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Electrochemical conversion of CO_2 to formic acid utilizing SustainionTM membranes



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ABSTRACT

Formic acid generated from CO_2 has been proposed both as a key intermediate renewable chemical feedstock as well as a potential chemical-based energy storage media for hydrogen. In this paper, we describe a novel three-compartment electrochemical cell configuration with the capability of directly producing a pure formic acid product in the concentration range of 5–20 wt% at high current densities and Faradaic yields. The electrochemical cell employs a Dioxide Materials Sustainion[™] anion exchange membrane and a nanoparticle Sn GDE cathode containing an imidazole ionomer, allowing for improved CO_2 electrochemical reduction performance. Stable electrochemical cell performance for more than 500 h was experimentally demonstrated at a current density of 140 mA cm⁻² at a cell voltage of only 3.5 V. Future work will include cell scale-up and increasing cell Faradaic performance using selected electrocatalysts and membranes.

1. Introduction

The concept of CO_2 utilization as an alternate means of reducing carbon emissions and atmospheric CO_2 in place of carbon capture and sequestration (CCS) has been attracting increasing interest in recent years [1–9]. CO_2 conversion into viable feedstocks for chemicals and fuels offers both a carbon neutral manufacturing process cycle and the potential for achieving an economically significant reduction in atmospheric CO_2 when applied on a global scale using renewable energy resources, such as solar, wind, nuclear, and tidal technologies. The focus of this paper is on the experimental work in developing a new method of electrochemically converting CO_2 directly into a pure aqueous formic acid product, which can be directly utilized as a renewable chemical feedstock.

The reduction of CO_2 to formate/formic acid has been investigated by many researchers over the past 30 years and is summarized in several excellent review papers [10–13]. The research can be divided into studies involving metal electrodes and metal catalysts in the form of flat plates, high surface area electrode materials, and metal organic catalysts [14–42], and in the implementation of gas diffusion electrodes (GDEs) [43–46] operating in both aqueous and non-aqueous electrolytes.

Presently, though, several limitations need to be overcome before the process can be commercialized. It has generally been found that the Faradaic efficiency of CO_2 conversion to formate/formic acid is significantly lower at lower aqueous pH conditions (pH 3–5) than at higher pH conditions (pH 7–11). The reason is that the competing cathodic hydrogen generation reaction can dominate at low pH, significantly lowering the cell formic acid/formate Faradaic efficiency. Because of this limitation, no one has operated an electrochemical system generating only formic acid. These systems have always produced alkali metal formate salts because of the cell electrolyte requirement. A formate salt product from these cells would have to go through a second step acidification process in order to produce formic acid.

Another formic acid/formate operating issue is that better gas diffusion electrodes need to be developed. GDEs have the advantage in that they allow direct contact between gaseous CO_2 and the electrochemical catalysts, improving mass transfer and allowing the reduction reactions to occur at significantly higher concentrations of CO_2 . But the GDEs that have been reported so far have issues with liquid flooding, even after hours of operation, so they need improvement.

In this paper, we discuss the development of two key improvements that can lower the barriers to commercialization. First, we have modified the GDE structure that is commonly used, by adding an anion exchange membrane, allowing the operation of a GDE cathode without liquid flooding. Second, we modified the cell design so that the cathode is held at a pH of 7–11 so that hydrogen formation is suppressed, and employed an acidic center compartment where the resultant product formate stream is acidic, so we can directly produce formic acid rather than a formate salt product. Only deionized water water is used in the cell design, and not requiring any salt additions as electrolytes.

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Fig. 1. Formic acid 3-compartment cell configuration. CO2 reduction is facilitated by the presence of an imidazolium ionomer present in the nanoparticle Sn catalyst at the GDE cathode.

2. Experimental methods

Key to the work was the development of a novel 3-compartment formic acid cell design. The anode compartment operates on a DI water feed, the GDE cathode operates in a pH range of 7–11, and the formic acid stream in the center compartment operates at a pH of 1–5 with an input stream of DI water. The center compartment is bounded by a cation membrane on the anode compartment side and by an anion membrane on the cathode compartment side. These two membranes adjoin the cell center compartment without adding a significant voltage resistance. Details on the cell construction and configurations are detailed below.

2.1. Three-compartment formic acid cell configuration

The 3-compartment formic acid cell configuration detail is shown in Fig. 1. Table 1 provides a summary detail of the various anode, cathode, and center flow compartment configurations that were evaluated. The formic acid cell consisted of three compartments: a cathode compartment where the cathode operates at a pH of 7–11 using a Sustainion™ anionic ionomer, a center flow compartment that is held at a pH between 1 and 5 using strongly acidic ion-exchange bead electrolyte media, and an anode compartment that is even more acidic using a zero gap spacing with the anode where a Nafion membrane ionomer serves as the electrolyte. CO₂ gas was introduced into the cathode compartment and flowing into the GDE cathode catalyst structure, where CO_2 reacts with water coming from the center compartment through the anion membrane to the GDE catalyst/membrane interface to form formate ions. The generated formate ions ionically pass through the anion exchange membrane into the center flow compartment. The reaction in the anode compartment is the oxidation of water into protons (H⁺) and oxygen, with the protons passing through a PFSA (perfluorinated sulfonic acid) cation exchange membrane into the center flow compartment. The protons and formate ions combine in the center flow compartment to produce formic acid. Deionized water is passed into the center flow compartment to remove the formic acid product from the cell. The formic acid cell design does not require any

supporting salt electrolytes, only deionized water is used for both the anode compartment and center flow compartment.

2.2. Three-compartment formic acid cell test system and isometric cell drawing

Fig. 2 shows the formic acid cell experimental test system set-up. Fig. 3 shows an isometric drawing of the formic acid cell assembly.

2.3. Equipment and chemicals

2.3.1. Equipment

BK Precision 9121A power supply (B&K Precision Corporation); PHD 2000 Infusion syringe pump (Harvard Apparatus); NE-9000 peristaltic pump (New Era Pump Systems, Inc.); Dakota Data Instruments GC Series CO₂ mass flow controller, 0-50 mL/min; Oakton pH 700 pH meter (Oakton Instruments); Oakton Cond 6+ Handheld Conductivity meter (Oakton Instruments); GC: HP 6890 Plus + GC (Agilent); modified fuel cell hardware (Fuel Cell Store, 5 cm²) was used as the electrochemical cell. A GDE cathode was prepared by spraying a Sn catalyst layer (99.9%, 60-80 nm, US Research Nanomaterials, Inc.) containing 5% carbon nanotubes (Sigma-Aldrich, multi-walled carbon nanotubes, > 90% carbon, Item 659258) suspended in an isopropanol/water mixture onto a 50% PTFE proofing Toray paper (TGP-H-120 50%, Fuel Cell Earth) containing 2 wt% Sustainion[™] ionomer. The anode was either a GDE electrode prepared by spraying a nanoparticle IrO_2 catalyst (99.99%, Alfa Aesar) onto 5% PTFE proofing Toray paper (TGP-H-120 5%, Fuel Cell Earth) or a titanium anode expanded metal screen having an IrO2-based catalyst coating supplied by Water Star, Inc. (Parkman, OH).

2.3.2. Chemicals and materials

Deionized water (DI water) ($18.2 \text{ M}\Omega \text{ cm}^{-1}$, from Milli-Q water system); formic acid (reagent grade > 95% Sigma–Aldrich); sodium hydroxide (standardized 0.1 N, LabChem Inc. for titrations); 1% phenolphthalein solution (LabChem); Amberlite^{*} IR120 (hydrogen form, Sigma–Aldrich); Dowex^{*} 50WX2 (hydrogen form,

Table 1

Formic acid cell assembly configuration summary.

Cathode configurations	
Cathode	POCO Graphite block with serpentine flow path
GDE cathode	Toray paper, 50% PTFE proofing
GDE catalyst	Sn Nanoparticles (99.9%, 60-80 nm, US Research Nanomaterials, Inc.), catalyst layer air atomized onto GDE cathode with varying amounts of PTFE
	suspension and 5% imidazolium-based ionomer, and 5% carbon nanotubes.
CO ₂ flowrate	20 mL/min, not humidified for ambient temperature operation
Anode configurations	
Anode 1	POCO Graphite block with serpentine flow path. The anode was a GDE electrode with a 2 mg cm $^{-2}$ IrO ₂ catalyst (99.99%, Alfa Aesar) onto 5% PTFE proofing Toray paper
Anode 2	Titanium Grade 2 anode block with serpentine flow path. Anode screen having IrO ₂ -based metal oxide coating on expanded titanium (Water Star) was spot welded onto the titanium anode block
Center flow compartment	
Ion exchange media	Amberlite * IR120 strong acid ion exchange resin fill, 620–830 μ m beads, and other selected ion exchange resins
Center compartment	1 mm thickness, 2.25 cm × 2.25 cm, 0.50 mL (empty), estimated 40% void volume, i.e., 0.2 mL free volume with ion exchange resin
Center compartment frame	Polycarbonate, machined flow path for solution flow in/out
DI water feed	Selected rate of 0.03-1 mL/min into center flow compartment
Anolyte recirculation rate: DI	water, 8–12 mL/min
Anion membrane	
Dioxide Materials Sustainion [™] X	K37 imidazolium-based anion exchange membrane:
60-80 micron thickness (wet), i	on exchange capacity of 1.05 mEq/g (950 EW), membrane conductivity in water, through plane, of about 60–70 mS cm $^{-1}$
Cation membranes	
DuPont Nafion® Membranes Tes	sted: 212, 115, 324
Cell active membrane geomet	ric area: 5 cm ²

Cell operating temperature: Ambient, 20–25 °C

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Sigma–Aldrich); Dow Amberlite[®] IRN-77 (ion exchange resin, nuclear grade, VWR Scientific); Duolite[®] Resin C433 (Alfa Aesar); Dupont Nafion[®] 115, 212, and 324 membranes (Ion Power Inc.). Liquid CO₂ (NuCO₂, Stuart, FL) was used as the gas supply and vaporized for use in the lab.

2.3.3. Analytical

Formic acid concentrations were determined by titration using a 0.1 N standardized NaOH reagent, phenolphthalein indicator, and a Class A 50 mL buret. Formic acid sample size weights/volumes for the titration were sized large enough to obtain titration volumes of about 20 mL or more, so as to minimize the error in the formic acid concentrations to less than 1%.

2.4. Formic acid cell compartment reactions and ion transport

The formic acid cell has a complex set of reactions that occur at the anode, the GDE cathode, and the center flow compartment. The center

flow compartment is bounded by a cation exchange on the anode side and an anion exchange membrane on the cathode side. Fig. 4 shows the proposed main and secondary reactions as well as ion transport that may occur during cell operation.

2.4.1. Main reaction

The electrochemical reduction of CO_2 starts when CO_2 reacts with water on the cathode forming formate (HCOO⁻) and hydroxide (OH⁻) ions:

$$CO_2 + H_2O + 2e^- \rightarrow HCOO^- + OH^-$$
 (1)

Simultaneously, the oxidation of water occurs at the anode, forming oxygen gas and protons (H^+) :

$$2H_2O \to 4H^+ + 4e^- + O_2 \tag{2}$$

Both the formate ions and hydroxide ions migrate through the anion exchange membrane into the center flow compartment where they meet the protons produced from the anode compartment which pass



Fig. 2. Formic acid cell experimental test system set-up.



Fig. 3. Formic acid cell exploded isometric assembly drawing.



Fig. 4. Formic acid cell configuration showing proposed electrochemical reactions and ion transport.

through the cation membrane to yield formic acid and water:

$$\mathrm{H}^{+} + \mathrm{OH}^{-} \to \mathrm{H}_{2}\mathrm{O} \tag{3}$$

 $\mathrm{H}^{+} + \mathrm{HCOO}^{-} \rightarrow \mathrm{HCOOH}$ (4)

2.4.2. Side reactions

Side reactions that can occur on the cathode:

$$CO_2 + H_2O + 2e^- \to CO + 2OH^-$$
 (5)

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$$
 (6)

$$CO_2 + OH^- \to HCO_3^- \tag{7}$$

The bicarbonate ion (HCO_3^-) can move through the anion exchange membrane where it reacts with protons produced on the anode to produce CO_2 :

$$\mathrm{H}^{+} + \mathrm{HCO}_{3}^{-} \rightarrow \mathrm{CO}_{2} + \mathrm{H}_{2}\mathrm{O} \tag{8}$$

Formic acid losses by oxidation at the anode:

$$2\text{HCOOH} + \text{O}_2 \rightarrow 2\text{CO}_2 + 2\text{H}_2\text{O} \tag{9}$$

2.5. Center flow compartment conductive media selection

The 3-compartment formic acid cell design requires a thin center flow compartment spacing and a high-conductivity electrolyte to minimize the cell IR drop. The conductivity of aqueous formic acid alone, without any added acid or anion salt carrier such as sulfate or bicarbonate, is extremely low, only being between 5 and 10 mS cm⁻¹ for formic acid concentrations ranging between 5 and 20 wt% (see Fig. S4). A higher-conductivity electrolyte was required to minimize the IR resistance across the thin center flow compartment. We decided on using an ion exchange resin media fill to improve the electrolyte/ solution conductivity.

The use of an ion exchange media to improve cell voltage and performance in electrochemical cells has been successfully employed in electrodeionization [47–52], electrodialysis [53,54], and other electrochemical systems [55,56].



Fig. 5. Graphic plot of the conductivity of hydrogen form ion exchange resin slurries saturated with water and various formic acid concentration solutions.

In order to determine suitable ion exchange resin media for the cell, the ionic conductivity of four types of ion exchange resin media were experimentally measured in water and in 5, 10, 15 and 20 wt% formic acid solutions. The hydrogen-form resins (as received) were saturated with the various solutions and then carefully packed into the space between the conductivity probe and the sensor probe plastic shield. The Oakton Conductivity instrument has a plastic shield that has to be in place to correctly measure conductivity (see Fig.S6 in the Supporting Information to see the conductivity sensor and its plastic cover shield). The various ion exchange resin/saturated formic acid solution media mixture conductivities were then individually measured. The measured ionic conductivities of the aqueous resin media mixtures are detailed in Table S2 (Supporting Information) and are summarized graphically in Fig. 5.

The use of cation ion exchange resin media provided a substantial conductivity increase over aqueous formic acid alone. The ion exchange resin/formic acid matrix mixtures showed an increase in ionic conductivity over formic acid solutions alone by a factor of about 6–10. The hydrogen-form sulfonic acid resins, such as the Amberlite^{*} IR120 and the Dowex^{*} 50WX2, provided the highest ionic conductivities. Amberlite^{*} IR120 was chosen as the primary center flow compartment ion exchange material for testing in the formic acid cell center flow compartment in our experimental runs. Dowex^{*} 50WX2, which has a very fine median particle size range of 100–200 mesh (75–150 µm) demonstrated a very high pressure drop in the center flow compartment when evaluated, and was not further utilized in the experiments.

2.6. Cation ion exchange membrane selection

The 3-compartment formic acid cell design required the selection of a suitable cation ion exchange membrane. The fundamental requirements for the cation exchange membrane are that it have a high ionic conductivity, resistance to oxidation reactions at the anode, and ability to block or limit the transport of formic acid/formate ions into the anode compartment. Typical low-cost hydrocarbon based cation membranes, such as those employed in electrodialysis systems, such as those produced by Tokuyama Soda under the Neosepta[®] trade name as well as other manufacturers, are not resistant to oxidation. The only type of membranes that are both highly conductive and have a high oxidation resistance are the PFSA based membranes, such as those sold by DuPont under the Nafion[®] trademark as well as other brands sold by other various manufacturers worldwide. PFSA membranes are available in different thicknesses, equivalent weights (EW), and with/without an internal fabric/mesh reinforcement.

2.7. Sustainion[™] anion exchange membrane

The Sustainion[™] membrane used in the formic acid cell is based on the development of a series of new proprietary anion exchange membranes. These membranes have a stable polystyrene backbone that has been functionalized with an imidazolium group, resulting in a unique membrane that is both very conductive and alkaline stable. Details of the synthesis and membrane are extensively discussed in recently issued patents and publications [55-62]. The electrochemical CO₂ reduction reaction, occurring with the tin catalyst on the cathode, is theorized to be facilitated by the addition of an imidazole-based ionomer incorporated into the cathode catalyst layer. The formation of a CO₂-imidazolium complex is proposed to lower the free energy required for the reduction reaction [63]. In addition, the Sustainion™ membrane at the membrane-cathode catalyst interface may also be involved in the reduction reactions. The Sustainion[™] membranes are also being used in other electrochemical cell applications, such as the reduction of CO₂ to CO and in water electrolysis cells, producing H₂ and O₂, where they allow electrochemical operation at very high current densities at low voltages [62-65].

3. Results and discussion

3.1. Single-pass operation cell performance

The formic acid cell was operated in two different modes, namely, a single-pass mode and a center compartment recirculation mode. In single-pass operation mode, DI water was directly metered into the center compartment using a syringe pump operating at selected flow rates. In a standard formic acid cell configuration using a graphite anode flow field and Nafion^{*} 115 membrane, the cell performance results are shown in Figs. 6 and 7. The calculated residence time in the center compartment ranged from about 4 min at the 0.05 mL flowrate and about 2 min at the 0.10 mL DI water flowrate using a ion exchange void volume value of about 40%.

In Fig. 6, we can see that the cell voltage increased with increasing current density, operating at a voltage of 3.15 V at 100 mA cm^{-2} and 3.75 V at a current density of 200 mA cm⁻². The high current density obtained at such relatively low cell voltages was largely attributed to utilizing a GDE cathode and SustainionTM anion membrane in the novel cell configuration described previously.

It was observed that the flow rate of DI water into the central compartment significantly affected the formic acid cell performance in terms of formic acid product concentration and Faradaic efficiency. Fig. 7 shows the formic acid concentration and Faradaic efficiency as a function of the center compartment flow rate in a typical single-pass operation mode having a graphite anode flow field, IrO₂-coated GDE



Fig. 6. Formic acid cell current density versus voltage profile for a typical cell configuration operated at different current densities in a single-pass operation mode into the center compartment at a DI water flow rate of 0.1 mL/min.



Fig. 7. Faradaic efficiency and formic acid concentration as a function of center compartment flow rate in single-pass operation mode with graphite anode flow field, IrO_2 coated GDE anode, and Nafion^{*} 115 membrane. Error bars show the range of results at the various flow rates.

anode, Sn GDE cathode and Nafion^{*} 115 membrane. At low flowrates, e.g. 0.05 mL/min, the cell produced about 9.7 wt% formic acid at a 47% Faradaic efficiency. The Faradaic efficiency improved with increasing flowrate, increasing to 88% at 0.5 mL/min. However, the formic acid product concentration was only about 2 wt% at this flowrate as shown in Fig. 7. A number of the experimental runs, more than 20, were conducted at the 0.05 mL/min and 0.10 mL/min flow rates to make comparisons with the other factors that we investigated in potentially improving the performance the formic acid cell. The runs were conducted for varying time periods ranging from 8 h to 120 h and longer. These factors included anode and cathode modifications, selection of ion exchange media employed in the center compartment, and the evaluation of various SustainionTM anion exchange membrane formulations.

Operationally, as the formic acid concentration in the cell center compartment increased, an increasingly larger fraction of the formic acid product might cross over into the cell anolyte compartment through the cation membrane where formic acid may be lost via reaction (8). Faradaic formic acid losses due to formic acid crossover and decomposition factors are further discussed in Section 3.5.

3.2. Recirculated center flow compartment mode operation cell performance

Cell performance using a recirculated mode operation, where various concentrations of formic acid were circulated through the center flow compartment for a period of time, was evaluated. Typically, formic acid concentration in the recirculated solution increased with time since there was no DI water added to the recirculation stream. However, the concentration increase slowed after several hours of operation, indicating a lower Faradaic efficiency. To further study the relationship between formic acid concentration and Faradaic efficiency, several formic acid solutions with different concentrations were used as starting solutions for the cell. The cell was then operated for a period of 2 h, and the final formic acid concentrations were determined by titration in calculating the Faradaic efficiency. As shown in Table 2, the Faradaic efficiency decreased with higher formic

Table 2

Effect of formic acid concentration on Faradaic efficiency in the recirculated center flow compartment mode operation.

Starting formic acid concentration (wt%)	0	9.9	19.5
Final formic acid concentration (wt%)	2.3	11.2	20.4
Faradaic efficiency (%)	85	47	32

Table 3

ion.
io

Anode GDE, IrO_2 loading: 5 mg cm ⁻² on Toray paper, POCO graphite block with serpentine flow path Anolyte: Deionized water
Cathode
GDE, nanoparticle Sn, Sn loading: 5 mg/cm^2 with 5% PTFE, 5% carbon nanotubes, and 5% imidazolium-based ionomer
CO ₂ gas flow rate: 20 mL/min
Center flow compartment
Resin fill: Amberlite [®] IR120
DI water single-pass mode input flow rate: 0.03 mL/min
Anion membrane
Dioxide Materials Sustainion [™] X37 imidazolium-based anion membrane
Cation membrane
DuPont Nafion [®] 212
Cell active membrane projected area: 5 cm ²
Cell operating temperature: Ambient, 20-25 °C
Cell current density: 140 mA cm ⁻²

acid concentrations used in the starting solutions. For example, an 85% Faradaic efficiency was obtained by recirculating an initial volume of DI water solution through the center compartment. The solution increased to a 2.3 wt% formic acid concentration after 2 h. The Faradaic efficiency dramatically dropped to 47% when a starting 9.9 wt% formic acid solution was recirculated through the center compartment. The cell performance using a recirculation mode operation through the center compartment was found to be significantly lower as compared to single-pass operation mode in obtaining the same formic acid product concentration.

3.3. Formic acid cell extended time performance runs

A first extended formic acid cell run was conducted to determine cell voltage and performance stability over time. The detailed cell configuration is given in Table 3. The cell was continuously operated in a single-pass operation mode using deionized water for a total of about 550 h. The test results are shown in Fig. 8.

The formic acid cell voltage was found to be surprisingly stable, operating in a range of 3.3–3.4 V over 550 h of operation. The formic acid concentration gradually decreased with time, starting at an 18 wt % concentration and decreasing to 15 wt% after 550 h. The formic acid cell average Faradaic efficiency was determined to be only about 30% during the run. The cell performance agreed with the trend in Fig. 8, where the cell operates at lower Faradaic efficiencies when producing a very high formic acid product concentration at specified flow rates in single-pass operation mode. The formic acid cell, on disassembly, was



Fig. 8. First extended run formic acid cell performance using graphite flow field, nanoparticle Sn cathode GDE, Nafion * 212 cation membrane, and IrO₂ coated GDE

Table 4

Table 4 Second formic acid cell extended time run electrolyzer configuration.
Anode
Titanium Grade 2 anode block with serpentine flow path. Anode screen having
IrO ₂ -based metal oxide coating on expanded titanium (Water Star) was spot welded onto the titanium anode block
Anolyte: Deionized water
Cathode
GDE, nanoparticle Sn, Sn loading: 5 mg cm $^{-2}$
5 wt% PTFE, 5 wt% carbon nanotubes,, 5 wt% imidazolium-based ionomer
CO ₂ gas flow rate: 20 mL/min
Anion membrane
Dioxide Materials Sustainion™ X37 imidazolium-based anion membrane
Cation membrane
DuPont Nafion [®] 324
Center flow compartment

Resin fill: Amberlite^{*} IR120 DI water single-pass mode input flow rate: 0.10 mL/min Cell operating temperature: Ambient, 20–25 °C Cell active membrane projected area: 5 cm² Cell current density: 140 mA cm⁻²

found to have significant oxidation erosion in several locations of both

the graphite anode graphite flow field and GDE. A big potential Faradaic efficiency loss factor in the formic acid cell is the significant transport of formate ions into the anode compartment

is the significant transport of formate ions into the anode compartment through the cation membrane. The effect of cation membrane selection is discussed in Section 3.4.

A second extended time cell run was conducted, but instead using a Ti metal anode flow field and an IrO_2 -based coating on expanded titanium which was spot welded onto the Ti anode flow field. This anode configuration would negate any anodic oxidation issues related to the use of a graphite flow field/carbon paper based GDE as anode substrates when generating oxygen. A Nafion^{*} 324 membrane was also evaluated in the testing in looking at reducing formic acid crossover as discussed in Section 3.4.

The detailed results of the revised formic acid cell configuration and cell performance are presented in Tables 4 and 5 and in Fig. 9. After 142 h of operation, the cell voltage increased from 3.3 V to 3.7 V. Surprisingly, the concentration of the formic acid product increased with time, starting at a concentration of 8.1 wt% concentration and increasing to 9.4 wt% after 142 h of operation.

The improvement in cell performance is also reflected by the improved Faradaic efficiency as shown in Table 5. The cell Faradaic efficiency started at 80.5% and increased to 94.0% at the end of the cell run. On disassembly, the cell anode indicated no anode or cathode deterioration. The significant improvement in the cell formic acid Faradaic performance may be the combined outcome of using both the Nafion^{*} 324 membrane and the IrO_2 -based titanium anode on the Ti flow field.

3.4. Formate ion transport into anode compartment

As mentioned above in Sections 3.1 and 3.3, the transport of formate ions into the anode compartment through the cation exchange membrane may be a significant potential source of Faradaic efficiency loss in the formic acid cell.

In order to determine the amount of formate ion transport through the cation exchange membrane into the anolyte compartment, with subsequent oxidation at the anode, two tests were conducted. Analysis of the recirculating anolyte solution during a number of the runs

Table 5

Faradaic efficiency of 142 h extended cell run with titanium flow field and IrO_2 coated titanium mesh anode and Nafion^{*} 324 membrane.

Cell operation in hours	3.4	25.5	47.2	119.6	142
Faradaic efficiency	80.5%	81.0%	82.0%	91.8%	94.0%



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Fig. 9. Second extended run cell performance using a titanium flow field, IrO_2 coated titanium mesh anode, and Nafion^{*} 324 membrane.

showed only small traces of formic acid, but this would not be a definitive determination of formic acid transport into the anode compartment since all of the transported formate could be oxidized immediately at the anode. A better method would be to determine the amount of CO_2 produced by the oxidation of formate ions that would be present in the anolyte oxygen product gas stream. Table 6 shows the data on the area ratio of CO_2 and O_2 found in the anolyte gas by GC with the cells operating at formic acid product concentrations and using various cation membranes selected in the tests.

From the data, the thickness of the Nafion PFSA type cation membranes was found to be a critically important factor in minimizing the transport of formate ions through the membrane into the cell anolyte compartment. The thinner Nafion[®] 212 was initially chosen in our experimental runs (the 500 h extended run) to obtain lower cell voltages, but this data showed that the transport of formic acid through a thicker membrane was significantly reduced, and thus an important factor in achieving improved formic acid cell Faradaic performance.

Nafion^{*} 324, which is a bilayer PFSA membrane having an 1100 EW and a 1500 EW layer, showed the lowest transport of formate ion into the anolyte, and would be the preferred cation membrane for use in the formic acid cell.

The permeation rate of formic acid based on Nafion^{*} membrane thickness has been previously reported [66]. Nafion^{*} 112 showed a 2–3 times higher formic acid flux rate than Nafion^{*} 117 (178 μ m thickness) in a two compartment permeation cell having formic acid on one side of the membrane and deionized water in the other compartment. The permeation cell was not used in an operating electrochemical cell. The amount of the swelling of the Nafion^{*} ionomer at high concentrations of formic acid was cited as a factor in the formic acid permeation or flux rate.

Table 6

Summary of GC analysis results of the formic acid cell anolyte gases using different cation membranes when operating the center flow compartment at various formic acid concentrations.

Membrane	Membrane thickness (µm)	Formic acid concentration (wt%)	$A_{\rm CO_2}/A_{\rm O_2}$
DuPont Nafion [®] 212	50.8	15	2.3
DuPont Nafion®	127	5	0.29
115		8.7	0.31
		15.6	0.56
		16.8	0.70
DuPont Nafion [®] 324	150	8.5	0.03

We propose that the dramatically reduced formic acid transport that we found using the Nafion[®] 324 was due to the ionomer properties of the Nafion[®] 1500 EW membrane layer. This membrane polymer has a much lower water content than the other Nafion[®] membranes that we evaluated and would have a reduced number of sulfonic acid functional groups per gram of ionomer. This ionomer environment should slow down the transport of the negatively charged formate anions. In addition, as is well known, formic acid at higher concentrations forms formate–formate dimers, which can form neutral charged molecules. Neutral molecules can easily pass through membranes. The formic acid conductivity versus concentration curve, as shown in Fig. S4 in the supporting information, shows a conductivity maxima at about 30 wt% formic acid. Formic acid concentrations above 30 wt% should show increasing concentrations amounts of the neutral formic acid dimer species.

3.5. Gas formation in center flow compartment

Gas bubbles were observed in the formic acid solution product stream exiting the cell center flow compartment. One potentially formed gas is CO_2 , which may be produced by the transport of carbonate ions (CO_3^-) or carbonic acid from the cathode compartment through the anion membrane into the center flow compartment. These carbonate and bicarbonate species should decompose to CO_2 in the low pH environment of the formic acid/strong acid ion exchange media in the center flow compartment. Other gases that may be generated are CO and H₂ from the potential decomposition of formic acid in the center flow compartment. Strong acidic conditions exist in the hydrogen form cation exchange resin at the cation exchange membrane interface, where a large flux of protons is entering the center flow compartment.

Table 7 shows the GC analysis of the center flow compartment product gas. The data show that CO_2 was the predominant gas product, with small amounts of CO and H_2 . The total volume of CO_2 gas generated was not measured, so the total amount of formic acid decomposition into H_2 or CO could not be quantified.

No gases were noted in or exiting the center flow compartment when the current to the cell was shut off when the solution flow was continued through the compartment. In addition, no gases were evolved from any of the formic acid/strong acid ion exchange resin mixtures that were prepared in the ionic conductivity experiments in Section 2.5.

The decomposition of formic acid, whether by acid or catalytic decomposition routes, may occur by two different pathways [67,68] as in reactions (10) and (11).

$$HODOH → CO2 + H2$$
 ΔG = −48.4 kJ mol⁻¹ Decarboxylation

HCOOH → CO + H₂O $\Delta G = -28.5 \text{ kJ mol}^{-1}$ Dehydration(11)

The small amounts of CO and H_2 that were found in the center flow compartment off-gas were found in approximately equimolar amounts. It is well known that various catalysts, such as Pt and Pd, will decompose formic acid solutions according to reaction (10), producing CO₂ and H₂. The coproduction of some CO indicates that the decomposition reaction may have an equal selectivity where both products are formed. Decomposition reaction (11), forming CO and water, typically

Table 7

Cummon or a	of CC	opolyzoia	rooulto	ofa	a formation	in	the	contor	flow	aomnortmor	.+
Summary (01 00	anaiysis	results	UI ga	as iormation	ш	uie	center	110 W	compartmen	íL.
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Gas products from center flow compartment			Peak ar	ea from GC	analysis	$A_{\rm H_2}/A_{\rm CO_2}$	$A_{\rm CO}/A_{\rm CO_2}$
compartment			A _{H2}	$A_{\rm CO}$	$A_{\rm CO_2}$		
H_2	CO	CO_2	14.7	19.2	1465.3	0.010	0.013

occurs during acid decomposition of formic acid, for example when concentrated sulfuric acid is added to formic acid as a well-known laboratory method of generating CO.

Other potential sources of CO and H_2 , may be from the cathode compartment, as dissolved aqueous side-product species. The very low solubilities of CO (0.03 g/kg of water) and H_2 (0.0016 g/kg water) [69] make this unlikely, however. Gas permeation through the anion membrane from the catholyte reaction was also unlikely so long as the anion membrane was intact, having with no physical gas permeation.

The experimental results indicate that there may be some electrochemical formic acid decomposition reactions that may be occurring, most probably at the cation membrane interface with the center compartment ion exchange resin, which is the strongest acid location. A large flux of protons enters the center flow compartment at this interface. Potential formic acid losses may be about 10% or less based on the GC data in Table 7.

The formic acid product from the cell, ranging from 5 to 20 wt% on concentration, was found to be stable, showing no signs of gas evolution or solution decomposition during storage.

3.6. Formic acid cell compartment voltage potential measurements

The operating voltage potentials of the formic acid cell anode, center compartment, and cathode were measured to determine the voltage potentials in the cell and the voltage polarization plot for the cell. A voltage polarization plot for the cell was also conducted and shown in Fig. 10.

The formic acid cell measured potentials were as follows:Cell Open Circuit Voltage: 1.80 volts

Measurements made operating at 140 mA cm⁻² current density:

Anode Potential: 1.40 - 1.45 volts

Cathode Potential: 1.40 – 1.50 volts Center Compartment: 0.40 – 0.60 volts (voltage drop including both membranes)

Total cell volts: 3.40

Total cell resistance by impedance measurements: 800 m Ω .

The voltage polarization plot for the formic acid cell is shown Fig. 10. The voltage OCP (open circuit potential) was found to be about 1.80 V. There appears to be a mixed cathodic cell reaction occurring at cell voltage potentials between 1.8 and 3.0 V, at current densities of $0-40 \text{ mA cm}^{-2}$.



Fig. 10. Cell voltage polarization plot of the formic acid cell.

3.7. Formic acid cell operation using a hydrogen-consuming anode

The formic acid cell was configured with a hydrogen-consuming anode to determine the lowest possible cell voltage that could be obtained, in addition to getting further confirmation of the cell operating cathode potentials. For this purpose, a Pt/C catalyst instead of IrO₂ catalyst was deposited onto a Nafion^{*} 115 membrane as well as the GDE anode. Other components were the same as those used in the formic acid cell assemblies previously described. The cell was operated at a voltage of 1.83–1.88 V at a current density of 160 mA cm⁻² (800 mA current) continuously for a period of 68 h. The measured cathode potential, when operating the cell at 140 mA cm⁻², was measured to be in the range of -1.38 V to -1.48 V, which was consistent with the cell cathode potential measurements detailed in Section 3.6. The formic acid cell, operating in a single-pass operation mode with a water flowrate of 0.10 mL/min, produced a 9.2 wt% formic acid product at a Faradaic efficiency of 81%.

4. Summary

A novel 3-compartment electrochemical cell design with the capability of generating a pure formic acid product from the reduction of CO2 is detailed. The cell configuration consisted of an anode compartment, a center flow compartment containing a cation exchange resin electrolyte bounded by a PFSA cation exchange membrane on the anode side and a proprietary Sustanion[™] anion exchange membrane on the cathode side, and an imidazole-nanoparticle Sn catalyst-based GDE in the cathode compartment. The Sustainion[™] anion membrane used in the formic acid cell has a stable polystyrene backbone that is functionalized with an imidazolium functional group, resulting in a membrane that is both very conductive and alkaline stable. The addition of an imidazole-based ionomer into the nanoparticle Sn based cathodecatalyst enabled CO₂ reduction reaction at the cathode GDE-anion membrane interface. The electrochemical cell operated at a current density of 140 mA cm⁻² range at a cell voltage of only 3.5 V with formic acid Faradaic efficiencies of up to 94%. High formic acid Faradaic efficiencies were found to be critically dependent on the selection of the cation membrane utilized on the anolyte compartment side of the cell. Thicker Nafion membranes were effective in minimizing crossover formate ion losses into the anode compartment. Nafion® 324 was found to provide the lowest formate/formic acid crossover into the anolyte compartment. Two modes of cell operation, a center compartment single-pass versus recirculation modes were investigated, with the single pass mode being preferred. The novel formic acid cell design indicates a potential route for future commercial use of formic acid as a sustainable chemical feedstock for generating downstream chemicals, as well being a viable chemical-based energy storage medium in hydrogen storage/generation.

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The authors filed a U.S. patent application on the electrochemical process and designs discussed here, which was recently published [70]. The authors all have a financial stake in the outcome on the sale of the Sustainion^m membranes discussed.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jcou.2017.04.011.

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