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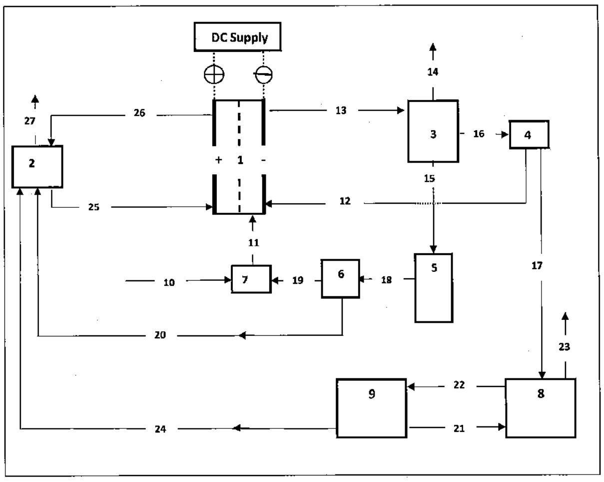
Figure 2. Formic acid – by ERC. Ammonia recycle process



(57) Abstract: A process for the conversion of carbon dioxide to formic acid by an integrated series of electrochemical and thermo-chemical reactions. Carbon dioxide is reduced to ammonium formate in an electrochemical reactor and the ammonium formate is converted to formic acid in a thermochemical reactor. The process recycles all intermediate reaction products to achieve the net conversion of carbon dioxide and water to formic acid and oxygen.

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Title of the Invention

PROCESS FOR THE CONVERSION OF CARBON DIOXIDE TO FORMIC ACID

Field of the Invention

This invention pertains to the field of processes for the electro-chemical reduction of carbon dioxide, in particular, an improved process for the electro-reduction of carbon dioxide to produce formic acid.

Background of the Invention

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It is well known that carbon dioxide can be converted to formate salts by electro-chemical reduction in processes such as those described in references 1 to 7. However, the development of such processes for continuous operating in commercial use is hindered by inherent aspects of their chemistry. First, the CO_2 feed to the process must be recovered and concentrated from industrial waste gas streams. Second, the electro-chemical reaction generates bicarbonate salts that consume reactants and present a disposal problem. Third, to obtain practical concentrations of formate salts the catholyte must be recycled, with resulting problems due to the accumulation of bicarbonate salts in the catholyte loop. Further, the direct electro-reduction of CO_2 to formic acid (H_2CO_2) is difficult. Many authors erroneously report the production of "formic acid" from ERC (Reference 5, pages 102-109) when in fact the product is a formate salt, such as potassium formate $KHCO_2$. This egregious misrepresentation comes from experimental work on ERC at $pH > 6$ where formic acid, with an acid dissociation constant of 1.6E-4 at 20 ^oC, cannot exist at equilibrium in aqueous solution at a concentration above about 1E-8 molar.

These issues are partially recognized in the prior art; for example, in reference 1, the bicarbonate salt is separated from the recycling catholyte by crystallization; while in reference 2, the formate salt from ERC is concentrated and/or converted to formic acid by secondary processes such as salt splitting, electro-dialysis, or nano-filtration. However none of the prior art recognizes the commercial significance of the issues surrounding bicarbonate, and engages their resolution in a single integrated system for the production of formic acid.

Summary of the Invention

The present invention is an improved process for electro-reduction of CO_2 (ERC) to obtain formic acid, which resolves the problems of CO_2 feed gas concentration and bicarbonate disposal, while consuming only carbon dioxide and water.

In some aspects, the present invention provides an electrochemical process producing formic acid wherein ammonium formate is used as an intermediary in the conversion of carbon dioxide and water to formic acid in an electrochemical reactor. In another aspect, the ammonium formate is generated in a catholyte in the electrochemical reactor.

In another aspect, the ammonium formate is reacted with an acid ammonium salt to produce said formic acid.

In another aspect, the ammonium formate is reacted with an acid ammonium salt to obtain formic acid and an ammonium salt, separating said formic acid and decomposing said ammonium salt to obtain ammonia.

In another embodiment, the invention comprises a process for the conversion of carbon dioxide and water to formic acid in an electrochemical reactor comprising the electrochemical conversion of carbon dioxide and water to ammonium formate; and the reaction of ammonium formate with an acid ammonium salt to produce formic acid.

In another aspect, the ammonium formate is accompanied by ammonium bicarbonate which is subsequently decomposed to ammonia and carbon dioxide for recycle within the process.

In another aspect, the produced formic acid is accompanied by an ammonium salt which is subsequently decomposed to ammonia and an acid ammonium salt for recycle within the process.

In another embodiment, the invention comprises a process for producing formic acid from carbon dioxide that comprises the steps of:

a. the electrochemical conversion of carbon dioxide to ammonium formate and ammonium bicarbonate in an electrochemical reactor;
b. the separation and decomposition of ammonium bicarbonate to ammonia and carbon dioxide, which are recycled to said electrochemical reactor;
c. reaction of the ammonium formate with an acid ammonium salt to generate and separate the product formic acid and forming an ammonium salt;
d. decomposition of said ammonium salt from step c into an acid ammonium salt and ammonia;
e. recycle of the acid ammonium salt from step d to step c; and
f. recycle of the ammonia from step d to the electrochemical reactor of step a.

In another aspect, the acid ammonium salt is ammonium hydrogen sulphate or ammonium hydrogen phosphate. The ammonium salt is ammonium sulphate or ammonium phosphate.

In another aspect, the present invention provides an electrochemical process for conversion of carbon dioxide to ammonium formate comprising the separation of ammonium bicarbonate from a recycling catholyte, decomposing the ammonium bicarbonate to ammonia, and recycling the ammonia within the process.

In another aspect, the present invention provides an electrochemical process for conversion of carbon dioxide to ammonium formate comprising the separation of ammonium bicarbonate from a recycling catholyte, decomposing the ammonium bicarbonate to carbon dioxide, and recycling the carbon dioxide within the process.

In another aspect, the present invention provides an electrochemical process for the conversion of carbon dioxide to ammonium formate and formic acid that includes the separation of ammonium formate from a recycling catholyte and converting the ammonium formate to formic acid. In another aspect, the ammonium bicarbonate is separated from the recycling catholyte by crystallization.

Brief Description of the Drawings

Figure 1 shows a conceptual flowsheet of a generic continuous process for the electro-reduction of CO_2.

Figure 2 shows a conceptual flowsheet of a process for the electro-reduction of CO_2 (ERC), according the present invention, to produce formic acid. The process converts CO_2 to ammonium formate by electrochemical reaction. The ammonium formate is subsequently converted to formic acid by thermochemical reaction. The process recycles all intermediate reaction products so as to effectively convert carbon dioxide and water to formic acid and oxygen.

Figure 3 shows the experimental result for Example 3.

Figure 4 shows the experimental result for Example 4.

Detailed Description of the Invention

Figure 1 shows a process for the electrochemical reduction of carbon dioxide to obtain CO_2 reduction products by cathode reactions with the generic form:

$$xCO_2 + (y-2(z-2x))H^+ + ye^- \rightarrow CxHyOz + (z-2x)H_2O \qquad \text{Reaction 1}$$

where x, y and z may take integer values respectively of 1 to 3, 0 to 8 and 0 to 2, as exemplified in **Table 1.**

Table 1

x	y	z	CxHyOz	Name
1	4	0	CH_4	methane
2	4	0	C_2H_4	ethene
2	6	0	C_2H_6	ethane
1	0	1	CO	carbon monoxide
1	2	2	CH_2O_2	methanoic acid
1	1	2	CHO_2^-	methanoate
1	4	1	CH_4O	methanol
1	2	1	CH_2O	methanal
2	6	1	C_2H_6O	ethanol

The process of **Figure 1** has an electrochemical reactor **A** where carbon dioxide (CO_2) is reduced according to Reaction 1, along with the associated reactor feed, recycle and product separation systems.

In **Figure 1** the electrochemical reactor **A** may have single or multiple electrochemical cells of parallel plate or cylindrical shape, wherein each cell is divided into an anode chamber with anode **B** and a cathode chamber with cathode **C** by a separator **D**. An electric power source **E** supplies direct current to the reactor at a voltage about 2 to 6 Volt/cell. The process uses anode and cathode feed tanks **F** and **G** along with the respective product separators **H** and **I.** In the continuous process an anode fresh feed **J**, optionally mixed with recycle **U**, forms anolyte liquid **K** which is passed to the anode chamber **B** where it is converted to anode output **L**, to be subsequently separated to products **M** and **N** and an optional anolyte recycle **U**. Meanwhile a cathode fresh feed **O**, optionally mixed with recycle **V**, forms catholyte liquid **Q** which is mixed with CO_2 gas **P** and passed to the cathode chamber **C** where the mixture (**P+Q**) is converted to cathode output **R**, to be subsequently separated to products **S** and **T** and an optional catholyte recycle **V**.

In the reactor **A**, the cathode **C,** where the CO_2 is reduced, includes a porous electrode with an electro-catalytic specific surface in the range about 100 to 100,000 m^2/m^3, which may include nano-structured surface embellishments, and may be in the form of a reticulate, foam, felt, matt, mesh, frit, fixed-bed, fluidized-bed, gas diffusion electrode (GDE), solid polymer electrode (SPE) or the like. The cathode is fed by a mixture of a CO_2 containing gas **P** and a catholyte liquid solution **Q** in a volumetric flow ratio from about 10 to 1000, measured at 1 bar(abs), 273 K. The gas **P** and liquid **Q** may be introduced separately to the cathode, or mixed before entering the cathode, then pass through the cathode in two-phase co-current flow. The co-current fluid (**P+Q**) flow path through the porous cathode may be preferably in the so-called "flow-by" mode with fluid flow orthogonal to the electric current or optionally in the so-called "flow-through" mode with fluid flow parallel to the electric current. The reactor may be oriented horizontally or sloped or preferably vertically, with the cathode fluid (**P+Q**) flow preferably upward but optionally downward. The separator **D** may be a layer of an electronically non-conductive material that is inherently ionically conductive, or made ionically conductive by absorption of an electrolyte solution. The preferred separator is an ion selective membrane such as those sold under the trade names Nafion, Fumasep, VANADion, Neosepta and Selemion and PEEK as detailed in **Table 4**, and is preferably a cation exchange membrane (CEM) such as Nafion N424, with a selectivity above about 90%. The separator may also include a layer of porous hydrophilic material such as asbestos, Zirfon^{R}Perl (Agfa-Gevaert N.V.), Scimat (Freudenberg NonWovens), Celgard (Celgard LLC) and like materials used as separators in water electrolysers and electric batteries.

Depending on the desired anode products **M,N,U** and process conditions the electronically conductive anode material may be selected from those known to the art, including for example nickel, stainless steel, lead, conductive oxide (e.g. PbO_2, SnO_2), diamond, platinised titanium, iridium oxide and mixed oxide coated titanium (DSE), and the like. The anode may be a two-dimensional electrode or a three-dimensional (porous) electrode in the form of a reticulate, foam, felt, matt, mesh, frit, fixed-bed, fluidized-bed, gas-diffusion (GDE) or solid-polymer electrode (SPE).

The desired cathode products **S,T,V** and process conditions determine the choice of the electronically conductive cathode electro-catalyst material(s), which may be selected from the exemplary lists in **Tables 2 and 3**.

The anode reaction is complimentary to the cathode electro-reduction reaction 1 and may be chosen from a wide range of electro-oxidations exemplified by reactions 2 to 10.

		Product
$4OH^- \rightarrow O_2 + 2H_2O + 4e^-$	Reaction 2	oxygen
$2Cl^- \rightarrow Cl_2 + 2e^-$	Reaction 3	chlorine
$2SO_4^{2-} \rightarrow S_2O_8^{2-} + 2e^-$	Reaction 4	persulphate
$2CO_3^{2-} \rightarrow C_2O_6^{2-} + 2e^-$	Reaction 5	percarbonate
$2H_2O \rightarrow O_2 + 4H^+ + 4e^-$	Reaction 6	oxygen
$C_6H_6 + 2H_2O \rightarrow C_6H_4O_2 + 2H^+ + 2e^-$	Reaction 7	benzoquinone
$C_8H_{10}O + H_2O \rightarrow C_8H_8O_2 + 4H^+ + 4e^-$	Reaction 8	methoxybenzaldehyde
$H_2 \rightarrow 2H^+ + 2e^-$	Reaction 9	proton
$CH_4 + H_2O \rightarrow CH_4O + 2H^+ + 2e^-$	Reaction 10	methanol

The primary reactants at the anode may be soluble ionic species as in reactions 2 to 5, neutral species as in reactions 6 to 10, "immiscible" organic liquids as in reactions 7 and 8 or gases as in reactions 9 and 10. Immiscible liquid and gas reactants, along with an aqueous liquid anolyte, may engender multi-phase flow at the anode which may include respectively a gas/liquid foam or liquid/liquid emulsion.

The anolyte **K** may be a non-aqueous solution of an electrolyte, but preferably an aqueous solution of an acid or base and/or salt with alkali metal or ammonium cations. Corresponding reagents may be for example: sulphuric, hydrochloric, hydrobromic, phosphoric or methanesulphonic acid; sodium, potassium, rubidium, caesium or ammonium hydroxide or a sodium, potassium, rubidium, caesium, or ammonium salt of the above acids. The anolyte may optionally include species to be engaged in oxidative redox couples, such as Ag^{2+} / Ag^{1+}, Ce^{4+}/ Ce^{3+} , Co^{3+} / Co^{2+} , Fe^{3+} / Fe^{2+} , Mn^{3+} / Mn^{2+}, V^{5+} / V^{4+} , organic couples such as quinone/hydroquinone and the like, in bare, complexed or chelated forms, with a redox potential matched to that of the desired anode process.

The desired cathode products **S,T,V** and process conditions determine the choice of the electronically conductive cathode electro-catalyst material(s), which may be selected from the exemplary lists in **Table 2** or from organo-metal complexes of cobalt, copper, iron, nickel, palladium and rhenium such as those in **Table 3,** on electronically conductive supports.

Table 2. Cathode metal electro-catalyst materials

FORMATE AND FORMIC ACID PRODUCTION			
Bismuth/Aluminum	High Purity Bismuth	Indium/Tin Alloy	Tin/Cadmium Alloy
Bismuth/Antimony Alloy	High Purity Cadmium	Lead/Aluminum Alloy	Tin/Rhodium Alloy
Bismuth/Cadmium Alloy	High Purity Indium	Lead/Antimony Alloy	Tin/Tantalum Alloy
Bismuth/Indium	High Purity Lead	Lead/Cadmium Alloy	Titanium/Antimony Alloy
Bismuth/Lead Alloy	High Purity Tin	Lead/Rhodium Alloy	Titanium/Bismuth Alloy
Bismuth/Tantalum Alloy	Indium/Aluminum Alloy	Lead/Tantalum Alloy	Titanium/Cadmium Alloy
Bismuth/Tin Alloy	Indium/Antimony Alloy	Lead/Tin Alloy	Titanium/Indium Alloy
Cadmium/Aluminum Alloy	Indium/Cadmium Alloy	Leaded Nickel Alloy	Titanium/Lead Alloy
Cadmium/Antimony Alloy	Indium/Lead Alloy	Tin/Aluminum Alloy	Titanium/Tin Alloy
Cadmium/Tantalum Alloy	Indium/Tantalum Alloy	Tin/Antimony Alloy	
CO PRODUCTION			
Gallium/Aluminum Alloy	High Purity Gallium	Palladium/Silver Alloy	Waspaloy Superalloy
Gallium/Antimony Alloy	High Purity Gold	Palladium/Tantalum Alloy	Zinc/Aluminum Alloy
Gallium/Tantalum Alloy	High Purity Palladium	Palladium/Zinc Alloy	Zinc/Antimony Alloy
Gold/Aluminum Alloy	High Purity Silver	Silver/Aluminum Alloy	Zinc/Gallium Alloy

Gold/Antimony Alloy	High Purity Zinc	Silver/Antimony Alloy	Zinc/Nickel Alloy
Gold/Gallium Alloy	Palladium/Aluminum Alloy	Silver/Gallium Alloy	Zinc/Tantalum Alloy
Gold/Silver Alloy	Palladium/Antimony Alloy	Silver/Nickel Alloy	
Gold/Tantalum Alloy	Palladium/Gallium Alloy	Silver/Tantalum Alloy	
Gold/Zinc Alloy	Palladium/Gold Alloy	Silver/Zinc Alloy	
HYDROCARBON PRODUCTION			
Copper/Aluminum Alloy	Copper/Tantalum Alloy	Titanium Superalloy	Titanium/Nickel Alloy
Copper/Antimony Alloy	High Purity Copper	Titanium/Aluminum Alloy	Titanium/Tantalum Alloy
Copper/Nickel Alloy	High Purity Titanium	Titanium/Antimony Alloy	
Copper/Nickel/Tin Alloy	Titanium Metal Matrix Composite	Titanium/Copper Alloy	

Table 3. Organo-metal electro-catalysts

Organometallic Complexes:		
Name	**Title of Paper**	**Products**
$[Ru(bpy)_2(CO)_2]^{2+}$	Electrochemical CO2 reduction catalyzed by ruthenium complexes [Ru(bpy)2(CO)2]2+ and [Ru(bpy)2(CO)Cl]+. Effect of pH on the formation of CO and HCOO-	CO, $HCOO^-$
$[Ru(bpy)_2(CO)Cl]^+$	Electrochemical CO2 reduction catalyzed by ruthenium complexes [Ru(bpy)2(CO)2]2+ and [Ru(bpy)2(CO)Cl]+. Effect of pH on the formation of CO and HCOO-	CO, $HCOO^-$
$[Re(dmb)(CO)_3]_2$	Involvement of a Binuclear Species with the Re−C(O)O−Re Moiety in CO_2Reduction Catalyzed by Tricarbonyl Rhenium(I) Complexes with Diimine Ligands: Strikingly Slow Formation of the Re−Re and Re−C(O)O−Re Species from Re(dmb)$(CO)_3$S (dmb = 4,4'-Dimethyl-2,2'-bipyridine, S = Solvent)	CO
Iron Porphyrin	Electrocatalytic and Homogeneous Approaches to Conversion of CO2 to liquid Fuels	CO

$Re(bipy)(CO)_3Cl$	Electrocatalytic and Homogeneous Approaches to Conversion of CO2 to liquid Fuels	CO
$Ph_3PCo(tpfc)$	Electrocatalytic and Homogeneous Approaches to Conversion of CO2 to liquid Fuels	CO
ClFe(tpfc)	Electrocatalytic and Homogeneous Approaches to Conversion of CO2 to liquid Fuels	CO
ClFe(tdcc)	Electrocatalytic and Homogeneous Approaches to Conversion of CO2 to liquid Fuels	CO
$[M(bpy)_2(CO)H]^+$ (M = Os, Ru)	Electrocatalytic and Homogeneous Approaches to Conversion of CO2 to liquid Fuels	CO, $HCOO^-$
$Rh(dppe)_2Cl$	Electrocatalytic and Homogeneous Approaches to Conversion of CO2 to liquid Fuels	$HCOO^-$
$[Pd(triphos)(PR_3)](BF_4)_2$	Electrocatalytic and Homogeneous Approaches to Conversion of CO2 to liquid Fuels	CO
$[Ni_3(\mu_3\text{-}I)(\mu_3\text{-}CNMe)(\mu_2\text{-}dppm)_3]^+$	Electrocatalytic and Homogeneous Approaches to Conversion of CO2 to liquid Fuels	CO, CO_3^{2-}
$[Cu_2(\mu\text{-}PPh_2bipy)_2\text{-}(MeCN)_2[PF_6]_2$	Electrocatalytic and Homogeneous Approaches to Conversion of CO2 to liquid Fuels	CO, CO_3^{2-}
$[Re(CO)_3(K^2\text{-}N,N\text{-}PPP)Cl]$	Electrocatalytic Reduction of Carbon Dioxide by a Polymeric Film of Rhenium Tricarbonyl Dipyridylamine	CO
4-tert-butylpyridinium	Using a One-Electron Shuttle for the Multielectron Reduction of CO2 to Methanol: Kinetic, Mechanistic, and Structural Insights	$HCOO^-$, CH_3OH, CH_2O
$[Ni(cyclam)]^{2+}$	Molecular Approaches to the Electrochemical Reduction of Carbon Dioxide	CO
$[Co(I)Porphyrin]^-$	Molecular Approaches to the Electrochemical Reduction of Carbon Dioxide	CO
Silver Pyrazole Supported on Carbon	Nitrogen Based Catalysts for the Electrochemical Reduction of CO2	CO
Silver Phthalocyanine Support on Carbon	Nitrogen Based Catalysts for the Electrochemical Reduction of CO2	CO

Silver tris[(2-pyridyl)methyl]amine	Nitrogen Based Catalysts for the Electrochemical Reduction of CO2	CO
Iron Tetraphenyl Porphyrin	A Local Proton Source Enhances CO2 Electroreduction to CO by a Molecular Fe Catalyst	CO
Iron 5, 10, 15, 20-terakis(2', 6'-dihydroxylphenyl)-porphyrin	A Local Proton Source Enhances CO2 Electroreduction to CO by a Molecular Fe Catalyst	CO
Iron 5, 10, 15, 20-tetrakis(2', 6'-dimethoxyphenyl)-porphyrin	A Local Proton Source Enhances CO2 Electroreduction to CO by a Molecular Fe Catalyst	CO

Table 4. Membrane materials

NAFION:				
Name	**Thickness (mm)**	**Type**	**Base Material**	**Note**
Nafion N115	0.127	CEM	Sulphonated Fluoropolymer	
Nafion N117	0.183	CEM	Sulphonated Fluoropolymer	
Nafion N1110	0.254	CEM	Sulphonated Fluoropolymer	
Nafion N324	0.152	CEM	Sulphonated Fluoropolymer	Teflon Reinforced
Nafion N424	0.178	CEM	Sulphonated Fluoropolymer	Teflon Reinforced
Nafion N438		CEM	Sulphonated Fluoropolymer	PTFE Monofilament Reinforced
VANADion:				
Name	**Thickness (mm)**	**Type**	**Base Material**	**Note**
VANADion 20	0.254	CEM	Fluoropolymer with Ionomer Coating	
VANADion 20L	0.254	CEM	Fluoropolymer with Ionomer Coating	Low Oil Composite Membrane
HYDRion:				

Name	Thickness (mm)	Type	Base Material	Note
HYDRion N115	0.127	CEM	Fluoropolymer with Iridium or Platinum Coating	
HYDRion N117	0.178	CEM	Fluoropolymer with Iridium or Platinum Coating	
HYDRion N1110	0.254	CEM	Fluoropolymer with Iridium or Platinum Coating	

Fumatech:

Name	Thickness (mm)	Type	Base Material	Note
Fumasep FKE	0.050-0.070	CEM	Fluoropolymer	Specifically for Electrolysis
Fumasep FKS	0.110-0.130	CEM	Polyethylene Terephthalate	
Fumasep FKB	0.080-0.100	CEM	Fluoropolymer	PEEK Reinforced
Fumasep FKL	0.110-0.120	CEM	Fluoropolymer	PEEK Reinforced
Fumasep FAB	0.100-0.130	AEM	Fluoropolymer	Very Low Resistance, PEEK Reinforced
Fumasep FAA-3-PK-130	0.130	AEM	Fluoropolymer	High Mechanical Strength, PK Reinforced
Fumasep FBM	0.200-0.250	BPM		Very High Effectiveness, High Mechanical Strength

NEOSEPTA:

Name	Thickness (mm)	Type	Base Material	Note
Neosepta CIMS	0.150	CEM		
Neosepta ACM	0.11	AEM		
Neosepta CMX	0.170	CEM		High Mechanical Strength
Neosepta AMX	0.140	AEM		High Mechanical Strength
Neosepta ACS	0.180	AEM		

Neosepta AFN	0.160	AEM		Very Low Resistance (0.5 ohms.cm2)
SELEMION Hydrocarbon:				
Name	**Thickness (mm)**	**Type**	**Base Material**	**Note**
SELEMION CMV	0.120	CEM	Ionomer	
SELEMION AMV	0.120	AEM	Ionomer	
SELEMION AMT	0.200	AEM	Ionomer	
SELEMION DSV	0.100	AEM	Ionomer	Very Low Resistance (~1 ohms)
SELEMION AAV	0.120	AEM	Ionomer	Low Proton Leakage
SELEMION ASV	0.120	AEM	Ionomer	Monovalent-Ion-Selective
SELEMION APS4	0.150	AEM	Ionomer	Oxidant-Proof

The catholyte **Q** may be a non-aqueous solution of an electrolyte, but preferably an aqueous solution of an acid or base and/or salt with alkali metal or ammonium cations. Corresponding reagents may be for example: sulphuric, hydrochloric, hydrobromic, phosphoric, methanesulphonic or formic acid; sodium, potassium, rubidium, caesium or ammonium hydroxide or a sodium, potassium, rubidium, caesium, or ammonium salt of the above acids, including the bicarbonate and carbonate salts. The catholyte may optionally include species to be engaged in reductive redox couples, such as, Cr^{3+} / Cr^{2+} , Cu^{2+} / Cu^{1+} , Sn^{4+} / Sn^{2+} , Ti^{3+} / Ti^{2+} , V^{3+} / V^{2+} , organic couples such as quinone/hydroquinone and the like, in bare, complexed or chelated forms, with a redox potential matched to that of the desired cathode process. In some cases the catholyte may contain chelating and/or surface active agents (surfactants) such as for example amino-carboxylates (e.g. EDTA, DTPA), phosphonates and quaternary ammonium salts.

The feed gas **P** may contain about 1 to 100 volume % CO_2 and the cathode reactant mixture (**P+Q**) may enter and/or traverse the porous cathode in a two-phase flow pattern such as described in reference 8 as: "bubbly", "plug", "slug", "dispersed" or "froth" (i.e. a foam).

Methods for separating the anode and cathode products may be; for example, gas/liquid or liquid/liquid disengagement, crystallization, filtration, liquid extraction, and distillation.

Figure 2 shows an embodiment of the process of Figure 1, in which formic acid is produced through the use of electrolytes comprising the ammonium cation (NH_4^+).The process of **Figure 2**, its main components and variants, are the basis for the present invention, which is described below.

In Figure 2 the items referenced by reference numerals **1** to **9** are process units specified as follows: an electrochemical reactor **1**, a mixer/separator **2**, a separator **3**, a divider **4**, a thermochemical reactor **5**, a separator **6**, a mixer **7**, a thermochemical reactor/separator **8**, and a thermochemical reactor/separator **9**. The reference numbers **10-27** refer to process streams whose functions are described below.

In this process the fresh CO_2 containing gas **10** is mixed with recycled CO_2 **19** in unit **7** , to give gas stream **11** which is fed to the cathode mixed (inside or outside the reactor) with a recycle ammonium bicarbonate/formate liquid catholyte solution **12.** The cathode product **13** is separated in unit **3** to a gas **14,** ammonium bicarbonate recycle solids **15** and ammonium formate solution **16,** part of which may be recycled to the catholyte **12**. In unit **5** the ammonium bicarbonate is decomposed to carbon dioxide, ammonia and water by reaction 11 which proceeds at a temperature above about 60 °C.

$NH_4HCO_3 \rightarrow CO_2 + NH_3 + H_2O$ Reaction 11

The mixed gas stream **18** is then separated to CO_2 gas **19** and an aqueous ammonia solution **20**. The CO_2 gas **19** is mixed with the fresh CO_2 **10** for recycle to the cathode in **11,** while the aqueous ammonia **20** is recycled to the anolyte loop via unit **2,** where it is mixed with ammonia **24** from unit **9** and anolyte recycle **26** to give the anode feed stream **25**. The anolyte **25** may include an acidic ammonium salt aqueous solution from which oxygen gas and protons are obtained by the anode reaction 6, while protons (H^+) and ammonium cations (NH_4^+) pass through the separator into the catholyte. For example, the anolyte may comprise sulphuric acid, ammonium sulphate and/or ammonium hydrogen sulphate (NH_4HSO_4) or the analogous phosphates (H_3PO_4, $(NH_4)_3PO_4$, $(NH_4)_2HPO_4$, $NH_4H_2PO_4$). In general the anolyte may comprise any acid and ammonium salt which undergoes thermal decomposition to ammonia in a reaction analogous to reaction 13 and whose anion is not electro-active under the prevailing conditions at the anode.

Alternatively the anolyte pH and the ammonium balance may be controlled through other electro-oxidation reactions, such as reactions 2 to 10 above, for example by generating chlorine in reaction 3 from an anolyte solution of ammonium chloride (NH_4Cl) and hydrogen chloride (HCl) or by producing benzoquinone by reaction 7 in an emulsion with sulphuric acid and ammonium sulphate.

For convenience the process described below uses anolytes based on sulphuric acid (H_2SO_4) with the sulphate (SO_4^{--}) and bisulphate (HSO_4^-) anions.

In some embodiments manipulating the concentrations of H^+ and NH_4^+ in the anolyte may be used to control the bulk catholyte pH. Control of the bulk catholyte pH, for example in the range about 5 to 9, may be desirable to avoid ammonia vapour losses and to maintain a high Faradaic efficiency for CO_2 reduction in the cathode.

In unit **8** the ammonium formate solution **17** from unit **4** is converted to formic acid by reaction 12, with ammonium hydrogen sulphate **21** recycled from unit **9**. The product formic acid **23** is separated from the reaction product mixture in unit **8** by means such as vacuum evaporation/distillation.

$NH_4HCO_2 + NH_4HSO_4 \rightarrow (NH_4)_2SO_4 + H_2CO_2$ Reaction 12

The ammonium sulphate from reaction 12 passes to unit **9** where it is decomposed to ammonium hydrogen sulphate and ammonia gas by reaction 13.

$(NH_4)_2SO_4 \rightarrow NH_4HSO_4 + NH_3$ Reaction 13

The reactions 12 and 13 occur respectively at about 100 ^oC and 150 to 300 ^oC and are preferably driven by waste heat from an associated process such as cement manufacture or power generation.

Ammonium hydrogen sulphate from unit **9** is recycled to unit **8** in stream **21** while the ammonia **24** is recycled to the anolyte loop via unit **2**. To promote reactions 12 and 13 streams **21** and **22** may include sulphuric acid and/or catalysts such as compounds of molybdenum or tungsten (e.g. ammonium molybdate or tungstate). The ammonia streams **20** and **24** together may be arranged to close the nitrogen balance (as NH_3 and/or NH_4^+) and thus allow the overall conversion of carbon dioxide in stream **10** to formic acid in stream **23,** according to the net reaction 14.

$CO_2 + H_2O \rightarrow H_2CO_2 + 1/2O_2$ Reaction 14

Optionally, the production of ammonium formate **17** according to the overall reaction 15 may be achieved by eliminating the process units **8** and **9** from the flowsheet of Figure 2.

$CO_2 + NH_3 + H_2O \rightarrow NH_4HCO_2 + \frac{1}{2} O_2$ Reaction 15

This method allows the production of ammonium formate with nearly stoichiometric conversion of CO_2 and NH_3 and H_2O to NH_4HCO_2 i.e. one mole CO_2 plus one mole NH_3 per mole NH_4HCO_2.

Example 1

A single-cell continuous parallel plate trickle-bed electrochemical reactor was assembled with superficial area dimensions of 0.1 m long by 0.01 m wide for both the anode and the cathode. The 3D cathode, contained by a 3 mm thick gasket, was a bed of pure lead wool with a fibre diameter, porosity and specific surface respectively about 0.2 mm, 80% and 3000 m^2/m^3, contacted with a lead plate current collector and separated from a 316 stainless steel anode by a Nafion 1110 cation membrane, which was supported in by 2 layers of a 8 mesh per inch polypropylene screen held in a 3mm thick anode gasket. The 3D cathode was fed with a single pass [CO_2 gas + liquid electrolyte] mixture consisting of 100 vol% CO_2 gas at 150 Sml/minute and 1 ml/minute of an aqueous solution of 2M ammonium sulphate with about 0.1 M ammonium hydroxide and about 1 mM sodium DTPA. The anode was fed with a recycling flow of 2 M ammonium sulphate plus 0.1 M ammonium hydroxide solution at 30 ml/minute via a 1.5 litre pump tank. The reactor was operated at 120 kPa(abs), 295 K with a current of 0.5 A and voltage about 5.4 V. At 1 hour operating time the cathode product solution contained about 0.05 M ammonium formate, corresponding to about 30% Faradaic efficiency for formate.

In a similar test with an anolyte of 1 M potassium carbonate a 100 ml batch of ammonium sulphate cathoyte was recycled for 5 hours to give a final formate concentration of about 0.1 M.

Example 2

A single-cell continuous parallel plate trickle-bed electrochemical reactor was assembled with superficial area dimensions of 0.1 m long by 0.03 m wide for both the anode and the cathode. The 3D cathode, contained by a 3 mm thick gasket, was a packed bed of approximately 0.3 mm diameter tin granules, contacted with a tin plate current collector and separated from a platinised titanium anode by a Nafion 117 cation membrane, which was supported in by polypropylene screen held in a 3mm thick anode gasket. The 3D cathode was fed with a single pass [CO_2 gas + liquid electrolyte] mixture consisting of 100 vol% CO_2 gas and an aqueous solution of 2M ammonium chloride + 0.5 M ammonium bicarbonate. The anode was fed with a recycling flow of 1.9 M ammonium sulphate + 0.8 M sulphuric acid. The reactor was operated at 120 kPa(abs), 295 K for a period of 60 minutes to give the results summarized in **Table 5**.

Table 5. Electroreduction of CO_2 to ammonium formate, using an acid anolyte

Current	Operating time	Voltage	Catholyte exit pH	Formate current efficiency
Amp	minutes	V		%
1	15	4.0	7.59	90
2	20	4.5	7.64	60
4	45	5.2	7.74	41
6	60	6.1	7.88	31

Example 3

About 5.1 grams of ammonium bicarbonate crystals in a glass reactor was continuously heated in a water bath at 70 °C. The contents of the reactor were weighed periodically to quantify ammonium bicarbonate decomposition. The results plotted in Figure 3 show an average rate of ammonium bicarbonate decomposition, according to Reaction 11, of 1.3 gram/hour. A similar experiment at 45 °C gave an average decomposition rate of about 0.6 gram/hour.

Example 4

About 5.1 grams of ammonium sulfate crystals was heated on a hot-plate at 250 °C and weighed periodically to measure the decomposition. The results plotted in Figure 4 show an average rate of decomposition, according to Reaction 13, of about 1.8 gram/hour.

Example 5

US patent 857046 discloses the production of concentrated formic acid from formate salts using sodium bisulfate. In the present invention the sodium bisulphate ($NaHSO_4$) is replaced by ammonium bisulphate (NH_4HSO_4) to produce formic acid by Reaction 12.

WHAT IS CLAIMED IS:

1. An electrochemical process producing formic acid wherein ammonium formate is used as an intermediary in the conversion of carbon dioxide and water to formic acid in an electrochemical reactor.

2. The process of claim 1 wherein said electrochemical reactor having a catholyte and wherein said ammonium formate being generated in said catholyte.

3. The process of claim 1 or 2 further comprising reacting said ammonium formate with an acid ammonium salt to produce said formic acid.

4. The process of claim 1 or 2 further comprising reacting said ammonium formate with an acid ammonium salt to obtain formic acid and an ammonium salt, separating said formic acid and decomposing said ammonium salt to obtain ammonia.

5. A process for the conversion of carbon dioxide and water to formic acid in an electrochemical reactor comprising:

   a. the electrochemical conversion of carbon dioxide and water to ammonium formate; and
   b. the reaction of said ammonium formate with an acid ammonium salt to produce formic acid.

6. The process of claim 5 wherein said ammonium formate is accompanied by ammonium bicarbonate which is subsequently decomposed to ammonia and carbon dioxide for recycle within said process.

7. The process of claim 5 where the produced formic acid is accompanied by an ammonium salt which is subsequently decomposed to ammonia and an acid ammonium salt for recycle within said process.

8. A process for producing formic acid from carbon dioxide that comprises the steps of:
   a. the electrochemical conversion of carbon dioxide to ammonium formate and ammonium bicarbonate in an electrochemical reactor;
   b. the separation and decomposition of ammonium bicarbonate to ammonia and carbon dioxide, which are recycled to said electrochemical reactor;
   c. reaction of the ammonium formate with an acid ammonium salt to generate and separate the product formic acid and forming an ammonium salt;
   d. decomposition of said ammonium salt from step c into an acid ammonium salt and ammonia;
   e. recycle of the acid ammonium salt from step d to step c; and
   f. recycle of the ammonia from step d to the electrochemical reactor of step a.

9. The process of any one of claims 5 to 8 wherein the acid ammonium salt is ammonium hydrogen sulphate or ammonium hydrogen phosphate.

10. The process of any one of claims 5 to 8 wherein the ammonium salt is ammonium sulphate or ammonium phosphate.

11. An electrochemical process for conversion of carbon dioxide to ammonium formate comprising the separation of ammonium bicarbonate from a recycling catholyte, decomposing the ammonium bicarbonate to ammonia, and recycling the ammonia within said process.

12. An electrochemical process for conversion of carbon dioxide to ammonium formate comprising the separation of ammonium bicarbonate from a recycling catholyte, decomposing the ammonium bicarbonate to carbon dioxide, and recycling the carbon dioxide within said process.

13. An electrochemical process for the conversion of carbon dioxide to ammonium formate and formic acid that includes the separation of ammonium formate from a recycling catholyte and converting the ammonium formate to formic acid.

14. The electrochemical process of claim 11 or 12 wherein said ammonium bicarbonate is separated from said recycling catholyte by crystallization.

Figure 1. Electro-reduction of carbon dioxide (ERC) process conceptual flowsheet

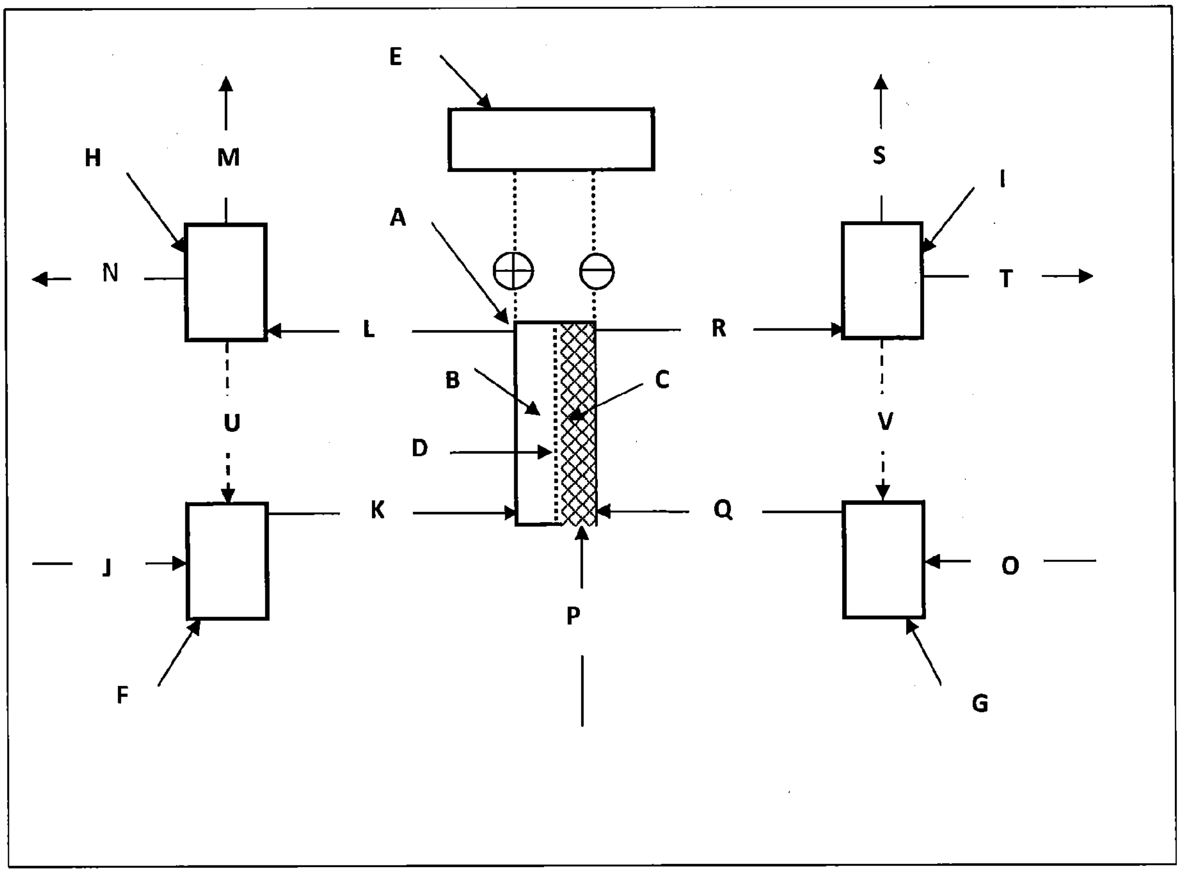


Figure 2. Formic acid – by ERC. Ammonia recycle process

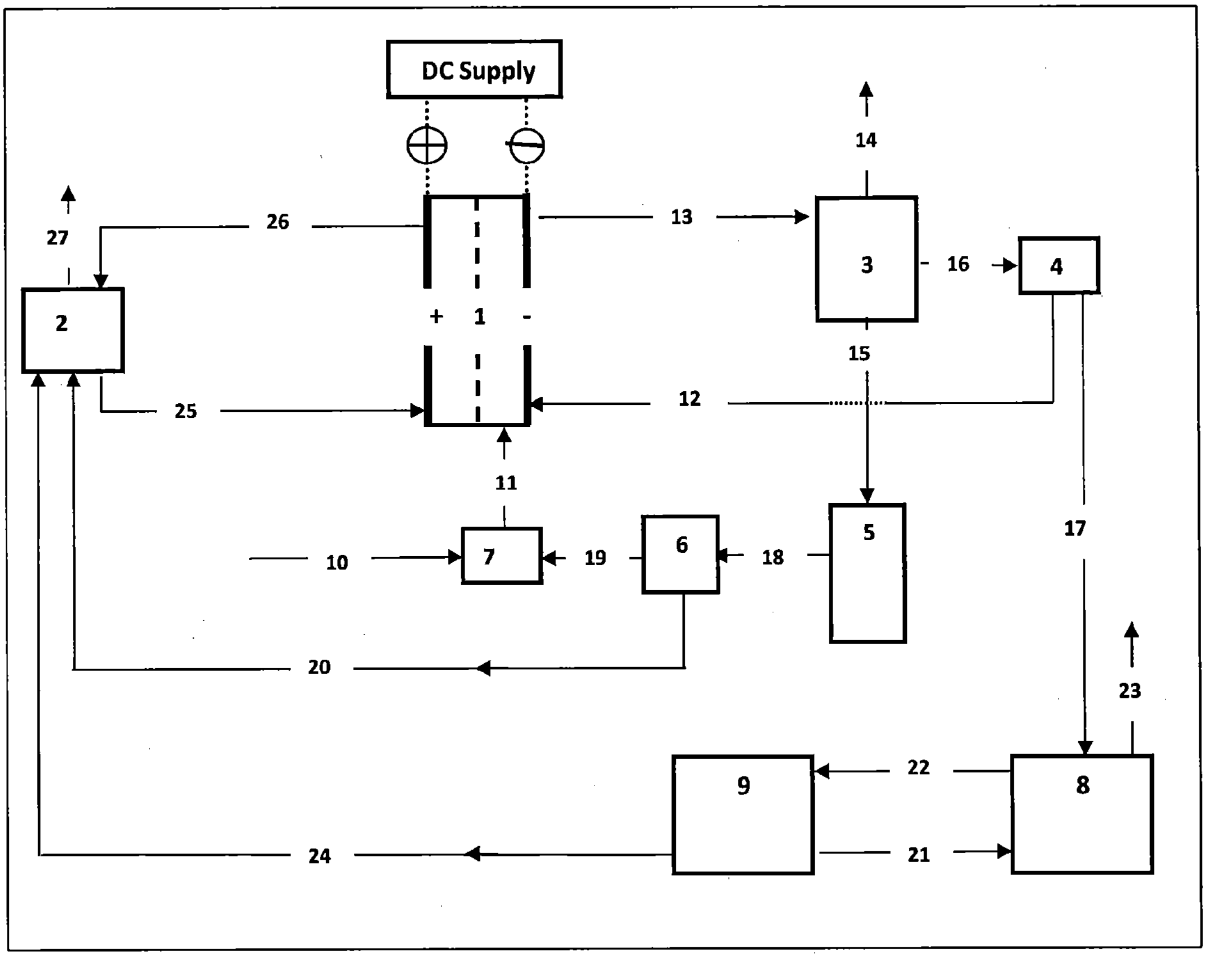


Figure 3. Example 3. Thermal decomposition of ammonium bicarbonate at 70 °C.

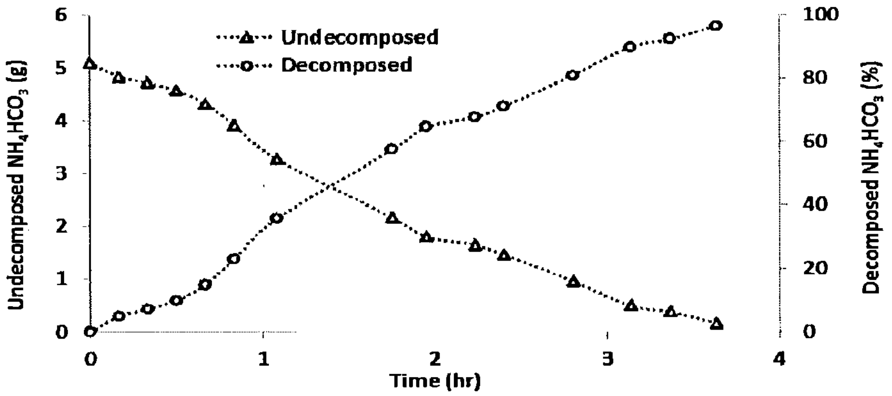
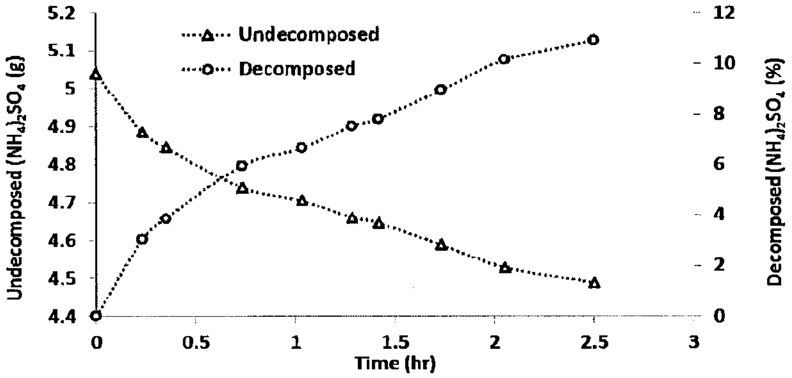


Figure 4. Example 4. Thermal decomposition ammonium sulphate at 250 °C.



INTERNATIONAL SEARCH REPORT

International application No.
PCT/CA2015/050232

A. CLASSIFICATION OF SUBJECT MATTER
IPC: ***C25B 3/04*** (2006.01) , ***C25B 15/08*** (2006.01)

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC: ***C25B*** (2006.01)

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic database(s) consulted during the international search (name of database(s) and, where practicable, search terms used)
Orbit Patent Database, Canadian Patent Database, Academic Search Research and Development
Ammonium, formate, formic acid, carbon dioxide, electrochem*, electroly*, reduction, anode, cathode, thermal decomp*,

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X Y	CA 2 625 656 (OLOMAN et al) 19 April 2007 (19-04-2007) (* paragraphs 27-37 and examples 5 and 9 *)	1, 2, 3 and 5 4, and 6-14
Y	US 2013/01050304 (KACZUR et al) 2 May 2013 (02-05-2013) (* Whole Document *)	4, and 6-14
A	US 2014/0367273 (KACZUR et al) 18 December 2014 (18-12-2014) (* Whole Document *)	

☐ Further documents are listed in the continuation of Box C.

☑ See patent family annex.

* Special categories of cited documents:
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Date of the actual completion of the international search	Date of mailing of the international search report 10 June 2015 (10-06-2015)
Name and mailing address of the ISA/CA Canadian Intellectual Property Office Place du Portage I, C114 - 1st Floor, Box PCT 50 Victoria Street Gatineau, Quebec K1A 0C9 Facsimile No.: 001-819-953-2476	Authorized officer Chris Bowen (819) 994-3555

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