Challenges in scale-up of electrochemical CO₂ reduction to formate integrated with product extraction using electrodialysis

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Abstract

BACKGROUND: The concept of carbon dioxide (CO₂) conversion to formate has attracted increasing interest in recent years and various small-scale studies are present in the literature. However, upscaling of electrochemical CO₂ reduction comes with many challenges and there are very few reports available on it. In this study, we present a scalable three-chamber reactor system for electrochemical CO₂ reduction to formate, a precursor suitable for the production of fuels, pharmaceuticals and fertilizers and its extraction as pure formic acid by electrodialysis.

RESULTS: The reactor produced 11.7 g L⁻¹ formic acid in 6 h, i.e. 1.95 g L⁻¹ h⁻¹ at −1.8 V applied potential, 5 mol L⁻¹ KOH as an electrolyte, GDE (gas diffusion electrode) cathode with SnO₂ catalyst and Naflon™ 200 membrane. The maximum Faradaic efficiency achieved was 38%. In addition, recovery of the formate is equally important as its production for use as feedstock to form chemicals. We therefore also investigated the extraction of formic acid through conventional electrodialysis (CED) and bipolar membrane electrodialysis (BMED). The formic acid was extracted with 88% recovery using CED and 46% with BMED. Furthermore, BMED resulted in recovery of >95% K⁺ as base and 12 L pure CO₂ for possible recycling to the electrochemical cell.

CONCLUSION: We consider this study to provide essential empirical evidence on factors influencing the scale-up and subsequent performance of a liquid electrolyte-based electrochemical CO₂ reduction reaction (CO₂RR) system to formate and its extraction at scale. However, optimized systems and operating strategies still need further investigation, and constituent materials, particularly in terms of membranes and cathode catalyst, need to be developed.

INTRODUCTION

Carbon dioxide (CO₂) is the predominant greenhouse gas, which is increasing in concentration in the atmosphere and increasingly contributing to global warming.1,2 It has been predicted that by 2050 CO₂ concentration in the atmosphere will reach over 500 ppm – nearly double the concentration pre Industrial Revolution.3,4 Since the beginning of the industrial era, oceanic uptake of CO₂ has also resulted in acidification of the ocean; the pH of ocean surface water has decreased by 0.1 (high confidence), corresponding to a 26% increase in acidity, measured as hydrogen ion concentration.5 At the same time, CO₂ has also been recognized as a potentially cheap and relatively abundant carbon resource available for conversion to various chemicals, which in turn is advantageous to the development of a circular economy. Therefore, the concept of CO₂ utilization has attracted increasing interest in recent years.6-8 The electrochemical conversion of CO₂ to various C1 and C2 compounds, e.g. HCOOH, CO, CH₄, C₂H₄ in aqueous solution, has been studied by various researchers.9-12 Electrical energy can be derived from biomass or wastes and other renewable energy sources, or potentially the electrical energy input can be sourced from microbial fuel cell (MFC) technology, where a biocatalyst converts chemical energy stored in organic matter in the waste water directly into electricity.13 Formate/formic acid is used as a precursor in many industries,
including pharmaceutical synthesis, textile finishing, animal feed, as a hydrogen storage material and in alternative fuel production.\textsuperscript{10,14–16} However, most of the research conducted on CO\textsubscript{2} reduction to formate focuses mainly on small-scale reactors and/or production optimization using a variety of metallic catalysts, electrolyte solutions and cell designs.\textsuperscript{9,15,17–19} In the transfer of applications from laboratory to industry deployment, it is important to study the scalability of the process. Scale-up is not straightforward as there are many factors that play a significant role in process efficiency. Frequently, identical reactions can exhibit a different performance at different scales. The products may also differ greatly, for example at different current densities, which may result from simplistic physical scale-up to industrial capacities. The electrochemical CO\textsubscript{2} reduction reaction (CO\textsubscript{2}RR) is challenging as it takes place at high overpotentials, which compete with the reduction of protons to hydrogen and a variety of other products, including CO and hydrocarbons. Various studies reporting methods to overcome the lack of product specificity are present in the literature. Furthermore, a number of catalysts such as copper, bismuth and indium have been tested for their selectivity towards formate production. Tin-based catalysts are known for their specificity towards formate production and are used by several researchers.\textsuperscript{17,18,20} For industrial application, high yields and high current densities are often required,\textsuperscript{21} but this has to be balanced against the effects of high current densities on the stability of electrodes and membrane materials over time, which are equally important and require investigation. In terms of reactor configurations, there are studies based on two-chamber reactor set-ups using KHCO\textsubscript{3} as an electrolyte, but this electrolyte has drawbacks related to its low CO\textsubscript{2} solubility and its low saturation point, with consequent low mass transfer rates.\textsuperscript{19} To overcome these drawbacks, three-chamber reactor systems have been investigated. Gas diffusion electrodes (GDE) have been used to allow direct contact between the catalyst and gaseous CO\textsubscript{2} in order to improve mass transfer. Recently, an alternative system with solid electrolyte was tested for its effectiveness in comparison to liquid electrolytes and extraction of pure formic acid in vapor form.\textsuperscript{19} However, this system needs more research on the stability of the solid electrolyte and ion-exchange membranes under low water conditions, preventing product crossover. On the other hand, there has been extensive research on liquid electrolyte-based small-scale systems, and a system that generates 10 g L\textsuperscript{-1} h\textsuperscript{-1} formate with 90% FE (Faradaic efficiency), using SnO\textsubscript{2} as catalyst has been demonstrated.\textsuperscript{16,22} This arrangement was subsequently further modified\textsuperscript{23} into a three-chamber configuration for better CO\textsubscript{2} mass transfer and is considered for scale-up herein.

In addition, the product recovery or extraction of formic acid from the product stream becomes even more important and challenging than optimization of the CO\textsubscript{2} reduction process. If improved, it contributes to the economic viability of the overall process. The formic-acid-containing electrochemical systems are highly alkaline electrolytes that form complex interactions, as well as cross-associations with water. The high pH makes the solutions unsuitable for the desired microbiological processes, and causes deterioration of electrodes and membrane materials over time, contributing impurities to the final products. It is therefore important to extract and purify the formate or other final product, in order that further biological or non-biological conversions to useful products can proceed. Several methods for the extraction of organic acid are presented in the literature, and electro dialysis (ED) is one of the most promising. ED is the process of separating charged particles under applied voltage/current. Conventional electrodialysis (CED) has already been tested to recover formic acid,\textsuperscript{24} and bipolar membrane electrodialysis (BMED) has been tested to simultaneously recover pure formic acid and KOH. The high cost of KOH for reuse after extraction by BMED makes its recovery very desirable.\textsuperscript{25,26}

There are very few reports in the literature on upscaling electrochemical CO\textsubscript{2} reduction to formate.\textsuperscript{27} Likewise, there is little consideration of the effect of long-term electrochemical reactions on the materials and performance of the electrochemical cells used. Based on the literature, the upscaling of electrochemical CO\textsubscript{2} reduction still requires various challenges to be overcome. These include addressing low selectivity, maintaining small current densities while delivering a reasonable selectivity, and the cost of the catalytic materials.\textsuperscript{16,23} Therefore, in this study, we present a plausibly scalable step towards electrochemical CO\textsubscript{2} reduction to formate and its subsequent recovery using CED and BMED in continuous operation of the electrochemical process. The results are promising, and further research and improvement in the system would be worth pursuing. The study also highlights various expected challenges to maintaining similar performances to small-scale reactors during scale-up: specifically, those due to materials used and the operating regime of the system presented.

**MATERIALS AND METHODS**

**Three-chamber electrochemical cell construction and operation**

A three-chamber electrochemical cell was configured using a flat plate reactor configuration, as shown in Fig. 1(a). The working volume of each of the three constituent chambers, each of dimensions 10 × 10 × 1 cm, was nominally 100 mL. The anode and cathode chambers were separated by a cation-exchange membrane of either Nafion™ 211, Fumapem R F-950 (Fuel Cell Store, College Station, TX, USA) or CM-1-7000 (Membanes International Inc., Ringwood, NJ, USA), as specified below. An SnO\textsubscript{2}/C (4–5 mg cm\textsuperscript{-2}) coated carbon paper with gas diffusion layer (GDL; H2315 I2 C6, Freudenberg, Germany) was used as the working electrode (cathode) and a nickel electrode (NI-M40-100, fuel-cellmaterials, Lewis Center, OH, USA) was used as counter electrode (anode). The procedure presented previously\textsuperscript{16} was followed in the preparation of the cathode with SnO\textsubscript{2}/C catalyst. SnO\textsubscript{2} (nanopowder, ≤100 nm, Sigma-Aldrich, St Louis, MO, USA) and carbon black (Vulcan XC 72R, Cabot Corp., Boston, MA, USA) particles were mixed together in 3.5 (w/w) ratio. First, SnO\textsubscript{2}/C was combined with isopropanol (Sigma-Aldrich) and Nafion solution (Nafion suspension, 5 wt%, Sigma-Aldrich) to make a catalyst paste. The catalyst solution was sonicated for 90 min and the paste was then layered on the GDL.

The electrolytes used for the anode and cathode chambers were 5 mol L\textsuperscript{-1} KOH and 2/5 mol L\textsuperscript{-1} KOH, respectively, at pH 14. Depending upon the operation of the reactor, different potentials of −1.0, −1.5, −1.8 and 2.0 V with respect to a reference electrode Ag/AgCl (3 mol L\textsuperscript{-1} KCl) were applied, and anode, cathode membrane and cell potentials were also individually and periodically sampled every minute and logged simultaneously. The electrolyte was recirculated at a flow rate of 75 mL min\textsuperscript{-1} using a peristaltic pump (Watson-Marlow, Falmouth, UK) at 25 rpm in both anode and cathode chamber. The CO\textsubscript{2} was supplied via the third chamber (gas chamber) using a socratic mass flow controller (Model Number-MC-500SCCM-D/S 5 mol L\textsuperscript{-1}, PCT Ltd, Norfof, UK) with a variable flow rate.
Electrodialysis set-up and operation

Two different ED set-ups were used to extract formic acid and KOH, namely CED and BMED. Conventionally, ED is a membrane separation process used to transport ionic solutes from one solution to another through anion- and cation-exchange membranes separated by a spacer, forming individual cells between two electrodes. The ED stack consists of two electrodes (one anode and one cathode) across which an electrical potential is established by an external power supply. Between the electrodes, alternating anion-exchange membranes (AEMs) and cation-exchange membranes (CEMs) are placed and are separated by spacers to create diluate and concentrate chambers, through which liquids flow in the CED (Fig. 2(a,c)).

In BMED, the basic concept and configuration of the set-up remain similar to CED but, in addition to the AEM and CEM membranes, a bipolar membrane is also inserted to create three flow paths, i.e. ACID, BASE and SALT, to separate acid and base from salt. The bipolar membrane is added to the stack, as shown in Fig. 2(b) where a water-splitting reaction takes place and the formation of acid and base occurs in the respective flow paths. The separate flow paths were connected to the membrane stack using a peristaltic pump (model 323, Watson-Marlow) and marprene tubing with 6.4 mm bore and 1.6 mm wall (Watson-Marlow) at 100 rpm, allowing flow of separate solutions. In the present study, the bipolar membrane produces H\(^+\) and OH\(^-\) ions, converting the salt (KCOOH in KOH) to its corresponding acid (HCOOH) and base (KOH), as shown in Fig. 2(b). The CED stack with 20 cell pairs model number ED 64002 and BMED stack with 10 cell pairs, model number ED 64004-T10-1211-ED1 were manufactured by PCCell GmbH (Heusweiler, Germany).

Electrochemical and chemical analyses

The electrochemical CO\(_2\)RR experiments were conducted in the reactor set-up described above and shown in Fig. 1(b). The voltage and current were determined by potentiostatic polarization using an electrochemical interface (Solartron Analytical, Farnborough, UK) controlled by dedicated software (CorrWare™, Scribner Associates Inc., Southern Pines, NC, USA), with Ag/AgCl (3 mol L\(^-1\) KCl) as a reference electrode. The current output at a specific applied potential was recorded every second. The individual potentials were recorded using Keithley data acquisition/logging (model DAQ6510/7700, 50 MHz, 20 CH, Farnell elements 14, Leeds, UK). CO\(_2\) consumption was measured using a wet gas tip meter, constructed and calibrated in the laboratory, connected to the outlet of the gas chamber, and tip counts were recorded using a personal computer equipped with LabVIEW™ and NI USB-6009 (National Instruments, Austin, TX, USA). These concentrations of formic acid in the reactor were determined after every hour by ion chromatography (Metrohm Ltd, Herisau, Switzerland) with 0.1 mmol L\(^-1\) H\(_2\)SO\(_4\) as regenerant and 1.3 g L\(^-1\) LiCl\(_2\) as eluent, equipped with a Metrosep Organic Acids 250/7.8 column (Cat. No. 6.1005.200). Other gaseous product emanating from the gas chamber and collected in a gas bag at the end of each experiment were fed into a quadrupole mass spectrometer (Cyionics Ltd, Pontypool, UK) fitted with an IOTA residual gas analyser.

Figure 1. Schematic for the (a) reactor assembly and (b) reactor set-up. CEM, cation-exchange membrane; GDE, gas diffusion electrode; PS, power supply; RE, reference electrode and V is voltage.
Calculations
The Faradaic efficiency (FE) of formate was calculated according to the following equation:

\[
    \text{FE} = \left( \frac{2 \times F \times V \times C}{1000 \times M \times Q} \right) \times 100\%
\]

where 2 = number of electrons required to form 1 mol formate, \( F \) is Faraday's constant (96 485 C mol\(^{-1}\)), \( V \) is volume of catholyte, \( C \) is mass concentration of formate generated by the reaction (mg L\(^{-1}\)), \( M \) is molar mass of formic acid (46.05 g mol\(^{-1}\)), and \( Q \) is total amount of charge consumed by the entire reaction as monitored by the potentiostat.

Current density was calculated by taking the ratio of the output current and the geometrical (or projected) surface area of the cathode (100 cm\(^2\)) exposed to the solution. The output current fluctuated during the experiments; therefore the total charge (\( Q \)) was obtained by integrating the current over time as in the following equation:

\[
    Q = \int_{0}^{t} i \, dt
\]

RESULTS AND DISCUSSION
Formic acid production versus applied potential
To understand the effect of applied potential on formic acid production, different applied potentials with respect to Ag/AgCl (3 mol L\(^{-1}\) KCl), a reference electrode, i.e. \(-1.0\) V, \(-1.5\) V, \(-1.8\) V, \(-2.0\) V, were successively applied, each for 2 h. The data presented in Fig. 3 are the average values and range of the duplicated experimental runs at each potential. As shown in Fig. 3(a), the applied potential exhibited a clear correlation with formate concentration and increased with an increase in the applied potential, i.e. from 0.4 to 2.9 g L\(^{-1}\). The FE% for formic acid also increased from 16% to 30% up to \(-1.8\) V applied potential, but then decreased to 22% at \(-2.0\) V. This may be due to the competitive hydrogen evolution reaction becoming more significant beyond \(-1.8\) V. While the highest formate production rate (1.45 ± 0.55 g L\(^{-1}\) h\(^{-1}\)) was achieved at an applied voltage of \(-2.0\) V, the FE was lower than at \(-1.8\) V. As can be seen in Fig. 3(b), the current consumption increases with increase in the applied voltage, and once settled was relatively stable throughout the duration of the experiment. This reflects the stability of the system and associated electrochemical reactions. In addition, to check the effect of applied potential on the reactions taking place at the electrodes, individual potentials, i.e. cell, anode, cathode and membrane potentials, were also measured. All individual potentials also remained stable over time, as presented in Fig. 3(c); for example, in the case of an applied potential of \(-1.8\) V, these potentials were measured at \(-2.2\) V cell, \(-1.8\) V cathode, 0.5 V anode and 0.01 V membrane potential. The current densities increased from 2.7 to 53.2 mA cm\(^{-2}\) but did not contribute fully towards the conversion to formate. The increase in current densities is also indicative of the increased rates of various electrochemical reactions, including the generation of other volatile...
fatty acids (VFAs) and any gas generation at the electrode surfaces. High current densities reflect high reaction rates but are also responsible for the specificity of the product formed. As the highest FE of 30% was achieved at −1.8 V applied potential, it is evident that this was the most efficient potential for formic acid production, and was thence used for all further experiments. Although all aforementioned observations suggested that the applied voltage of −1.8 V was optimal for formate production, high current flowing through the system influences the performance of the CO2RR by affecting reactor materials, as discussed below in more detail. After selecting the applied potential, longer runs of up to 6 h were also investigated and are presented in the next subsection.

**Effect of CO2 flow rate**

Should reactor dimensions be increased such that the static head in the chamber is also increased, then the partial pressure of CO2 will also need to be considered and optimized, probably by adjusting its flow rate. Once the applied potential was selected to be −1.8 V, the system was further evaluated by varying the CO2 flow rates according to the gas chamber mass flowmeter. Flow rates of 35, 100 and 150 mL min−1 were selected. The reactor was run for a maximum of 6 h, as shown in Fig. 4(a), to find the saturation point for formate production. Formate concentration was not seen to saturation but an approximately consistent increase of 1.2 g L−1 h−1 in formate concentration was evident. It was observed that an increase in CO2 flow rate in the gas chamber also increased the formic acid production. Samples were collected every hour to determine any changes in formic acid concentration, pH and conductivity. As shown in Fig. 4(a), the total amount of formic acid produced also increased with increasing flow rate of CO2 as did the FE, shown in Fig. 4(b). At the same time, the consumption of CO2 at each flow rate was also measured using a tipping bucket flowmeter at the outlet of the gas chamber. The gas was collected in a gas bag at the vent of the tip meter. It can be seen from Fig. 4(b) that the volume of CO2 consumed increased from 5.03 to 14.05 L as CO2 flow rate increased from 35 mL min−1 to 150 mL min−1, respectively. This implies that higher flow rate produce a higher CO2 pressure in the gas chamber which may improve the mass transfer rate. There may also be higher visodynamic forces caused by higher CO2 flow rates, increasing mixing and mass transfer at the electrode surfaces, which could enhance efficiency. An increased concentration of formic acid from 6.9 at 35 mL min−1 to 9.9 g L−1 with maximum FE of 36% at 150 mL min−1 CO2 flow rate was achieved. The pH decreased from 14 to 10.5, 10.1 and 9.9 in 35, 100 and 150 mL min−1 CO2 flow rate, respectively, after 6 h running. The decrease in pH occurred due to the intrusion of CO2 into the catholyte, through the GDL. The greater drop in pH at higher

![Figure 3](http://www.soci.org/article-figures/)

**Figure 3.** (a) Applied potential versus formate production and FE; (b) applied potential versus current consumption; (c) individual potentials at an applied potential of −1.8 V versus Ag/AgCl (3 mol L−1 KCl).
Flow rates reflect the carbonic acid resulting from CO₂ ingress. Under alkaline conditions, a continuous indirect feed of gaseous CO₂ on the cathode side will be converted into carbonate and eventually bicarbonate, gradually lowering the pH. The accumulation of formate and its consequent higher concentration over time also results in a decrease of catholyte pH. As the pH of the catholyte plays an important role in the selectivity of the product formed, as is also described previously, it is important to maintain alkaline pH in order to achieve maximum efficiency towards a selected product, i.e., formate in this study. Liquid phase conductivity also decreased with the consumption and depletion of ions in the catholyte. The conductivity of the cathodic chamber gradually decreased at all the applied flow rates, from >200 mS cm⁻¹ (0 mL min⁻¹, 0 h) to 176.8 mS cm⁻¹ (35 mL min⁻¹), 144.4 mS cm⁻¹ (100 mL min⁻¹) and 121.4 mS cm⁻¹ (150 mL min⁻¹, after 6 h), which reflects an accumulation of products and the intrusion of CO₂ into the cathode chamber, as evidenced in Fig. 4(d). The gaseous products collected in a gas bag were measured at the end of the 6 h run for each batch experiment. Other byproducts were found in small concentrations, namely H₂ and CO, and these varied very slightly, which may be attributable to increase in CO₂ flow rates.

Effect of membrane type

After selecting the optimal applied potentials and CO₂ flow rate, different membranes were also tested considering the high current densities and design of the reactor. To understand the membrane influence on the system, three different types of membrane were considered, i.e., Nafton™ 211, Fumapem R F-950 and CM1-7000, each operated under the same conditions. Nafton™ membrane is frequently used to separate the anode and cathode compartments of fuel cells and water electrolysers. Nafton™ 211 is described as chemically stabilized perfluorosulfonic acid/PTFE copolymer in the acid (H⁺) form. Fumapem F-950 membrane is a long-side-chain per fluorinated sulfonic acid (LSC-PFSA) cation exchange membrane (CEM) with low resistance, high mechanical stability, selectivity and chemical stability. Both Fumapem F-950 and Nafton™ 211 have been tested in various small-scale reactors for CO₂ electroreduction. Nafton™ 211 and Fumapem F-950 are dimensionally thin membranes with thickness 25.4 and 50 μm, respectively and, considering the flat plate design of the current reactor, difficulties were experienced in keeping these membranes mechanically stable and in place. The membranes were deformed by the flow of electrolyte and the differential pressure between anode and cathode chambers. To overcome this,
CMI 7000 was considered, which is a strong acid polymer membrane with gel polystyrene and divinylbenzene cross-link structure that includes numerous sulfonic acid groups. CMI 7000 displays mechanical durability, albeit with a high ohmic resistance.

During 6 h batch run with individual membrane the formate concentration increased without much change in the conductivity and pH. The FE with Nafion™ 211 increased to 38% as compared to Fumapem F-950, at 36%. Due to the thickness of the CMI 7000 and added ohmic resistance, its effect on membrane potential can be clearly seen in Fig. 5(a). In the CMI 7000 membrane test, the potential at the membrane was around 1.5 V. As a result, the applied voltage was also increased to 4 V. For both Fumapem F-950 and Nafion™ 211, the potential difference between the membrane and reference was less than 0.01 V for Nafion™ 211 and 0.05 V for Fumapem F-950, and cell voltage was also far lower, at around 2.2–2.5 V. The membrane potential had an effect on formate production, and after 6 h the final formate concentrations were 8.8, 10 and 11.7 g L⁻¹ with CMI 7000, Fumapem F-950 and Nafion™ 211, respectively. Due to the increase in cell voltage with CMI 7000, the temperature of the electrolyte also gradually increased from 22 to 25 °C over the 6 h, which resulted in a lower FE of <20%. It was observed for all the membranes that, with longer and/or multiple runs, the membranes and GDL with associated catalyst were unable to maintain their performance, which can be seen in Fig. 5(b). The error bars show the range over duplicate runs. Therefore, the importance of sourcing a suitable membrane for industrial application, which can resist high currents and are stable when operated over the long term, becomes evident. The possibility of using different catalysts to overcome this issue may be considered for long-term and continuous operation of the system, as is also described in previous reports.⁹,³²

**Recovery of formic acid and KOH using electrodialysis**

Recovery of formic acid produced from electrochemical CO₂ reduction is as important as the optimization of the electrochemical CO₂RR. For the extraction of pure formic acid we tested two different ED set-ups, i.e. CED and BMED. The catholyte from the electrochemical cell (ECcell) contains some visible impurities; therefore, before introducing the solutions into the ED unit, they were filtered through a 0.2 μm filter to prevent blockages in the ED cell membranes. As discussed above, the main reason of using BMED in this study was to simultaneously recover formic acid and KOH. As shown in Fig. 6(a), standard stock KOH solutions containing 6.2 g L⁻¹ formic acid were initially tested in BMED.

Using BMED, 90% of the formic acid was recovered in the acid stream from a standard stock solution in less than 30 min, while 95% K⁺ as base KOH was recovered in the base stream. However, when the solution containing synthesized formate from the CO₂RR ECcell was introduced into the BMED, the current consumption was higher as the separation took a longer time, as did the current depletion to complete. This resulted in low recovery of formic acid, perhaps due to the high alkalinity and complex chemical composition of the electrochemically derived solutions. The recovery of up to 46% formic acid (Fig. 6(b)) in the acid stream and >95% KOH recovery in the base stream was achieved as shown in Fig. 6(c,d). This was observed as increasing K⁺ concentration and pH in the base line, CO₂ intrusion into the cathode chamber in the ECcell was also responsible for low recovery. This is due to the CO₂ passing through GDE to the cathode chamber, which then forms CO₃⁻ or HCO₃⁻ ions during BMED. When combined with H⁺ in the acid line, this converts into pure CO₂. The evolution of CO₂ also resulted in product leakage and thus lower recovery. The pure CO₂ produced from 200 mL of catholyte in 6 h was collected in a gas bag and amounted to 12 L. While this can be detrimental to the extraction process and power consumption, the pure CO₂ can nevertheless be reused in various industrial applications and the solutions can possibly be rerun through ED for subsequent extraction. Considering the lower formic acid recovery, i.e. 46% from BMED, CED was also investigated for the extraction of formic acid alone, which has also been presented by various other researchers.²⁶,³³

The CED set-up has been discussed above and results in the concentration of acid after its extraction from the dilute chamber. Similarly to BMED, when standard KOH solution containing formate was run through the CED the recovery was higher and more rapid, i.e. <20 min with low current consumption. However, when the sample from the ECcell was run through CED, 88% of formic acid was recovered but the current consumption remained high (Fig. 7(a)) as compared to the standard solutions, as well as ECcell sample through BMED (Fig. 6(a)). This may again suggest that the complexity of the electrochemical synthesis solutions after CO₂ reduction has a bearing. If we only consider the recovery of formic acid, then CED is more effective than BMED (Fig. 7(b)). However, overall recovery of formic acid, KOH and additional

**Figure 5.** Difference in (a) formate production and (b) membrane potentials with three different cation-exchange membranes.
Figure 6. (a) Difference in current consumption in bipolar membrane electrodialysis with standard stock KOH solution containing known formate concentration versus electrochemical cell solution containing formate obtained after 6 h of CO₂ reduction reaction; (b) transfer of formic acid from salt to acid line along with pure CO₂ production (approx. 12 L); (c) transfer of K⁺ ions from salt to base line; (d) changes in pH and conductivity in base solution to reflect increase in OH⁻ ions.

Figure 7. (a) Current consumption in conventional electrodialysis (CED) with solution from electrochemical cell after 6 h of CO₂ reduction reaction; (b) difference in percentage recovery of formic acid with CED and bipolar membrane electrodialysis (BMED).
production of pure CO₂ make BMED more advantageous. Based on the results it can be suggested that the combination of the electrochemical CO₂ reduction process with BMED for recovery of formic acid has the potential for further improvements. Various strategies can be applied to increase the formate extraction with low current input, plausibly by an improved combination of membranes and extraction processes and methodologies.

Challenges in scale-up

The transition from small-scale electrochemical CO₂ reduction to larger-scale industrial implementation is still at an early stage of development and yet to be realized. Efforts to develop an industrial/commercial CO₂ electrolyser have not been attempted, to the authors’ knowledge. The transition is not straightforward and needs significant research to optimize various elements and subprocesses that affect the overall performance of the system. Despite recent advances in such matters, upscaling CO₂RR still needs to be optimized in terms of electrode materials, selectivity, stability, energy efficiencies/current densities and reactor designs, if technological readiness level is to be increased for the process. Therefore, a fuller understanding of the different parameters that control this catalytic process is necessary. There have not yet been many attempts to upscale CO₂RR reported. In this study we have considered some key barriers. These, in addition to what is already known from the literature and future developments, may facilitate implementation at a larger scale. Based on the system presented in this study, the current densities required to achieve high formate concentrations are very high. As evidenced by Eqn 3, the current densities required to achieve similar productivities to those achieved in our modestly scaled reactor are significantly higher than those reported herein. If a target formate concentration for example 20 g L⁻¹ h⁻¹ is anticipated, using a counter chamber of volume 100 mL, where ratio of volume (cm³) / electrode surface area (cm²) is 1 cm. Assuming also that there are no limitations in the reduction process and an FE of 100% is achievable, then a current of 2.3 A cm⁻² will be required, as opposed a 0.23 A cm⁻² for a 10 times smaller volume reactor:

\[ Z = \frac{2 \times V \times C \times F}{M} \]  

where \( Z \) is the required current density (A cm⁻²), \( 2 \) = number of electrons required to form 1 mol of formate, \( V \) is the volume of catholyte, \( C \) is the target mass concentration of formate based on time and electrode surface area (g L⁻¹ h⁻¹ cm⁻²), \( F \) is Faraday’s constant (96 485 C mol⁻¹) and \( M \) is the molar mass of formic acid (46.05 g mol⁻¹).

The high electrical current through the reactor is shown to adversely affect the membrane properties and electrode materials. The tolerance limits in applied current for many membranes is <500 mA. Membranes become unstable with prolonged application of excessive current in operation, evidenced by changes in the catholyte colour and turbidity due to membrane deterioration and a light-brown colouration of the cathode due to its deterioration, as shown in Fig. 8(a,b). The membrane and GDL (Fig. 8(c)) with catalyst layer were only stable for three or four experimental runs of 6 h, after which the formate concentrations and current densities reduced, with a range as shown in Fig. 5(a). Therefore, further investigations on electrolyte concentrations, membranes and catalyst s are required for a better understanding of the CO₂ electroreduction process.

In addition, better results with GDL have been reported in the literature, but electrolyte penetration through the GDL once power is supplied has been also observed as a problem. The

![Figure 8](image-url) Changes in cathode colour: (a,b) light brown and turbid; (c) cathode deterioration over multiple runs; (d) electrolyte transfer through GDL during the electrochemical reaction.
GDL becomes completely covered with small droplets of electrolyte and, in longer runs, the gas chamber begins to fill with liquid, which interferes with the CO2 supply to the chamber (shown in Fig. 8(d)). According to previous reports,29,35 the flooding of GDL results in the reduction of reaction rates due to the repulsion of the OH− ions produced and the increase in pressure inside the pores, lowering the functionality of the GDE. This can also reduce the active area of the GDE for CO2 reduction and thus prevent electrochemical conversion. An accumulation of solid deposits on the gas side was also observed at the end of the 6 h runs, resulting in degradation of the GDL and overall electroreduction performance. This salt deposition was also observed in electroreduction of CO2 to CO by Jeanty et al.22 and was analysed to be K2CO3 and KHCO3, which means that although the electrolyte used in the current study was KOH, the transfer of gas through the GDL to cathode chamber or transfer of electrolyte through the GDL to the gas chamber leads to the accumulation of salts. Due to the design of the flat plate reactor, membrane distortion was also observed to be an issue. The gases generated under the applied potentials and the flexibility of the membrane caused its deformation towards the lower pressure chamber and resulted in varying anode and cathode chamber volumes. The reactor design therefore required further improvements to mitigate against membrane distortion and to improve maximum CO2 mass transfer by increasing the gas chamber pressure. High-pressure systems were tested by Ramdin et al.29 and showed positive effects on formate productivities.

We consider this study to provide essential empirical evidence on important factors influencing the scale-up and subsequent performance of a liquid electrolyte-based electrochemical CO2RR system to formate and its extraction at scale. However, optimized systems and operating strategies still need further investigation, and constituent materials, particularly in terms of membranes and cathode catalyst, need to be developed. Similar catalyst and membranes that perform better in small-scale system show lower efficiencies on scale-up and less stability, even for short periods of operation. In addition, ED shows encouraging results in extracting formic acid from complex electrochemical solutions. However, there are several possibilities to improve the recovery rate further. Modifications in the arrangement of ion-exchange membranes or by connecting different stacks together may result in better recovery and will be investigated in future studies. In addition, plans to better understand the complexities of the solutions obtained after CO2 reduction and their consequences are also in place.

CONCLUSIONS

This paper presents a study of some key factors believed to be important in the scaling up of electrochemical CO2 reduction to formate. The effects of applied potential, CO2 flow rates and membrane on FE, current density, pH and conductivity have been investigated. Maximum formic acid production was observed with Nafion™ 211 at 150 mL min⁻¹ CO2 flow rate and -1.8 V with 38% FE, which possibly can be improved further at this scale. However, more research is still required towards reactor design and materials because of their deterioration over time under high currents applied to the system. For future industrial usage, FE needs further improvement. The extraction of formic acid is as important as its production if it is to be utilized in further processes. CED and BMED were compared for recovery efficiency, and 88% formate with CED and 46% formate along with >95% KOH and 12 L of pure CO2 were recovered with BMED. However, due to the complexity of the cathodic solutions, complete extraction for formate requires further investigation.

ACKNOWLEDGEMENTS

This work was supported by the EPSRC Multi-Disciplinary Fuels RCUK Energy Programme; the Liquid Fuels and Bioenergy from CO2 Reduction (Lifes-CO2R) Project (EP/N009746/1); and the FLEXIS research project (grant number: WEFO 80835). Dinsdale would also like to acknowledge the Royal Academy of Engineering Fellowship Chair in Emerging Technologies (CIET1819/2/86).

CONFLICT OF INTEREST

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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