Development of a continuous reactor for the electro-reduction of carbon dioxide to formate – Part 1: Process variables

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Abstract

This paper reports an experimental investigation into the effects of five process variables on the performance of a bench-scale continuous electrochemical reactor used in the reduction of CO_2 to potassium formate, and interprets the data in terms of reactor engineering for a (speculative) industrial process for electro-reduction of CO_2. The process variables: temperature, catholyte species, catholyte conductivity, cathode specific surface area and cathode thickness were studied, along with CO_2 pressure and current density, in a set of factorial and parametric experiments aimed to unravel their main effects and interactions. These variables showed complex interdependent effects on the reactor performance, as measured by the current efficiency and specific energy for generation of formate (HCO_2^-). The "best" result has a formate current efficiency of 86% at a superficial current density of 1.3 kA m^{-2}, with a product solution of 0.08 M $KHCO_2$ and specific electrochemical energy of 260 kWh per kmole formate. The combined results indicate good prospects for process optimization that could lead to development of an industrial scale reactor.

Nomenclature

C	catholyte composition
CE	current efficiency (dimensionless)
E	cathode potential (VSHE)
E_{cell}	full-cell operating voltage (absolute value) (V)
E^o	Standard equilibrium electrode potential (VSHE)
GDE	gas diffusion electrode
i	geometric (superficial) current density (kA m^{-2})
i_{max}	maximum geometric (superficial) current density (kA m^{-2})
Me	cathode material
P	CO_2 pressure (Bar(abs) or kPa(abs))
$P_{cathode}$	cathode side pressure (kPa (abs))
T	temperature (K)
t	operating time (h)
X_1, X_2, X_3	factorial variables defined in Tables 6, 9, 10, 13, 14, 16 and 17
y	volume fraction (i.e. mole fraction) in gas phase (dimensionless)
τ	thickness of 3D cathode (m)

1. Introduction

The electrochemical reduction of carbon dioxide on Cd, Hg, In, Pb, Sn and Zn cathodes produces formate/formic acid with high selectivity [1]. This process is of particular interest since it could both mitigate greenhouse gas emissions and utilize CO_2 as a carbon source for the manufacture of organic compounds. Among such compounds formic acid appears as an energy storage medium that is being considered both as a fuel for direct formic acid (DFA) fuel cells and as a source of H_2 for hydrogen fuel cells [2, 3]. Formic acid is now manufactured by thermo-chemical processes based on the carbonylation of methanol or sodium hydroxide and by the oxidation of hydrocarbons [4] all of which have negative environmental consequences.

There is a substantial literature on the electro-reduction of CO_2 to formate/formic acid, extending back to the 1870s [1]. Table 1 presents a summary of some representative results from such work published since 1970 [5–16]. As indicated in Table 1 all (published) work prior to 2004 was done in laboratory scale batch reactors [17] operating at currents from a few mA up to about 2 A. Most of this work was concerned with the

Table 1. Representative results of prior work on electro-reduction of CO_2 to formate/formic acid

Source	Cathode	Mode	Cathode area/(10^{-4}) m^2	Catholyte (aqueous solution)	Conditions				Variable	i_{max}/kA m^{-2}	CE at i_{max}/%
					P/Bar	T/K	pH	t/h			
Udupa et al. [5]	Hg/Cu [rotary cylinder]	Batch	39	Na_2SO_4, $NaHCO_3$	1	293[a]	7–9	6	i, t	0.5	33
Ryu et al. [6]	Hg [pool]	Batch	7	$NaHCO_3$, $NaHCO_2$	0.1–0.8	274–333	7[a]	?	i, P, T	0.01	98
Ito et al. [7]	Cd, In, Pb, Sn, Zn [sheet[a]]	Batch	5[a]	[Li, Na, K, Rb] CO_3, PO_4, SO_4	1[a]	298	6.8	0.3[a]	C, E, i, Me	0.2	75
Russell et al. [8]	Hg [pool]	Batch	5	$NaHCO_3$, $NaHCO_2$	1	298	6.8	?	E	0.01	100
Hori and Suzuki [9]	Hg [pool]	Batch	5	[Li, K, Na] HCO_3, PO_4, Cl, ClO_4, SO_4	1	298	2–7	1	C, E, pH	0.01	100
Kapusta and Hackerman [10]	Hg, In, Sn [sheet[a]]	Batch	1	KCl, $KHCO_3$	1	296	6.5	?	C, E, P	0.1	99
Mahmood et al. [11]	Pb, In, Sn [GDE]	Batch	3	Na_2SO_4, H_2SO_4	1	293	2	0.5	i, Me, pH	1.15	97
Todoroki et al. [12]	Hg, Pb, In [wire, shot]	Batch	0.2	$KHCO_3$	1–60	293	7[a]	?	E, i, Me, P	5.6	100
Mizuno et al. [13]	In, Pb, Sn [coil]	Batch	3	$KHCO_3$	10–50[a]	293–373	7[a]	?	P, Me, T	?	100
Koleli and Balun [14]	Pb [fixed bed]	Batch	2	K_2CO_3	1–50	293–353	?	0.5	E, Me, P, T	0.02[a]	88
Akahori et al. [15]	Pb [wire]	Cont	1	K_2HPO_4, H_3PO_4	1[a]	288	6	?	E_{cell}, τ	0.02	100
Li and Oloman [16]	Sn/Cu [mesh]	Cont	45	$KHCO_3$	0.2–1.2	300	7–8	2	i, Me, P, t	1.78	36

Batch = zero catholyte liquid flow (some had gas flow); Cont = continuous catholyte liquid flow; Cathode area = geometric (superficial) cathode area; Fixed bed = bed of particles; Other symbols are as defined in Nomenclature.
[a]Ambiguous or unspecified, but assumed or calculated from context of source article; ? = not specified in source article.

separate effects of variables in subsets from the group [C, E, i, Me, P, pH, T] on the reaction kinetics and mechanism, along with the selectivity for generation of formate/formic acid. This literature contains both complimentary and contradictory observations concerning the effects of the process variables in the electro-reduction of CO_2.

The consensus is that the primary electro-active species CO_2(aq) is reduced to formate/formic acid (reaction 1) in parallel with the reduction of water to hydrogen (reaction 2) and tertiary reactions that convert CO_2 to CO (reaction 3) plus traces of hydrocarbons [6, 9, 10]. Reaction 1 is considered a kinetically "slow" process, occurring at cathode potentials (depending on the CO_2 pressure, current density and catholyte pH) from about −0.8 to −1.8 VSHE, with over-potential ranging from about −0.4 to −1.4 V. The intrinsic kinetics of reaction 1 are said to be independent of pH (2 < pH < 8), but a pH above 6 can have a strong effect on the mass transfer limiting current for this reaction, as CO_2(aq) is depleted through the CO_2(aq)/HCO_3^-/CO_3^{2-} equilibria.

cathodes where reaction 1 is favored over reaction 2. The most studied of this group are Hg, In, Pb and Sn, but it is not clear which of these metals is best because their performance seems to depend on other variables such as CO_2 pressure, catholyte composition, potential and temperature, whose effects have not been isolated. Similar ambiguity exists with respect to the catholyte composition and pH. Most authors prefer $KHCO_3$ (ca. 0.5 M) with pH 6–8 but others have excellent results in Na_2SO_4 at pH 2 and some claim good current efficiency in a catholyte of K_2CO_3, whose normal pH would be near 12. This situation is clouded by the fact that many sources refer to "formic acid' as the reaction product at pH above 6, where HCO_2H (pK_a = 3.8 at 298 K) should not exist at significant concentration. Apart from the pH, the nature of the cation is considered to be important due to the effect of specific adsorption in shifting the cathode potential to more positive values that promote reaction 1 over reaction 2, in the sequence $Li^+ < Na^+ < K^+$ on Hg [9], although the reverse sequence is observed on an In cathode [7]. With respect to the electrolyte anions some authors imply a unique

Cathode:		E^oVSHE @ 298 K in alkaline conditions
1.	CO_2(aq) + H_2O + 2e$^-$ → $HCOO^-$ + OH^-	−1.02
2.	$2H_2O$ + 2e$^-$ → H_2 + 2OH^-	−0.83
3.	CO_2 + H_2O + 2e$^-$ → CO + 2OH^-	−0.94

Useful selectivity for formate/formic acid is obtained on a group of so-called "high hydrogen over-potential" cathodes where reaction 1 is favored over reaction 2.

role for carbonate/bicarbonate [7, 18] while others [9, 10] claim that among carbonate, phosphate, acetate and

borate the partial current for reaction 1 is independent of the buffer anion. Analogous cation and anion effects on reaction selectivity are observed in the electro-reduction of CO_2 to CO, alcohols and hydrocarbons on copper [19, 20].

The effect of pressure is relatively straightforward. Though some sources indicate that the reaction rate is nearly independent of CO_2 pressure [6] most who have studied this variable (up to 6000 kPa(abs)) show a strong positive effect of CO_2 pressure on the cathode potential and the partial current density for reaction 1, consistent with a reaction order of about one with respect to CO_2 concentration in the catholyte [12, 14, 21]. The effect of temperature is more problematic. One source [6] shows a 20-fold increase in current density as the temperature rises from 275 to 333 K, without comment on the selectivity. Another [14] shows a monotonic increase in formate current efficiency on Pb with increasing temperature (298–353 K), while a third [13] indicates a parabolic effect of temperature on a Pb cathode, together with monotonic decreases in efficiency on In and Sn over the range 293–373 K.

Increasing current density typically lowers the formate CE [5, 7] by an effect that may be attributed mainly to CO_2 concentration polarization. However some data on Sn [7], as well as results from experiments on Pb at 5000 kPa(abs) CO_2 pressure [14] imply a parabolic dependence of formate CE on current density with a maximum CE at about –1.5 VSHE.

Some of the conflicting observations outlined above may be caused by changes of the rate determining step in the intrinsic kinetics of reaction 1 that occur, for example, at about –0.8 V over-potential on Hg [6, 22]. However we note that the above referenced works were based almost exclusively on uni-variate experiments that did not engage interactions among the studied variables and that often implicitly discounted other variables that affect the process. These other variables include the operating time, conductivity, CO_2 solubility and formate concentration in the catholyte, etc. – and importantly the fluid dynamic factors that determine the mass transfer capacity of the cathode. The latter can be critical because the low solubility of CO_2 in aqueous electrolytes (< 70 mM at STP) means that reaction 1 is usually under a CO_2 mass transport constraint. Unrecorded details such as these may be partly responsible for apparent contradictions in the literature regarding the conditions for electro-reduction of CO_2 to formate/formic acid.

At the time of writing (Dec. 2005) only two articles have appeared that describe the electro-reduction of CO_2 in a continuous reactor. Akahori et al. [15], who are apparently the first to report continuous operation, used a lead wire bundle cathode in a flow-by reactor with a cation membrane separator. This reactor obtained a formate current efficiency near 100% with single-phase flow of a CO_2 saturated catholyte solution at 1.4 ml min^{-1} and current about 2 mA (0.02 kA m^{-2}). The second source is our recent communication [16], summarized below, that introduced the trickle-bed reactor for the electro-reduction of CO_2 and studied the separate and combined effects of three variables (i, P, t) on the formate CE.

From this summary of previous work, it is evident that some research on the electro-reduction of CO_2 ought to focus on engineering issues related to the development of a continuous electrochemical reactor (and process) for potential industrial application. Such a reactor would operate over thousands of hours with high current density and formate efficiency (e.g., > 1 kA m^{-2}, > 70%), low specific energy (e.g., < 500 kWh kmol^{-1} formate) and acceptable capital cost.

In a previous communication [16], we reported a preliminary investigation into the electro-reduction of CO_2 in a laboratory bench-scale continuous reactor with a flow-by 3D cathode of 30$^\#$ mesh tinned-copper of geometric area of 0.0045 m^2 (45 cm^2) operated at currents up to 8 A. That work reported superficial current densities from 0.22 to 1.78 kA m^{-2} (22–178 mA cm^{-2}) with corresponding formate current efficiencies from 86 to 36%. The present paper examines a more extensive range of process variables relevant to the development of a continuous reactor for the electro-reduction of CO_2 to formate. In a later submission, we will describe our work on scale-up of the reactor, aimed at a (speculative) industrial process for the electro-reduction of CO_2.

2. Experimental methods

The configuration of the single-cell electrochemical reactor and the schematic process flow diagram used here are those described in our previous communication [16]. Minor changes in the reactor components were made for the present work, as follows:

(1) In place of one layer of tinned-copper 30$^\#$ mesh, one to four layers of tinned-copper 30$^\#$ or 60$^\#$ mesh, were used to increase the thickness and electro-active area of the 3D cathode.
(2) The platinized titanium anode feeder plate was replaced with a stainless steel sheet and the polypropylene screen anode spacer was replaced by a 10 mesh stainless steel screen separated from the Nafion membrane by a thin 10 mesh PVC screen.

The configuration of the single-cell electrochemical reactor was as follows:

Anode side		Separator	Cathode side	

ss sheet + ss mesh + PVC screen + Nafion 117 + tcc mesh(s) + tcc sheet
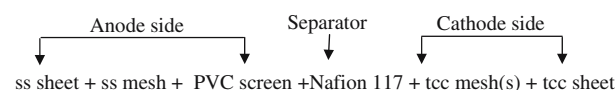
where "ss" = stainless steel and 'tcc' = tin coated copper. All the meshes, including ss mesh and tcc mesh(s), and the screen were impregnated with silicone on the margins for sealing. Table 2 lists the properties of both the 30$^\#$ and 60$^\#$ copper meshes (ARGUS Corp.,

Table 2. Properties of tinned-copper mesh[a]

Mesh	Mesh count per inch	Thickness/mm	Wire diameter/mm	Opening/mm	Open area/%	Specific surface/m^2 m^{-3}
Tin coated copper (tcc)	30	0.61	0.305	0.541	40.8	7000
Tin coated copper (tcc)	60	0.38	0.191	0.234	30.5	14,000

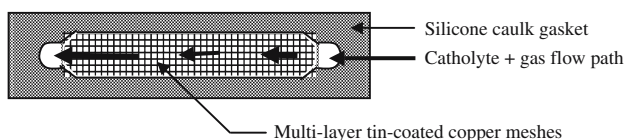[a]Thickness of tin coating = ca. 0.5 micron

*Fig. 1.* Multi-layer tin-coated copper mesh cathode.

USA) that were used as the substrate of the tinned-copper cathode.

The plating procedure for the tinned cathode was that described in the previous work. For multi-layer cathodes, the copper meshes were laid together, glued on the margins for sealing (as shown in Figure 1) and plated. Complete contact between layers was made by compression, to ensure sufficient electronic conductivity and uniform 2-phase flow distribution through the cathode.

In those experiments where temperature was investigated as a process variable pre-cooling or heating of both anolyte and catholyte was adopted to keep the reactor temperature at the desired levels. Considering the deterioration of the tinned copper cathode described previously [16], in the present work a new cathode was used for each run and the operating time of the reduction of CO_2 for every run was set at 10 min. Samples of the catholyte product were taken for analysis 10 and 12 min after initiating the current. The catholyte residence time in the reactor of a few seconds, followed by about 1 min in tubing prior to the sample point meant that, with the rate of degradation of the cathode, the sampling was done essentially at steady-state. No attempt was made to track the carbon balance in these runs. However, by accounting for [CO_2, CO] (gas phase) and [HCO_3^-, HCO_2^-] (liquid phase) our previous work [16] showed essentially 100% closure of the carbon balance under conditions similar to those used here.

3. Experimental design

Our previous communication [16] proposed a simplified model of the electro-reduction of CO_2 in an isothermal continuous reactor with a "trickle-bed" cathode and cation membrane separator, operating at steady-state. This model invokes the competing cathode reactions (1, 2) balanced by the anode reaction 4 (see below).

Anode: $E°$ VSHE @ 298 K
4. $O_2 + 4H^+ + 4e^- \leftarrow 4OH^-$ +0.41
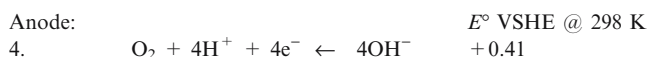
Reaction 1 proceeds under a CO_2 mass transport constraint while the rate of the thermodynamically favored and kinetically controlled reaction 2 depends largely on the pH and the "hydrogen over-potential" of the cathode. The model and associated experimental data show that the formate current efficiency in such a continuous reactor depends on effects and interactions of many process variables, the most salient of which are listed in Table 3.

Although not explicit in the model, the kinetics of reactions 1 and 2 are determined jointly by the cathode material and catholyte composition.

As indicated above, other work on the electro-reduction of CO_2 to formate/formic acid has been carried out almost exclusively in batch reactors (i.e. "cells"). That work has shown the feasibility of CO_2 reduction and shed light on some of the major variables, but its results are limited in two respects:

(a) it used uni-variate parametric experiments that do not capture the (sometimes critical) effects of interactions among the variables.
(b) it did not deal with factors that relate to engineering a continuous reactor, such as fluid flow rates, reactant conversion, pressure drop, temperature rise by Joule heating, ionic conductivity, current distribution and reactor voltage.

Our work aims to embrace most of the variables listed in Table 3 at an elementary level, with both factorial and parametric experiments. These experiments are designed to see the main effects and interactions of the variables, to support the reactor model and scale-up to a (speculative) industrial process.

In the preliminary work [16], we investigated the effects of three process variables: current (1–8 A), gas phase CO_2 concentration (16–100 vol%) and operating time (10–180 min) in operation of the 0.0045 m^2 bench-scale reactor near ambient conditions (115 kPa(abs), 300 K). That work also observed the effect of cathode material (Cu and Sn) on the competition between reactions 1 and 2. The present work investigates the further five variables listed in Table 4. Details of the individual experimental designs are given under Section 4.

Table 3. Major process variables in electro-reduction of CO_2 in a continuous reactor

1	3D cathode specific surface	8	Formate concentration
2	3D cathode thickness	9	Gas load[a]
3	Cathode material	10	Liquid load[a]
4	Catholyte composition	11	Operating time.
5	Catholyte conductivity	12	Superficial current density
6	Catholyte pH	13	Separator properties
7	CO_2 pressure	14	Temperature

[a]Fluid load = mass flow rate/superficial flow area.

Table 4. Experimental variables in the present work

Variable	Units	Range
Temperature	K	288–328
Catholyte composition	–	(K^+, Na^+), $(Cl^-, CO_3^{-2}, HCO_3^-)$
Catholyte ionic conductivity	$S\ m^{-1}$	1.1–19.4
3D cathode thickness	mm	0.4–1.9 (1–4 mesh layers)
3D cathode specific surface	$m^2\ m^{-3}$	7000–14,000 ($30^\#$–$60^\#$)

Table 5. Typical changes along reactor length at 6 A

Condition [in cathode]	Unit	In	Out
Total pressure	kPa(abs)	120	101
Temperature	K	286	288
Formate concentration	M	0	0.08
Liquid flow	$ml\ min^{-1}$	20.0	20.1
Gas flow	$ml\ min^{-1}$	165	150
pH	–	7.5	8.5
CO_2 pressure	kPa(abs)	118	70
HCO_3^- concentration	M	0.45	0.60
Cathode residence time	s	L^a = 5, G^b = 0.5	

[a] L = liquid, [b] G = gas.

The trickle-bed reactor used here operates in nearly plug flow [17, 23] with consequent changes in process conditions along the reactor length. Table 5 summarizes typical values of these changes in the cathode at 6 A, which is the maximum current used in the present work. There are also gradients in local cathode potential and current density, but these variations were not measured and are not described here.

Unless otherwise indicated all cathode conditions (except pH and temperature) in the experimental work reported below are those at the reactor inlet. The pressure is the total pressure at the cathode inlet and the pH and temperature are the catholyte outlet values. The effects of the cathode fluid loads and total pressure will be presented along with reactor scale-up issues in a subsequent communication.

Anolyte composition and flow were fixed at 1 M KOH, 30 $ml\ min^{-1}$ while the anolyte temperature was varied from about 285–335 K to control the catholyte temperature, as required by the experimental design.

4. Results and discussion

4.1. *Temperature (current and CO_2 pressure)*

Temperature is one of the most important variables with respect to engineering industrial scale electrochemical reactors operating at current densities of 1–5 kA m^{-2}, in which the energy balance can drive the electrolyte temperature up to the boiling point. Increasing temperature has three primary effects on reactor performance in CO_2 reduction:

(i) Increase of the exchange current densities of competing reactions by a ratio that depends on the relative activation energies.
(ii) Decrease in the solubility of CO_2 in the catholyte.
(iii) Increase in the mass transfer coefficient of CO_2 to the cathode surface.

Secondary effects of increasing temperature include: changes in the pressure gradient, liquid hold-up, electrolyte ionic conductivity, reactor voltage, current and potential distribution, etc. Temperature is thus engaged in complex interactions with current density and CO_2 pressure that determine the formate current efficiency and specific energy consumption. The two level, three factor (2^3) factorial experiment Set 1, summarized in Table 6 was employed to examine some of these effects. To separate the effect of temperature on the intrinsic kinetics from that on the solubility of CO_2 the experiment was designed so the solubility of CO_2 in water at the high temperature and high CO_2 pressure (328 K, 100%) matched that at the low temperature and low CO_2 pressure (288 K, 40%).

Figure 2 shows the experimental results from Set 1 in a factorial cube, with the statistical analysis of effects in Table 7.

These data confirm our previous conclusion [16] that (as expected) lowering the current and increasing the CO_2 volume fraction in the feed gas increased the formate CE, and show this result at both levels of temperature. The more complex effect of temperature can be examined by processing some of the experimental data to provide the information in Table 8.

In Table 8, comparing run 1 with run 4 and run 5 with run 8, exposes the combined effects of temperature and
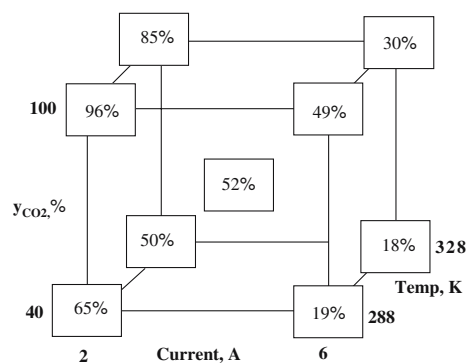
Table 6. Set 1. Factorial variables and levels

Variable	Symbol	Units	Level		
			High	Low	Centre (three replicates)
Current	X_1	A	6^a	2	4
Temperature	X_2	K	328	288	308
CO_2 conc in gas	X_3	Vol %	100	40	70

[a] 6 A ≡ 1.3 kA m^{-2} (130 mA cm^{-2}).
Operating conditions: cathode: 1 layer of tcc $30^\#$; gas flow = 180 ml STP min^{-1}; liquid flow = 20 ml min^{-1}; catholyte = 0.5 M KHCO$_3$; pressure: = 133 kPa(abs); pH = 7.5–9.5.

Fig. 2. Formate current efficiencies for factorial runs, Set 1 Other conditions as under Table 6.

three-fold higher mass transfer coefficient of CO_2 at 328 K than that at 288 K contributes more to the CE at 6 A than at 2 A.

The overall factorial results show that temperature generally has a negative 12% main effect on formate current efficiency, which indicates that the kinetic benefit of elevated temperature is outweighed by the corresponding drop in CO_2 solubility, at the CO_2 pressures used here. The negative effect of temperature has major implications for the reactor scale-up.

The only significant interaction is that between T and y_{CO2}. Temperature interacts negatively with y_{CO2} (-6%), which suggests that the benefit of increased y_{CO2} is slightly countered by increasing the temperature.

mass transfer on CE at 6 A and 2 A, respectively, without the confounding effect of CO_2 solubility. This is because the levels of T and y_{CO2} for both runs at each current were arranged for, respectively, the same solubility of CO_2.

The fact that CE increases with temperature at both currents suggests that increasing the temperature favours the generation of formate by the intrinsic kinetics, as observed by Koleli and Balun under 5000 kPa(abs) CO_2 pressure [14]. However, the relative increase of CE at 6 A (58%), is higher than that at 2 A (21%). This effect may be explained by the fact that the reaction kinetics dominate the process at 2 A while mass transfer is more important at 6 A [16], and thus that the

4.2. Electrolyte species

To explore the effect of some common electrolyte species, the cathodic reduction of CO_2 was investigated in aqueous solutions of $KHCO_3$, $NaHCO_3$, Na_2CO_3, KCl and NaCl as well as in some combinations of these electrolytes. Two sets of factorial experiments were carried out here, along with one parametric experiment.

4.2.1. Factorial experiments on K^+, Na^+, Cl^- and CO_3^{2-}
The 2^2 factorial experiment, summarized in Table 9, was carried out in an attempt to see the effects of cation species (K^+ and Na^+) and anion species (Cl^- and CO_3^{2-}) on formate CE. The catholyte concentrations were all

Table 7. Set 1. Factorial effects of current, temperature and CO_2 fraction on the formate CE

Effects	Main			Interaction			95% Confidence interval	Curvature	95% Confidence interval
	Current, A X_1	T, K X_2	y_{CO_2}, % X_3	$X_1 X_2$	$X_2 X_3$	$X_1 X_3$			
CE, %	−45	−12	27	2	−6	4	±5	1	±6

Confidence intervals are estimated from pooled replicates.

Table 8. Set 1. Effect of temperature coupled with mass transfer

Current	Run No	Temperature	y_{CO2}	CE/%	Relative increase of CE/%
6 A	Set 1–1	328 K	100%	30	(30–19)/19 = 58%
	Set 1–4	288 K	40%	19	
2 A	Set 1–5	328 K	100%	85	(85–65)/65 = 31%
	Set 1–8	288 K	40%	65	

Table 9. Set 2. Factorial variables and levels

Variable	Symbol	Level		
		High	Low	Centre
Cation	X_1	K^+ (0.5 M)	Na^+ (0.5 M)	Mixture[a]
Anion	X_2	Cl^- (0.5 M)	CO_3^{2-} (0.25 M)	Mixture

[a]Mixture = 1/4(0.25 M K_2CO_3 + 0.25 M Na_2CO_3 + 0.5 M KCl + 0.5 M NaCl).
Ionic conductivity = 3.4 to 6.5 S m^{-1}. Operating conditions: current = 2A; y_{CO_2} = 100%; cathode: 1 layer of tcc 30$^#$; gas flow = 180 ml STP min^{-1}; liquid flow = 20 ml min^{-1}; temperature = 299 K; pressure = 127 kPa(abs); pH = 6.5–8.0
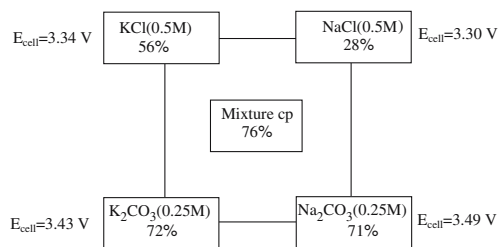
Fig. 3. Formate current efficiency and reactor voltage for factorial runs, Set 2. Other conditions as under Table 9.

held at 0.5 N and one layer of tcc 30# at a low current (2 A) was employed as cathode for all the runs to minimize the effects of conductivity and CO_2 solubility in the catholyte. The results of the factorial runs are given in Figure 3, and the effects of cations and anions on formate CE are summarized in Table 10.

The results of Table 10 show that, on average, changing the cation species from K^+ to Na^+ decreases the CE by 15%. This observation is qualitatively in agreement with previous reports on the effect of alkali metal cations on the reaction selectivity [9, 19].

On the other hand, changing the anion feed species from CO_3^{2-} to Cl^- results in a decrease of CE by 30% on average. It can also be seen from the comparison between the results of runs with 0.25 M K_2CO_3 and 0.25 M Na_2CO_3 that CO_3^{2-} is so much superior to Cl^- in terms of formate CE at 2 A that when CO_3^{2-} is used, the cation (K^+ or Na^+) has no effect. The negative effect of chloride relative to carbonate anions here may be due to the inability of Cl^- to buffer the cathode surface pH [24] and/or to the presence of adsorbed tin-chloride complexes [25] that shift the electrode kinetics in favour of reaction 2.

The high curvature shown in Table 10 reflects non-linearity in the experimental system – with good possibility for optimization around the catholyte composition.

4.2.2. K_2CO_3 vs $KHCO_3$ in the catholyte

The results of Figure 3 do not necessarily mean that alkali carbonate is a good choice of catholyte for electro-reduction of CO_2. This situation is complicated by the speciation between CO_3^{2-}, HCO_3^- and $CO_2(aq)$ with respect to the pH, which is considered to be a key factor for electrochemical reduction of CO_2 [9, 18, 24]. In the present system, the mixture of gas and liquid electrolyte feed passed through a 6-m long, 5 mm internal diameter tubing before entering the reactor. Absorption of CO_2 by the catholyte in the feed line would result in conversion of most of the carbonate to bicarbonate by reaction 5.

$$CO_3^{2-} + CO_2(aq) + H_2O \rightarrow 2HCO_3^- \quad (5)$$
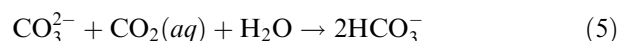
From the analysis of the liquid species, it was found that pumping 0.25 M CO_3^{2-} in the Set 2 experiments resulted in feeding 0.5 M HCO_3^- to the reactor. In other words, a catholyte with more than 0.25 M CO_3^{2-} could give lower formate CE because the unconverted CO_3^{2-} in the reactor would result in a competition between reaction 5 and reaction 1. Experimental results with a higher CO_3^{2-} feed concentration (shown in Table 11) support this hypothesis.

From this theoretical consideration and experimental result HCO_3^- appears to be a better anion than CO_3^{2-}. Thus $KHCO_3$ was adopted as the primary catholyte (in agreement with much prior literature) for subsequent study. The effect of $KHCO_3$ concentration on formate CE was then investigated by a set of parametric runs whose results are given in Table 12.

Table 12 shows a maximum formate CE at about 0.5 M $KHCO_3$ with higher bicarbonate concentration (up to 1.96 M) favouring hydrogen evolution. Hori [9, 19] attributed the effect of $KHCO_3$ concentration to the buffering action of HCO_3^- at the cathode surface (reaction 6), which decreases the surface pH as the bulk concentration of bicarbonate is increased and shifts the process selectivity in favour of reaction 2. This decrease

Table 10. Set 2. Factorial effects of electrolyte species on formate current efficiency

Effects	Main		Interaction	95% Confidence interval	Curvature	95% Confidence interval
	Cation X_1	Anion X_2	X_1X_2			
CE, %	−15	−30	−14	±5%	19	±4%

Confidence intervals are estimated from pooled replicates.

Table 11. Set 3. Comparison between HCO_3^- and CO_3^{2-}

Electrolyte	Conductivity/S m^{-1}	pH	E_{cell}/V	CE/%
0.45 M $KHCO_3$	4.8	8.07	5.48	50
0.45 M K_2CO_3	5.2	9.18	5.38	12

Operating conditions: current = 6 A; cathode: 1 layer of tcc 30#; gas flow = 180 ml STP min^{-1}; liquid flow = 20 ml min^{-1}; temperature = 300 K; pressure = 140 kPa(abs); y_{CO2} = 100%.

Table 12. Set 4. Effect of KHCO$_3$ concentration on formate CE

| KHCO$_3$ concentration/M	Conductivity/S m^{-1}	E_{cell}/V	CE/%
0.10	1.1	5.50	42
0.25	2.6	5.42	46
0.45	4.8	5.43	50
0.75	6.7	5.37	33
1.96	19.4	4.97	27

Operating conditions: current = 6 A; y_{CO2} = 100%; cathode = 1 layer of tcc 30$^{\#}$; gas flow = 180 ml STP min^{-1}; liquid flow = 20 ml min^{-1}; temperature = 299 K; pressure = 133 kPa(abs); pH = 7.5–8.0.

Table 13. Set 5. Factorial variables and levels

Variable	Symbol	Units	Level		
			High	Low	Centre
Conductivity	X_1	S m^{-1}	19.4	4.8	12.0
Number of layers	X_2	–	3	1	2

Operating conditions: current = 6 A; y_{CO2} = 100%; cathode: one or multi-layers of tcc 30$^{\#}$; KHCO$_3$ concentration = 0.45 M; gas flow = 180 ml STP min^{-1} × layers; liquid flow = 20 ml min^{-1} × layers; temperature = 299 K; pressure = 133 kPa(abs); pH = 7.0∼8.0.

in surface pH has been estimated in the modeling work of Gupta et al. [24] to be about 0.5 pH unit at the prevailing conditions. While it is probably true that the process selectivity is affected by surface speciation, the results of Table 12 may be more satisfactorily explained by the variation in catholyte conductivity together with the decrease of CO$_2$ solubility (ca. 30%) and increase of viscosity (ca. 30%) as the KHCO$_3$ concentration rises from 0.1 to 2 M [26–28]. At 6 A the experimental reactor is operating under CO$_2$ mass transfer control [16], so a decrease in the limiting current density for reaction 1 by 50% should cause a corresponding drop in the formate current efficiency.

$$HCO_3^- + OH^- \rightarrow CO_3^{-2} + H_2O \qquad (6)$$
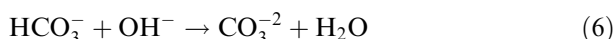
4.3. Catholyte conductivity and cathode thickness

Dilute solutions of KHCO$_3$ (e.g., 0.5 M) may be appropriate for academic studies of CO$_2$ reduction but they are not adequate for the superficial current densities of 1–5 kA m^{-2} required of a 3D cathode in an industrial process. The need for a low reactor voltage and a relatively uniform potential distribution in the trickle-bed electrode dictates a catholyte conductivity of at least 10 S m^{-1} and preferably as high as 50 S m^{-1}. Theoretical considerations indicate that the effect of catholyte conductivity becomes increasingly important as the thickness and superficial current density of the 3D cathode are increased.

In the present work, the effect of electrolyte conductivity was studied in conjunction with the cathode thickness (i.e., number of mesh layers) in the two level,
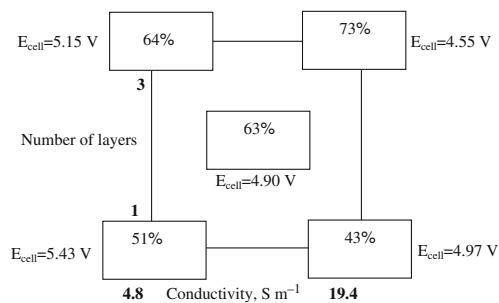

Fig. 4. Formate current efficiency and reactor voltage for factorial runs, Set 5. Other conditions as under Table 13.

two factor (2^2) factorial experiment summarized in Table 13. Here the feed concentration of KHCO$_3$ was held at 0.45 M and the catholyte conductivity was increased by adding KCl as supporting electrolyte, while the gas and liquid flows were adjusted to maintain constant fluid loads on the cathode. Figure 4 shows the results of this experiment and Table 14 presents a statistical analysis of the data.

In considering the results in Figure 4 and Table 14 it should be noted that other factors are involved here that may confound the observed effects. In particular we know from Set 2 that KCl (alone) gives a lower formate CE than KHCO$_3$ (alone) and further observe that the addition of any supporting electrolyte to raise conductivity reduces the solubility of CO$_2$ in the catholyte [29] and thus the CO$_2$ mass transfer limited current density.

It is seen that with one layer of cathode mesh, increasing conductivity had a negative effect on the formate CE, which indicates that the conductivity of 0.45 M KHCO$_3$ was high enough to support the 1 layer cathode and the added KCl played a negative role. However, with three layers of cathode mesh the positive effect of adding KCl surpassed its negative effect (e.g., CE increased from 64% to 73%). This is because multi-layers need higher ionic conductivity to support electro-activity over the available cathode thickness.

The above results for electrolyte conductivity and cathode thickness are a nice example of how interactions and confounding effects can cloud conclusions drawn from uni-variate experiments (e.g., as in Table 1). In the present case the results of Figure 4 give direction for process optimization around the cathode thickness, catholyte composition and conductivity.

4.4. Specific surface area of the cathode

Table 15 presents results of experiments that show the effect of increasing the specific surface of the cathode by changing from 30$^{\#}$ to 60$^{\#}$ mesh (see Table 2 for the mesh properties). The increase in specific surface is accompanied by lower porosity and higher pressure drop through the cathode, however Table 15 shows the expected rise in formate CE from increasing the mass transfer capacity of the cathode [16].

Table 14. Set 5. Factorial effects of conductivity and the number of layers

Effects	Main		Interaction	95% Confidence interval	Curvature	95% Confidence interval
	Conductivity X_1	Layers X_2	X_1X_2			
CE, %	1	21	8	± 7	5	± 6

Confidence intervals are estimated from pooled replicates.

Table 15. Effect of the cathode specific surface

		Number of layers	
		1	3
Mesh size	Specific surface, m^{-1}	CE, %	
30#	7000	51	64
60#	14,000	63	82

Operating conditions: catholyte = 0.45 M KHCO$_3$ for one layer and [0.45 M KHCO$_3$ + 1 M KCl] for three layers; current = 6 A; y_{CO2} = 100%; liquid flow = 20 ml min^{-1} ×layers, gas flow = 180 ml STP min^{-1} ×layers; temperature = 298 K; pressure = 138 kPa(abs); pH = 7.5–8.0.

Table 16. Set 6. Factorial variables and levels

Variable	Symbol	Units	Levels		
			High	Low	Centre
Number of layers	X_1	–	3	1	2
KCl conc	X_2	M	3	1	2

Operating conditions: cathode: one or multi-layers of tcc 60#; catholyte = 0.45 M KHCO$_3$ + KCl; current = 6 A; y_{CO2} = 100%; gas flow = 90 ml STPmin^{-1} ×layers; liquid flow = 10 ml min^{-1} × layers; temperature = 298 K; pressure = 140 kPa(abs); pH = 7.6∼ 9.5.
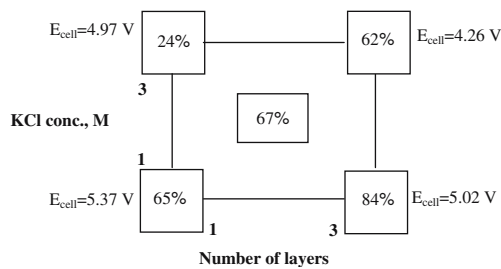

Fig. 5. Formate current efficiency and reactor voltage for factorial runs, Set 6. Other conditions as under Table 16.

4.5. *Concentration of the supporting electrolyte (KCl) and cathode thickness*

Following the results of Sections 4.3 and 4.4 a series of experiments was used to explore the effects of the concentration of KCl (as a supporting electrolyte) on the reactor performance with a 60# cathode. First the number of cathode layers and KCl concentration were tested jointly in a two level, two factor (2^2) factorial experiment and subsequently the KCl concentration and number of layers were examined separately in parametric runs. In all cases the gas and liquid flows were adjusted to maintain constant fluid loads on the cathode.

4.5.1. *Factorial runs*

Table 16, Figure 5 and Table 17 present the design, data and statistical analysis for the factorial experiment Set 6. Here it is seen that, over the tested range, KCl concentration has 32% negative main effect on formate CE, and the effect occurs with both one and three cathode layers, which implies that (under the experimental conditions) KCl concentration should not exceed 1 M for both one and three layers. The results confirm the positive effect of increasing the number of cathode layers and point to possible interactions and curvature. Also, both Figures 4 and 5 show the expected substantial decrease in reactor voltage (8–18%) from increasing both the number of layers and the catholyte conductivity.

4.5.2. *Parametric runs*

Several parametric runs were performed to seek the appropriate KCl concentration and to get information on the effective electro-active bed thickness. Tables 18 and 19 show results from the parametric runs.

Table 18 shows that under these conditions KCl concentration can be as low as 0.5 M without a negative effect on the formate CE. That is, the conductivity of

Table 17. Set 6. Factorial effects of KCl concentration and the number of cathode layers

Effects	Main		Interaction	95% Confidence interval	Curvature	95% Confidence interval
	Number of layers X_1	KCl conc X_2	X_1X_2			
CE, %	29	−32	10	± 8	5	± 7

Confidence intervals are estimated from pooled replicates.

Table 18. Effect of KCl concentration

KCl concentration/M	$P_{cath(inlet)}$/kPa(abs)	pH (outlet)	E_{cell}/V	CE/%
3.0	131	7.84	4.26	62
1.0	141	7.66	4.88	84
0.5	146	7.65	4.27	87

Operating conditions: current = 6 A; cathode: three layers of tcc 60[#]; catholyte = 0.45 M $KHCO_3$ + KCl; gas flow = 270 ml STP min^{-1}; liquid flow = 30 ml min^{-1}; temperature = 299 K; pressure = 133 kPa(abs). y_{CO2} = 100%.

Table 19. Effect of number of layers of tcc 60[#]

Number of tcc#60	$p_{cath(inlet)}$/kPa(abs)	pH (outlet)	E_{cell}/V	CE/%	$[HCOO^-]^a$/M
1	146	9.45	5.37	65	0.101
2	146	7.65	4.12	86	0.080
3	141	7.66	4.88	84	0.052
4	136	7.61	4.68	85	0.039

Operating conditions: current = 6 A; cathode: multi-layers of tcc 60[#]; catholyte = 0.45 M $KHCO_3$ + 1 M KCl gas flow = 90 ml STP min^{-1} × layers; liquid flow = 10 ml min^{-1} × layers; temperature = 299 K; pressure = 141 kPa(abs).
^{a}Formate concentration in catholyte product.

0.45 M $KHCO_3$ + 0.5 M KCl is high enough to provide ionic conductivity for three layers of tcc 60[#] (thickness = 1.1 mm).

It is seen from Table 19 that increasing the number of layers from two has no significant effect on the formate CE, which suggests that the effective bed thickness under these experimental conditions is no more than the thickness of two layers of tcc 60[#]. This value is in agreement with the theoretical calculation of the effective bed thickness [16] which gives 0.66 mm, compared to the thickness of two layers of tcc 60[#], i.e., 0.76 mm. The relatively low porosity of the tinned copper mesh, i.e., 0.41 and 0.31 for tcc 30[#] and tcc 60[#], respectively, limits the liquid hold-up in the reactor, thus constraining the effective electrolyte conductivity and electro-active bed thickness. From these results we surmise that the utilization of a more porous cathode material with high specific surface, such as a tin felt or foam, would improve the reactor performance.

5. Conclusions

The present study of five process variables for the electro-reduction of CO_2 in a continuous reactor, supported by the model described in our previous communication [16], allows the following observations, within the ranges of variables studied here:

(a) Increasing the reaction temperature from 288 to 328 K favours the intrinsic selectivity for formate over hydrogen. However, with the reaction under a CO_2 mass transfer constraint the positive effect of temperature on the intrinsic kinetics is countered by a corresponding decrease in the solubility of CO_2 in the catholyte, with the net result that at fixed CO_2 pressure the formate current efficiency decreases with increasing temperature.

(b) With respect to the catholyte composition the generation of formate is favoured by K^+ vs Na^+ cations and by HCO_3^- vs Cl^- anions. The presence of CO_3^{2-} in the catholyte suppresses formate generation – presumably due to the reaction with CO_3^{2-} that inactivates $CO_2(aq)$ as HCO_3^-. The negative effect of CO_2 speciation is evident at a catholyte pH over about 9. Under conditions near mass transport control, increasing the concentration of $KHCO_3$ in the catholyte from 0.1 to 2 M at 299 K in a single mesh layer cathode has a parabolic effect on the formate CE, with a maximum at about 0.5 M $KHCO_3$. Surface speciation may have a role here, but the observed non-linearity is attributed mainly to the competing effects of ionic conductivity and solubility of CO_2 in the catholyte.

(c) The effect of KCl as a supporting electrolyte in the $KHCO_3$ catholyte depends on the thickness of the 3D cathode. Increasing the catholyte conductivity from 4.8 to 19.4 S m^{-1} in a single mesh layer cathode (0.61 mm thick) decreases the formate CE, but has the opposite effect in a triple mesh layer cathode (1.9 mm thick). This interaction is attributed mainly to countervailing effects of KCl concentration on the CO_2 mass transfer limiting current density and the electro-active thickness of the 3D cathode.

(d) Within the limits of electro-active thickness, increasing the number of tinned-copper mesh layers in the 3D cathode with fixed fluid loads raises the formate CE. This effect is presumably due to the drop in CO_2 concentration polarization that results from a reduction in the real current density on the cathode surface.

(e) Increasing the specific surface area of the cathode from 7000 to 14,000 m^{-1} also raises the formate CE – again due mainly to the reduction in real current density on the cathode.

(f) Apart from the effects on formate CE, increases in the temperature, catholyte conductivity, cathode thickness or specific surface also reduce the reactor voltage and thus affect the specific energy consumption for formate generation (at a given superficial current density).

From a reactor engineering perspective, the "best" result of the present work was obtained after 10 min operation with a bi-layer 60# cathode and catholyte of [0.5 M KHCO$_3$ + 0.5 M KCl], operating on a gas of 100% CO$_2$ at 120 kPa(abs) and 299 K, with gas and liquid feed flows, respectively, 180 ml STP min^{-1} and 20 ml min^{-1}. The reactor performance indictors in this case were: Formate current efficiency = 86%, formate product concentration = 0.08 M, reactor voltage = 4.1 V, superficial current density = 1.3 kA m^{-2}, specific electrochemical energy consumption = 260 kWh per kmol formate.

Beyond these immediate results, our observations and those of other workers in this field indicate there is a rich opportunity for process optimization through the many variables affecting CO$_2$ reduction in a 3D electrode. This situation opens a path to process development that we will explore in a subsequent communication.

Acknowledgements

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