cathodic current associated with the beginning of the CO₂ reduction reaction.

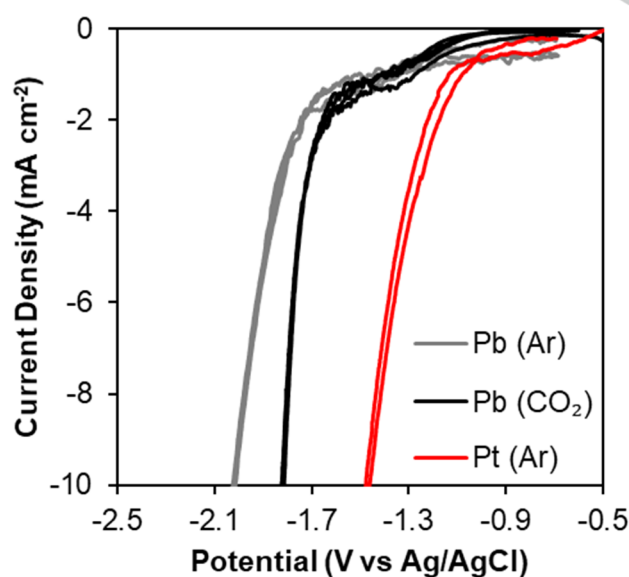


Figure 3. Electrochemical current density versus potential behavior at 50 mV s⁻¹ for a Pb or Pt wire in saturated KCl, pH ~ 1.5 methanol catholyte and 3 mM HCl under Ar or CO₂, 56 mM KCl in water anolyte separated by a Nafion membrane.

pH Dependence. The relative protonation/deprotonation of formic acid, the esterification of formic acid with methanol, and the rate of the electrochemical hydrogen evolution reaction (HER) are all strongly dependent on pH. To elucidate the effect of pH on these parameters and the corresponding CO₂ reduction product distribution, chronoamperometric measurements were conducted on the Pb cathode at -1.85 V vs Ag/AgCl for 30 min in dual methanol/water electrolyte systems across a range of pH values. As shown in Figure 4, the faradaic efficiency was strongly influenced by the initial pH. At higher pH values (> 4), hydrogen evolution was suppressed by the low proton concentration and nearly all of the CO₂ reduction product was the deprotonated formate, HCOO⁻. At an initial catholyte pH of 1, however, nearly all the CO₂ reduction product was methyl formate, HCOOCH₃, reaching a faradaic efficiency of ~ 60%. Decreasing the initial catholyte pH to 0 led to a concomitant decrease in the methyl formate faradaic efficiency to ~ 47%. This decrease in methyl formate FE was attributed to an increase in the HER partial current density with increased H⁺ concentration, supported by a notable increase in the total current density measured at pH 0 relative to pH 1 (Figure S5). A further decrease of the pH to -0.3 led to a dramatic increase in current density by an order of magnitude and total suppression of CO₂ reduction as HER became the dominant reaction pathway (Figure 4). Considering the requirement for acidic conditions to produce methyl formate, the stability of Pb at low pH under reductive potentials was another motivating factor in the choice of this metal as the electrocatalyst,^[21] and this stability is highlighted by low Pb concentrations in catholyte samples listed in Table S4 of the supplemental information.

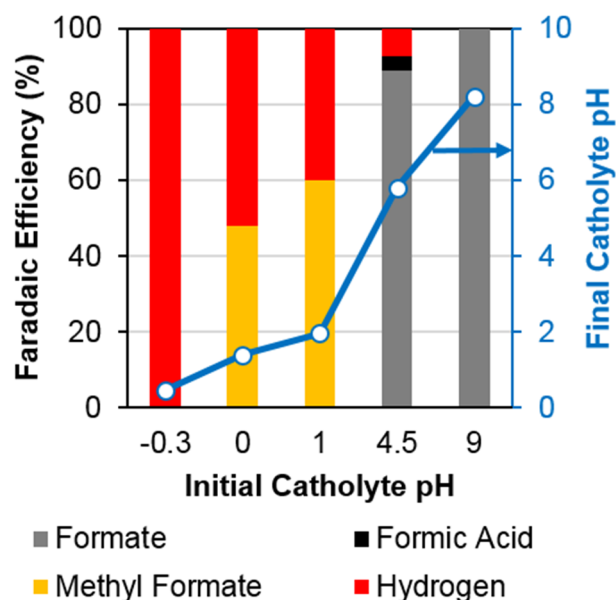


Figure 4. Faradaic efficiency versus initial catholyte pH for a Pb wire held at -1.85 V vs Ag/AgCl for 30 min in KCl-saturated methanol catholyte adjusted to different pH values with HCl (or 0.3 M KOH/CO₂ in methanol for pH 9) with 56 mM KCl in water anolyte. The blue curve corresponds to the measured catholyte pH at the end of the 30 min experiment.

The total CO₂ reduction product faradaic efficiency depends on the competing HER rate and the current density and mass flux of CO₂ to the electrode. Among the liquid products, however, the selectivity relationship between formate, formic acid, and methyl formate was controlled by the pH of the catholyte. HCOOH and

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HCOO⁻ interconvert with an aqueous pK_a of 3.745^[22] and an estimated methanolic pK_a of around 8.^[23] Figure 5 shows the percentage of the CO₂ reduction liquid product in the form of methyl formate as a function of the final pH condition measured in the catholyte for > 50 electrolysis experiments under a range of applied potentials and times. The catholyte at these conditions was measured to be 8 – 15% water in methanol due to water crossover from the anolyte. The NMR peak chemical shift for HCOOH/HCOO⁻, in which the position indicates the degree of ionization, is also plotted in Figure 5 and shows sigmoidal behavior of the chemical shift with pH.^[24] Based on this data, the pK_a of formic acid in methanol saturated with KCl and CO₂ at this water content can be estimated to be around 5. At pH values less than 3.2, no formate was ever detected based on the measured chemical shift peak position.

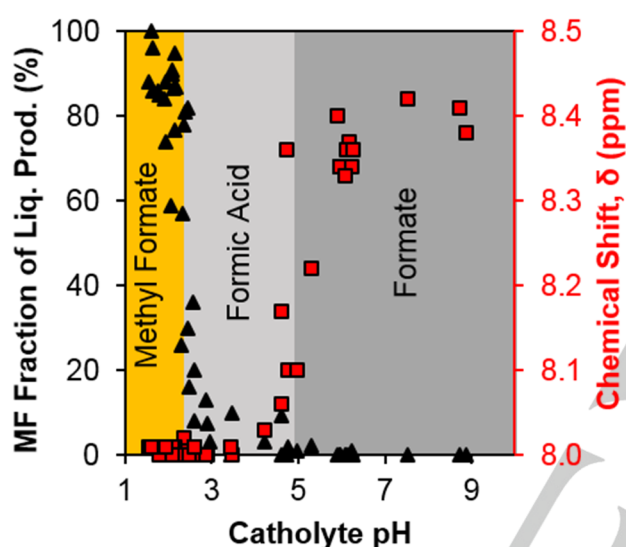


Figure 5. Conversion of the CO₂ reduction liquid product to methyl formate (black triangles) and measured NMR peak chemical shift (red squares) as a function of the final pH value in the saturated KCl in CH₃OH catholyte. The color-coded regions correspond to the dominant liquid product: methyl formate (yellow), formic acid (FA, light grey), and formate (dark grey).

The conversion between formic acid and methyl formate also demonstrated a strong pH dependence. From control experiments, a stock solution of formic acid in pure methanol converted to a few percent methyl formate over a couple days. However, with the addition of HCl to the methanol, the formic acid rapidly converted to methyl formate. Figure 5 (black triangles) shows the percent conversion of formic acid to methyl formate across a range of electrolysis experiments using an acidic methanol-catholyte/water-anolyte. Quantifiable methyl formate detection began at a catholyte pH less than 4, which is close to the threshold pH value where the protonated state of formic acid is dominant over the deprotonated formate. A greater fraction of methyl formate was observed with decreasing catholyte pH. This result is consistent with the requirement for protonated HCOOH to react with methanol via an esterification route to produce methyl formate (Figure 1). Thus, based on the pH of the catholyte, three regions can be identified in methanol for the preferred selectivity of the primary liquid products. Formate predominates at high (>5) pH, formic acid predominates at intermediate (3-5) pH, and methyl formate occurs at low (<3) pH.

Notably, the pH dependence of the liquid product distribution makes the formation of pH gradients across the membrane during electrolysis a complicating factor in identifying conditions for optimal methyl formate production. At the anode, the oxygen evolution reaction (OER) releases H⁺ from H₂O, while at the cathode protons are consumed in the reduction of CO₂ to HCOOH and HCOOCH₃ (Figure 1). Therefore, unless H⁺ can be exchanged from the anode to the cathode at a rate to match the electrochemical reaction, a H⁺ gradient will develop and increase the pH at the cathode. The results in Figure 4 confirm that the catholyte pH increased over time, with no methyl formate observed after the pH increased beyond ~ 4.5. Longer electrolysis times and higher current densities thus led to lower selectivity towards methyl formate compared to formic acid or formate due to the concomitant decrease in the acidity of the catholyte. The catholyte pH increased as more charge passed through the cell, consistent with electrochemical consumption of protons at the cathode that are not being sufficiently replenished by protons released from the anodic reaction. The development of a pH gradient, even at fairly low initial pH conditions, was attributed primarily to competitive migration of H⁺ and K⁺ across the Nafion membrane. KCl was included in the system as a necessary supporting electrolyte to increase the methanol solution conductivity and decrease the ohmic overpotential losses in the cell to a tolerable level. Moreover, although K⁺ exchange with the ionomer decreases the Nafion ionic conductivity, in this case it has the added benefit of significantly decreasing the permeability of the membrane to methanol crossover, as has been previously reported in detail.^[25] Although sufficient concentration of an acid such as HCl, H₂SO₄, or H₃PO₄ in otherwise pure methanol/water electrolyte could minimize pH gradient formation across the membrane, in practice acid concentrations high enough for satisfactory solution conductivity led to >90% faradaic efficiency for hydrogen evolution due to the abundance of H⁺ ions (Figure 4).

Despite the decreased permeability of the Nafion membrane in the presence of K⁺ cations, some methanol/water exchange does occur during the experiment, with a water content of 8 – 15 vol% measured in the catholyte after two hours of CO₂ reduction in a closed H-cell system. The presence of water complicates the measured pH in methanol, as described in the SI. Furthermore, increased H₂O concentration in the pH 1 – 2 methanol solvent leads to progressively lower conversion of formic acid to methyl formate, which is clearly exhibited by the NMR spectra (Figure 6). At 10 vol% water in the methanol, 82% of the formic acid converted to methyl formate, which decreased to only 9% in 90 vol % water. This effect may be at least partially attributable to Le Chatelier's principle in which increased water concentration and decreased methanol concentration would drive the equilibrium away from methyl formate towards formic acid (Figure 1). Thus, in addition to a low pH, a low water content in the catholyte is also essential to maintaining a high CO₂ reduction selectivity to methyl formate.

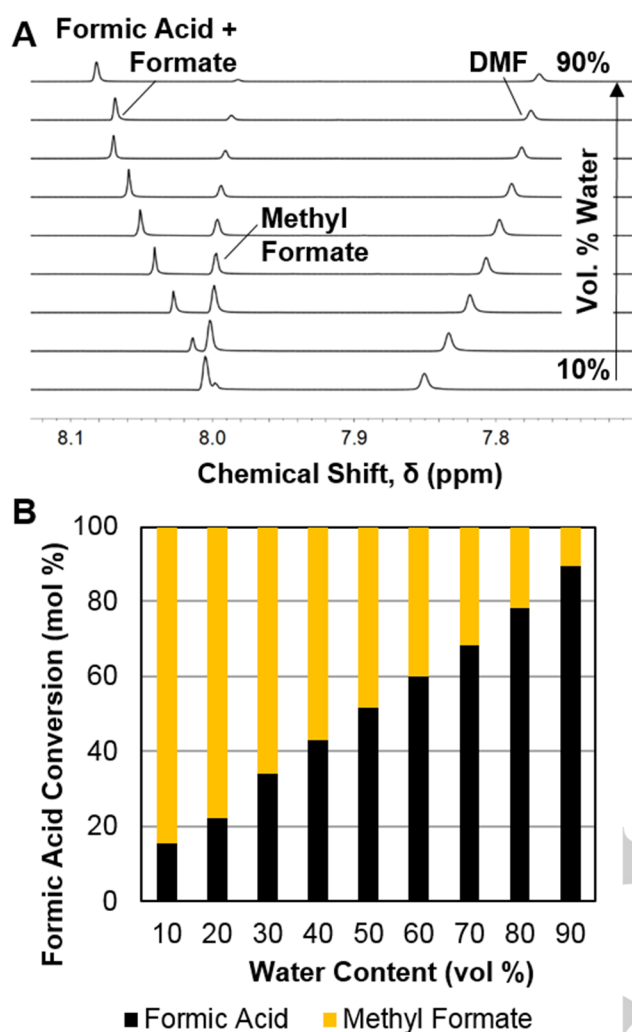


Figure 6. Effect of water in the catholyte. (A) NMR spectra and corresponding (B) molar percent conversion of formic acid to methyl formate for 100 mM formic acid dissolved in 3 mM HCl in methanol with increasing water content by volume %.

Potential Dependence. With an ideal starting pH of ~ 1.5 , further optimization for the high faradaic efficiency production of methyl formate was pursued by varying the applied potential to the Pb cathode from -1.6 V to -2.1 V vs Ag/AgCl as shown in Figure 7. The Pb wire was held at the specified potential for either 30 or 120 min, and the pH was measured before and after electrolysis. The pH values fluctuated during the course of the experiment due to a changing proton concentration from the faradaic reaction as well as the pH probe sensitivity to water content (see SI) as H_2O crossed to the catholyte during electrolysis (8–15 vol% H_2O over 120 min). In all cases, the magnitude of the current density increased at more negative, increasingly reductive potentials, as expected for the electrocatalyst J - E behavior (Figure 3) of a cathode following Butler-Volmer kinetics. A partial current density for CO_2 reduction products as high as -37 mA cm^{-2} was obtained at -2.1 V vs Ag/AgCl, which is relatively high considering the smooth Pb wire cathode has low surface roughness and was measured in an H-cell system rather than a high mass flux flow

cell electrolyzer. Furthermore, the total faradaic efficiency for CO_2 reduction products increased at more negative potentials, but the selectivity varied among the liquid products. Applying -1.85 V vs Ag/AgCl at the Pb wire for 30 min resulted in a modest quantity of methyl formate (40% FE) with a low fraction of formic acid (4% FE). At potentials more positive than -1.85 V vs Ag/AgCl, the charge passed in 30 min was insufficient to yield easily resolvable liquid products by NMR. Going more negative to -1.9 V, the selectivity for methyl formate increased to 58% FE, which further increased to as high as 75% FE at -2.0 V. After 30 min at -2.1 V, however, high faradaic efficiencies for formic acid (55% FE) and formate (41% FE) were measured with low methyl formate (2.5% FE). The sharp change in selectivity between -2.0 to -2.1 V vs Ag/AgCl after 30 min was attributed to the notable difference in the final catholyte pH, which markedly increased to pH ~ 5 when held at -2.1 V. The resulting balance between formate and formic acid with little methyl formate is consistent with the formic acid equilibrium observed in Figure 5 at pH 5. The stronger catholyte pH increase at -2.1 V, in turn, is due to the significantly increased current density at this potential (Figure 7A) which results in a faster rate of proton consumption at the cathode.

To further explore the transient behavior of the product distribution, faradaic efficiencies were also determined as a function of applied bias after 120 min (Figure 7D). Though not included on the plot, after two hours a small but consistent amount of CO was also detected at all the measured potentials (0.9–1.5% FE). A low overall current density of ~ 2 mA cm^{-2} was observed at -1.6 and -1.7 V, corresponding to the low current density plateau evident in the J - E behavior of the Pb wire (Figure 3). Over two hours at these lower potentials, a small amount of liquid product formic acid and methyl formate was detected, but the large majority of the charge passed was directed to hydrogen formation ($> 80\%$). Similar to the trends at 30 min, more negative potentials led to increased current density and selectivity towards CO_2 -derived products. H_2 was decreased from 49% FE at -1.8 V vs Ag/AgCl to 35% at -1.9 V to only 15% at -2.0 V. The change in hydrogen selectivity corresponded to a sharp increase in the partial current density for CO_2 reduction products while the partial current density of H_2 formation did not significantly change (Figure 7C). After 120 min, the highest methyl formate selectivity measured was 25% FE at -1.8 V vs Ag/AgCl. The CO_2 -derived product balance shifted away from methyl formate towards formic acid at more negative potentials, with a formic acid FE of 71% compared to only 4% FE for methyl formate at -2.0 V. This result is in stark contrast to the 12% FE formic acid, 75% FE methyl formate observed after 30 min at -2.0 V vs Ag/AgCl (Figure 7B).

The marked change in the product distribution with time can again be primarily attributed to pH effects. After 120 min at -2.0 V, for instance, the Pb wire passed more than four times the charge passed after only 30 min, leading to higher H^+ consumption and a correspondingly higher final catholyte pH. After 30 min at -2.0 V, the catholyte had pH 2.2 which would be predicted to give an equilibrium ratio of ~ 3 :1 methyl formate to formic acid according to Figure 5 and is consistent with the 75% FE methyl formate to 12% FE formic acid measured. In contrast, the greater charge passed after 120 min at -2.0 V resulted in a final catholyte pH of 3.7, which Figure 5 suggests would lead to majority formic acid

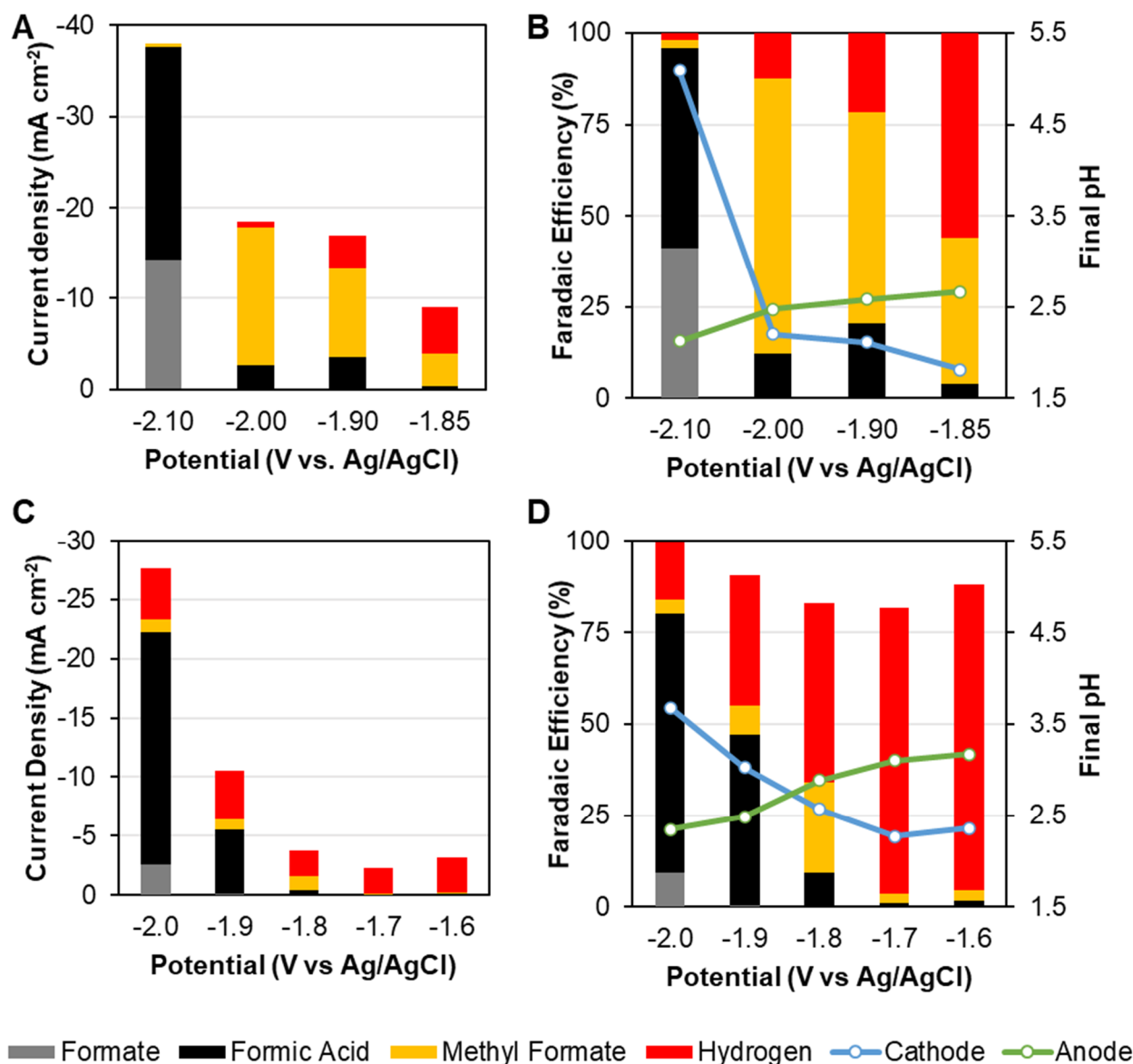


Figure 7. Electrochemical performance and product distribution data for CO₂ reduction at a Pb wire in saturated KCl, methanol catholyte with an initial pH ~1.5 and 56 mM KCl, 3 mM HCl in water anolyte. (A, C) Average partial current densities versus applied potential and (B, D) faradaic efficiency and corresponding final catholyte/anolyte pH (blue/green curves) versus applied potential. Product concentrations were measured after potentiostatic operation for (A, B) 30 min and (C, D) 120 min.

with a low conversion to methyl formate (<10%) and the onset of low levels of deprotonated formate. The chronoamperometric electrolysis results are in strong agreement, yielding 71% FE formic acid, 4% FE methyl formate, and 12% FE formate. Thus, maintaining a catholyte pH < 2.5 can be deemed a critical factor to achieving high selectivity of CO₂ electroreduction with methanol to methyl formate. Notably, while the aqueous anolyte pH changed over time as well, decreasing with higher charge passed, the magnitude of the pH shift was less than at the catholyte. This trend can be attributed to the logarithmic dependence of pH on proton concentration, meaning that an acidic pH value requires a greater concentration change to decrease than to increase, as well as the greater sensitivity of the methanol catholyte pH to low levels of water crossover.

While the CO₂ reduction liquid product selectivity can be attributed to the effect of the catholyte pH, the reason for the observed trend in H₂ formation is less clear. The rate of hydrogen evolution would generally be expected to increase with increasing H⁺ concentration, a trend which was indeed observed in this system as a function of pH when controlling for the other system variables (Figure 4). However, at a consistent initial pH with a fresh Pb working electrode, the H₂ faradaic efficiency steadily increased throughout the electrolysis as shown in Figure 8 despite simultaneously increasing pH at the cathode. At -1.8 to -2.0 V vs Ag/AgCl, the change in H₂ FE was modest, increasing by 10 - 30% FE over two hours. At -2.1 V vs Ag/AgCl, the hydrogen FE increased dramatically from 7% to 78% over two hours. Counterintuitively then, HER was increasingly promoted during the electrolysis despite the decreasing concentration of H⁺ ions at

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the cathode as reflected by the increasing catholyte pH. The exact reason for the increased H₂ FE with time is not totally clear at present, but we speculate that it is related to the observed formation of a brittle black layer on the Pb wire cathode during electrolysis. The film surface, which is noticeably rougher than the pristine Pb wire (Figure S7), may be more selective for HER than Pb, leading to increasing H₂ FE as the film forms and increases in surface area during the experiment. This type of phenomena has been seen previously for the deactivation of CO₂ reduction electrocatalysts like Ag and Cu as deposited contaminants and graphitic carbon on the surface shifted the selectivity toward hydrogen.^[26] Selectivity towards hydrogen has also been shown to increase on Pb cathodes due to slow reduction of a meta-stable surface oxide layer.^[27] Preliminary SEM and XPS surface characterization of the black film is shown in Figure S6 of the SI.

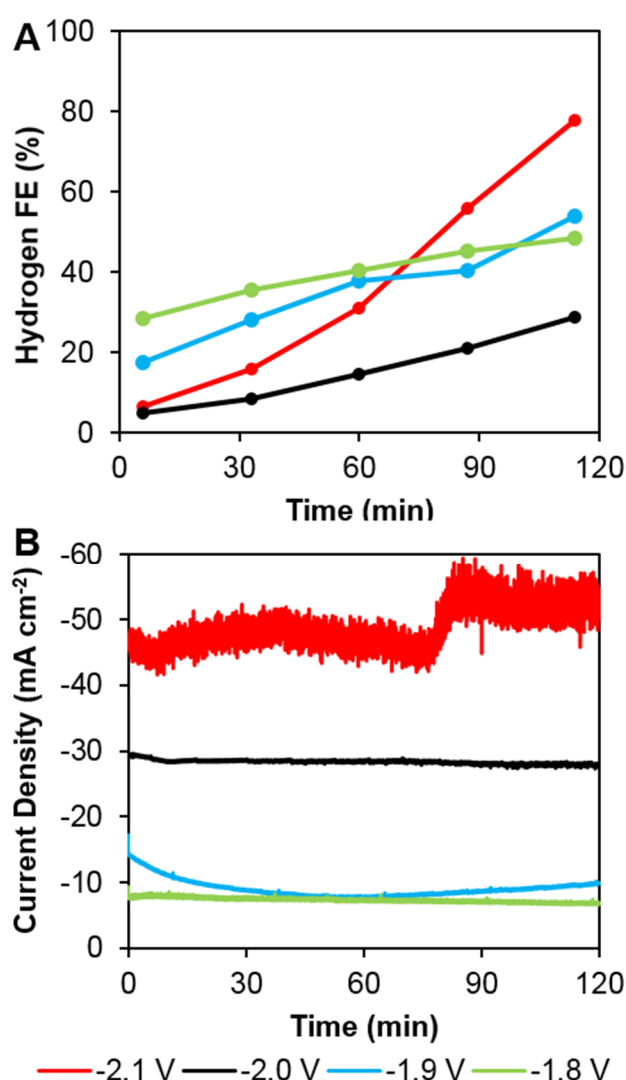


Figure 8. (A) Faradaic efficiency (FE) for hydrogen and (B) corresponding total current density versus time at a Pb wire cathode with CO₂ bubbling in saturated KCl, methanol catholyte with an initial pH ~1.5 and aqueous 56 mM KCl, 3 mM HCl anolyte. The legend shows the applied bias to the Pb electrode, V vs Ag/AgCl in each case.

Conclusion

CO₂ reduction in acidic methanol using a Pb cathode was investigated with a focus on determining optimal conditions for the production of methyl formate. To minimize methanol decomposition at the anode, a dual electrolyte system was employed with methanol catholyte separated from aqueous anolyte across an ion exchange membrane. The pH of the catholyte was determined to play a critical role in the selectivity among the CO₂ reduction liquid products based on both the pK_a of formic acid and the acid-catalyzed esterification of methanol and protonated formic acid to produce methyl formate. The applied bias was an important factor as well, with potentials negative of -1.8 V vs Ag/AgCl leading to increased CO₂ reduction faradaic efficiency to liquid products. High selectivity towards methyl formate was observed when the methanol catholyte pH was maintained below 2.5, reaching as high as 75% FE to methyl formate at -2.0 V vs Ag/AgCl. Increasing catholyte pH at longer electrolysis times, however, favored a shift towards formic acid and eventually formate production. In addition, the in-situ formation of a black surface layer during electrolysis coincided with a gradual increase in the rate of the competing hydrogen evolution reaction.

The results indicate that an electrolyzer capable of > 85% faradaic efficiency to methyl formate is possible with further optimization of the supporting electrolyte and cell design. Furthermore, the partial current density observed for CO₂ reduction products reached high values for H-cell measurements (-37 mA cm⁻²). The CO₂ reduction reactivity was not highly sensitive to water, permitting the use of an aqueous anolyte, but the sensitivity of the simultaneous esterification reaction necessitates minimal water crossover to the cathode to promote high methyl formate selectivity. Thus, the sustainable water oxidation half-reaction can be coupled to CO₂ reduction with methanol/formic acid esterification to provide the easily purified volatile product methyl formate. The process demonstrates the in-situ synthesis of a CO₂ reduction product not observed in aqueous electrolysis and highlights a pathway for similar routes to incorporate intermediate species with waste CO₂ to value-added chemicals. Future efforts to stabilize methyl formate production will focus on strategies to maintain a low catholyte pH, including the addition of buffer species, composite membranes to decrease water crossover, elimination of chloride in the anolyte to prevent anodic chlorine production, and the isolation of supporting electrolyte K⁺ cations at the cathode to promote proton migration from the anode.^[28]

Experimental Section

Electrochemical Measurements. All experiments used Pb wire (99.995%, 0.5 mm diameter, BeanTown Chemical) working electrodes with the Pb soldered to a copper wire that was encased in a glass tube and sealed using Loctite EA9460 epoxy. The exposed Pb wire was cut to a length of 4 cm and mechanically polished until shiny. A fresh electrode was used for each electrochemical experiment. Electrochemical experiments were performed in a custom two-chamber glass H-cell (Figure 1). A polytetrafluoroethylene ionomer sheet, Nafion 115 (Fuelcellstore.com), was cut to 4 x 4 cm, hydrated with deionized water, and used as a proton exchange membrane between the cell chambers. The cathode side of the membrane was patted dry prior to assembly. The cathode chamber contained the Pb

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working electrode and Ag/AgCl (1 M KCl) reference electrode, while the anode chamber contained a Pt mesh counter electrode. Unless stated otherwise, the cathode was initially filled with 25 mL of methanol (VWR, 99%) saturated with KCl (~ 56 mM) and the anode was filled with 25 mL of 56 mM KCl in 18 M Ω -cm water. For the studies of potential dependence, the catholyte had an initial pH ~ 1.5 derived from equilibration of the electrolyte with the Nafion membrane and estimated to be equivalent to 3 mM HCl (see SI for discussion of pH in methanol/water mixtures). The pH values were measured using a Laqua glass body pH probe filled with methanol which was saturated in KCl, and the probe was standardized using aqueous buffers. An MKS mass flow controller was used to flow 20 sccm of CO₂ or Ar (both 99.99%) pre-saturated with methanol through a medium porosity glass gas diffuser into the cathode in the vicinity of the Pb working electrode. The electrodes, gas diffuser, and head space exhaust were sealed in place by an air-tight cell cap (Pine Instrument Company). Either a BioLogic SP-200 or a Metrohm PGSTAT100N potentiostat with electrochemical impedance spectroscopy (EIS) were used for all measurements. Potentiostatic EIS measurements were performed before every CO₂ reduction experiment to determine the uncompensated solution resistance, and the potentiostat subsequently compensated for 85% of this resistance during electrolysis.

Product Analysis. CO₂ reduction products were measured by gas chromatography (GC, SRI 8610) and nuclear magnetic resonance (NMR, Agilent VNMR5 700 MHz) spectroscopy for the gas and liquid products, respectively. The cathode gas headspace was analyzed by in-line GC measurements with a thermal conductivity detector (TCD) and flame ionization detector (FID) which sampled 1 mL at an exhaust flow rate of 20 sccm every 27 min, giving 5 data points in a two-hour experiment. H₂ and CO were quantified based on calibration gases, and no other gaseous products were detected during the experiments. Liquid products were analyzed by ¹H NMR using the following sample preparation: 600 μ L of electrolyte solution and 200 μ L d₆-DMSO (Cambridge Isotopes, 99.9%) containing a DMF internal standard (to a final concentration of 3 mM DMF) were mixed until homogeneous. The sample was then analyzed in an NMR equipped with an HCN cryoprobe using a two-signal solvent suppression pulse sequence, and chemical shift values were referenced to residual DMSO at 2.50 ppm. The integration values of formate (chemical shift, δ ~ 8.42 ppm), formic acid (δ ~ 7.99 ppm), and methyl formate (δ ~ 8.00 ppm with a 3H singlet at 3.60 ppm) were measured against the DMF internal standard using a calibration curve. The peaks for the formyl C-H of formic acid and methyl formate often overlapped in the spectra, so the ratio of the two was determined by dividing one third of the integration of the peak at δ ~ 3.60 ppm by the integration at 8.00 ppm (see SI). Faradaic efficiency was calculated for chronoamperometric measurements by determining the charge required to produce the measured product concentration and dividing by the total charge passed during the time the sample underwent electrolysis as determined by the integration from the potentiostat.

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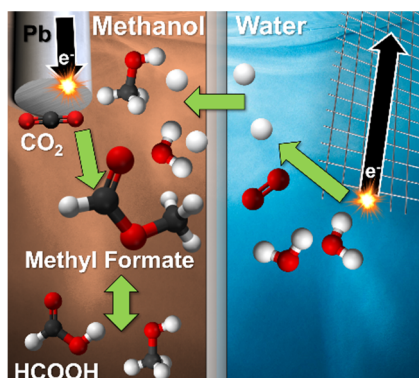
Prior work to identify species generated in a methanol electrolyte is based upon work supported by the U.S. National Science Foundation under Award Number CHE-1955268. The authors also acknowledge support from the Conn Center for Renewable Energy Research at the University of Louisville.

Keywords: methyl formate • CO₂ reduction • Pb catalyst • electrochemistry • pH

- [1] a) M. R. Singh, E. L. Clark, A. T. Bell, *PNAS* **2015**, *112*, E6111-E6118; b) National Research Council, *Limiting the Magnitude of Future Climate Change*, The National Academies Press, Washington, DC, **2010**; c) National Research Council, *America's Climate Choices*, The National Academies Press, Washington, DC, **2011**.
- [2] R. I. Masel, Z. Liu, H. Yang, J. J. Kaczur, D. Carrillo, S. Ren, D. Salvatore, C. P. Berlinguette, *Nat. Nanotechnol.* **2021**, *16*, 118-128.
- [3] a) J. Qiao, Y. Liu, F. Hong, J. Zhang, *Chem. Soc. Rev.* **2014**, *43*, 631-675; b) B. Kumar, J. P. Brian, V. Atla, S. Kumari, K. A. Bertram, R. T. White, J. Spurgeon, *Catal. Today* **2016**, *270*, 19-30; c) Y. J. Sa, C. W. Lee, S. Y. Lee, J. Na, U. Lee, Y. J. Hwang, *Chem. Soc. Rev.* **2020**, *49*, 6632-6665.
- [4] a) P. G. T. Fogg, Alcohols, in *Carbon Dioxide in Non-Aqueous Solvents At Pressures Less Than 200 kPa* (Ed.: P. G. T. Fogg), Pergamon, Amsterdam, **1992**, pp. 128-177; b) J. J. Carroll, J. D. Slupsky, A. E. Mather, *J. Phys. Chem. Ref. Data* **1991**, *20*, 1201-1209.
- [5] a) National Energy Technology Laboratory, "Rectisol", can be found under <https://netl.doe.gov/research/coal/energy-systems/gasification/gasification/rectisol>, **2021**; b) G. Hochgesand, *Ind. Eng. Chem.* **1970**, *62*, 37-43.
- [6] K. Z. House, A. C. Baclig, M. Ranjan, E. A. van Nierop, J. Wilcox, H. J. Herzog, *PNAS* **2011**, *108*, 20428-20433.
- [7] M. Muruganathan, Kaneco, S., Katsumata, H., Suzuki, T. and Kumaravel, M., Electrocatalytic Reduction of CO₂ in Methanol Medium, in *Green Carbon Dioxide* (Ed.: G. Centi, S. Perathoner), Wiley, **2014**, pp. 191-214.
- [8] a) A. Naitoh, K. Ohta, T. Mizuno, H. Yoshida, M. Sakai, H. Noda, *Electrochim. Acta* **1993**, *38*, 2177-2179; b) T. Saeki, K. Hashimoto, N. Kimura, K. Omata, A. Fujishima, *J. Electroanal. Chem.* **1996**, *404*, 299-302.
- [9] a) T. Saeki, K. Hashimoto, A. Fujishima, N. Kimura, K. Omata, *J. Phys. Chem.* **1995**, *99*, 8440-8446; b) T. Saeki, K. Hashimoto, N. Kimura, K. Omata, A. Fujishima, *Chem. Lett.* **1995**, 361-362; c) T. Yamamoto, H. Katsumata, T. Suzuki, S. Kaneco, *ECS Trans.* **2017**, *75*, 31-37; d) T. V. Magdesieva, I. V. Zhukov, D. N. Kravchuk, O. A. Semenikhin, L. G. Tomilova, K. P. Butin, *Russ. Chem. Bull.* **2002**, *51*, 805-812.
- [10] a) C. A. Huff, M. S. Sanford, *J. Am. Chem. Soc.* **2011**, *133*, 18122-18125; b) P. G. Jessop, T. Ikariya, R. Noyori, *Chem. Rev.* **1995**, *95*, 259-272; c) M. Yadav, J. C. Linehan, A. J. Karkamkar, E. van der Eide, D. J. Heldebrant, *Inorg. Chem.* **2014**, *53*, 9849-9854; d) I. Omae, *Catal. Today* **2006**, *115*, 33-52.
- [11] T. Saeki, K. Hashimoto, Y. Noguchi, K. Omata, A. Fujishima, *J. Electrochem. Soc.* **1994**, *141*, L130-L132.
- [12] J. Hietala, A. Vuori, P. Johnsson, I. Pollari, W. Reutemann, H. Kieczka, Formic Acid, in *Ullmann's Encyclopedia of Industrial Chemistry* (Ed.), Wiley-VCH, **2016**, pp. 1-22.
- [13] M. S. Yalfani, G. Lolli, T. E. Mueller, A. Wolf, L. Mleccko, *ChemSusChem* **2015**, *8*, 443-447.
- [14] V. Iablokov, N. Kruse, *ChemCatChem* **2019**, *11*, 1200-1204.
- [15] a) J. Chen, S. Qin, G. Song, T. Xiang, F. Xin, X. Yin, *Dalton Trans.* **2013**, *42*, 15133-15138; b) A. A. Abd-El-Latif, H. Baltruschat, *J. Electroanal. Chem.* **2011**, *662*, 204-212.

- [16] M. N. Mahmood, D. Masheder, C. J. Harty, *J. Appl. Electrochem.* **1987**, *17*, 1159-1170.
- [17] J. Reijenga, A. van Hoof, A. van Loon, B. Teunissen, *Anal. Chem. Insights* **2013**, *8*, 53-71.
- [18] R. Kishi, H. Ogihara, M. Yoshida-Hirahara, K. Shibamura, I. Yamanaka, H. Kurokawa, *ACS Sustainable Chemistry & Engineering* **2020**, *8*, 11532-11540.
- [19] X. Li, A. Faghri, *J. Power Sources* **2013**, *226*, 223-240.
- [20] S. Kaneco, R. Iwao, K. Iiba, K. Ohta, T. Mizuno, *Energy* **1998**, *23*, 1107-1112.
- [21] M. Pourbaix, *Atlas of Electrochemical Equilibria in Aqueous Solution*, Pergamon Press, Oxford, **1966**.
- [22] A. E. Martell, R. M. Smith, *Critical Stability Constants: Second Supplement*, 1 ed., Springer, US, **1989**.
- [23] F. Rived, M. Roses, E. Bosch, *Anal. Chim. Acta* **1998**, *374*, 309-324.
- [24] T. Rodima, V. Maemets, I. Koppel, *J. Chem. Soc. Perkin Trans.* **2000**, 2637-2644.
- [25] V. M. Barragan, C. Ruiz-Bauza, J. P. G. Villaluenga, B. Seoane, *J. Power Sources* **2004**, *130*, 22-29.
- [26] E. L. Clark, J. Resasco, A. Landers, J. Lin, L. T. Chung, A. Walton, C. Hahn, T. F. Jaramillo, A. T. Bell, *ACS Catal.* **2018**, *8*, 6560-6570.
- [27] a) M. J. W. Blom, V. Smulders, W. P. M. van Swaaij, S. R. A. Kersten, G. Mul, *Applied Catalysis B: Environmental* **2020**, *268*, 118420; b) C. H. Lee, M. W. Kanan, *ACS Catal.* **2015**, *5*, 465-469; c) R. L. Machunda, J. Lee, J. Lee, *Surf. Interface Anal.* **2010**, *42*, 564-567.
- [28] J. E. Huang, F. Li, A. Ozden, A. S. Rasouli, F. P. G. de Arquer, S. Liu, S. Zhang, M. Luo, X. Wang, Y. Lum, Y. Xu, K. Bertens, R. K. Miao, C.-T. Dinh, D. Sinton, E. H. Sargent, *Science* **2021**, *372*, 1074-1078.

Entry for the Table of Contents



An electrolytic cell with acidic methanol catholyte and an aqueous anolyte separated by a proton exchange membrane is utilized to produce a methanol unique C₂ product, methyl formate, from CO₂ on a Pb electrode. High selectivity (~75% FE) for methyl formate is attainable so long as the catholyte pH remains low.

Twitter for C. Grapperhaus: @UofL_DrG