(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
24 September 2015 (24.09.2015)

WIPO | PCT

(10) International Publication Number
WO 2015/139129 A1

(51) International Patent Classification:
C25B 11/03 (2006.01) *C01B 31/18* (2006.01)
C25B 1/00 (2006.01)

(21) International Application Number:
PCT/CA2015/050197

(22) International Filing Date:
17 March 2015 (17.03.2015)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
61/954,297 17 March 2014 (17.03.2014) US

(72) Inventors; and
(71) Applicants : **HUFF, Sean** [CA/CA]; #1506 - 288 West 1st Avenue, Vancouver, British Columbia V5Y 0E9 (CA). **KAZEMI, Sona** [IR/CA]; #1506 - 288 West 1st Avenue, Vancouver, British Columbia V5Y 0E9 (CA). **AZIZNIA, Amin** [IR/CA]; #1506 - 288 West 1st Avenue, Vancouver, British Columbia V5Y 0E9 (CA). **OLOMAN, Colin** [CA/CA]; 3176 West 36th Avenue, Vancouver, British Columbia, V6N 2R5 Canada (CA).

(74) Agent: **NEXUS LAW GROUP LLP**; P.O. Box 9, Suite 1140 - 625 Howe Street, Vancouver, British Columbia V6C 2T6 (CA).

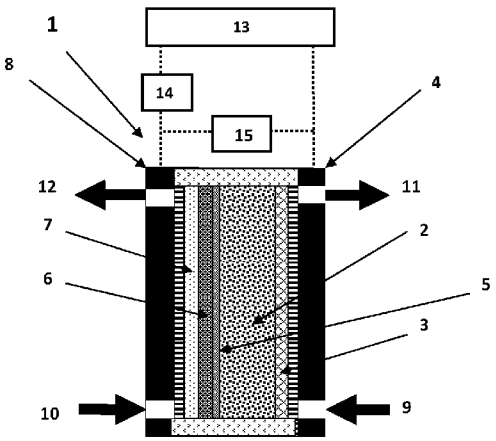
(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Published:
— *with international search report (Art. 21(3))*

(54) **Title**: GAS-CONTACTING ELECTRODES FOR USE IN CONTINUOUS ELECTROCHEMICAL REACTORS AND METHOD OF MAKING THE SAME

Figure 2 ERC reactor configuration



(57) **Abstract**: Novel gas-contacting electrodes for use in continuous electrochemical reactors with gaseous reactants to obtain gas or liquid products, and process for making such gas-contacting electrodes comprising the steps of forming a porous matrix by applying a mixture of a catalyst, a hydrophobe and a micro-sized pore-former onto a substrate; and treating the matrix to remove the pore-former. The removal of the pore-former may be by any one of the dissolution, decomposition, vaporization and reaction of pore forming particulates. The pore-former may be any compatible solid that can be removed from the matrix by dissolution, decomposition, vaporization or reaction, preferably in solid particulate form characterised by a particle size range and distribution that correspond to the desired pore size in the finished electrode. In some embodiments, the particle size of the pore-former in the mixture may be between 1 micrometer to millimeter.

WO 2015/139129 A1

GAS-CONTACTING ELECTRODES FOR USE IN CONTINUOUS ELECTROCHEMICAL REACTORS AND METHOD OF MAKING THE SAME

Field of the Invention

This invention concerns reactors, electrodes and methods for dealing with gaseous reactants in electrochemical processes involving liquid electrolytes. In particular, this disclosure is aimed at continuous reactors for the electro-chemical reduction of carbon dioxide.

Background of the Invention

The electro-reduction of carbon dioxide (ERC), which has been known for over 100 years, has now become a focus on efforts to convert CO_2 to useful materials, such as fuels and organic chemicals.

$xCO2 + (y-2(z-2x))H^+ + ye^- \rightarrow CxHyOz + (z-2x)H_2O$ Reaction 1

$2H^+ + 2e- \rightarrow H_2$ Reaction 2

Reactions 1 and 2 represent respectively the generic primary and specific secondary cathode reactions in the ERC process, which may generate organic products such as those in Table 1.

Table 1.

x	y	z	CxHyOz	Name
1	4	0	CH_4	Methane
2	4	0	C_2H_4	Ethane
2	6	0	C_2H_6	Ethane

1	0	1	CO	carbon monoxide
1	2	2	CH_2O_2	methanoic acid
1	4	1	CH_4O	methanol
1	2	1	CH_2O	methanal
2	6	1	C_2H_6O	ethanol

Electrochemical processes with gaseous reactants and liquid electrolytes involve three-phase systems (gas- liquid - solid) that bring difficulties to the design of the corresponding electrodes and continuous electro-chemical reactors. These difficulties arise from three main factors: (i) gases have zero electrical conductivity (ii) gases often have low solubility in aqueous liquids and mass transfer from gas to solid is slow (iii) the volumetric flow rates demanded by reaction stoichiometry are high for gases relative to those of the corresponding liquids. In the prior art these difficulties are engaged with gas-diffusion electrodes (GDE), solid-polymer electrolyte (SPE) electrodes or in three-phase systems exemplified by trickle-bed electrodes. In GDEs the gas and liquid are separated by a thin micro-nano porous hydrophobic and electronically conductive barrier containing the dispersed electro-catalyst and usually supported on an ion exchange membrane. In SPEs a thin porous electronically conductive layer containing the particulate electrocatalyst in an ionically conductive solid polymer matrix is coated on an ion exchange membrane that separates the gas from a liquid electrolyte or the opposing anode. Both GDEs and SPEs have a thickness (dimension parallel to current) less than 0.1 mm. In trickle-bed electrodes a two-phase [gas + liquid] mixture is pumped through a porous electrode – usually in the so-called “flow-by” mode, with an electrode thickness up to about 10 mm.

Electrochemical reactors with GDE, SPE and trickle-bed cathodes used in prior art for the electro-reduction of carbon dioxide have encountered various problems. For example, GDEs are plagued by liquid flooding, SPEs deteriorate due to in-situ crystallization of reaction products and trickle-beds require operation with a substantial pressure drop. In particular, GDEs and SPEs suffer from a drop of effectiveness due to the gradual loss of active surface area. In all the above cathodes it is found that obtaining partial current densities for CO_2 reduction above about 1000 A/m2 requires operation at super-atmospheric pressure.

Summary of the Invention.

The present invention offers novel gas-contacting electrodes for use in continuous electrochemical reactors with gaseous reactants to obtain gas or liquid products. Preferably, the reactors are employed for the electro-chemical reduction of carbon dioxide.

In accordance with some aspects the present invention provides a process for making a gas contacting electrode comprising the steps of forming a porous matrix by applying a mixture comprising a catalyst, a hydrophobe and a micro-sized pore-former onto a substrate; and treating the matrix to remove the pore-former. In some embodiments, the step of treating the matrix to remove the pore-former may be by any one of the dissolution, decomposition, vaporization and reaction of pore forming particulates. In some embodiments, the mixture may be applied to the substrate by any one of rolling, calendaring, hot pressing, cold pressing, printing, spraying, brushing and electrostatic

spraying. In some embodiments, the pore-former may comprise one or more of an inorganic and organic salt that is soluble in water but possess low solubility in alcohols. In some embodiments, the pore forming agents may be materials volatilised or decomposed by heat such as ammonium bicarbonate, aluminium chloride, naphthalene and urea. In some embodiments, the pore forming agents may be materials decomposed and solubilised by reaction, such as sodium carbonate (with acid), calcium carbonate (with acid) and aluminium (with acid or base). In some embodiments, the particle size of the pore-former in the mixture may be between 1 micrometer to 1 millimeter. In some embodiments, the amount of the pore-former in the mixture may be between about 10 and about 60% by weight. In some embodiments, the step of treating the matrix to remove the pore-former may be by any one of the dissolution, decomposition, vaporization and reaction of pore forming particulates. In some embodiments, the substrate may comprise a porous structure of any one ore more of a metal mesh, carbon cloth, carbon paper, porous carbon, porous metal, porous plastic and glass fiber.

In some aspects the present invention provides micro-porous gas-contacting electrodes produced in accordance with the above processes. In some embodiments, the micro-porous gas-contacting electrode may have pore diameters in the range about 1 micrometer to 1000 micrometer. In some embodiments, the catalyst in the micro-porous gas-contacting electrode may comprise a particulate in the size (equivalent diameter) range of 1 nanometer to 100 micrometer. In some embodiments, the catalyst in the micro-porous gas-contacting electrode may be supported or unsupported. Examples of catalyst supports are but not limited to carbon and titanium dioxide. In some

embodiments, the catalyst content may be from 10 to 80 wt%. In some embodiments, the micro-porous gas-contacting electrode may further comprise carbon black. The carbon black may be in an amount ranging from 0 to 70% by weight. In some embodiments, the micro-porous gas-contacting electrode may have pore surfaces that are embellished by nano-structured catalyst. The embellishments may be obtained by one or more of electro-phoretic deposition, micelle templated electro deposition and micelle templated electro-less deposition. In some embodiments, the embellishments may comprise one or more of cadmium, lead, tin, indium, thallium, copper, silver, gold, palladium and platinum. In some embodiments, the porosity may range from 20 to 95 %. In some embodiments, the thickness of the micro-porous gas-contacting electrode may range from 0.1 to 5 mm. In some embodiments, the pore sizes of the micro-porous gas-contacting electrode may range from 0.01 to 1 mm.

In some aspects, the present invention provides an electrochemical reactor comprising a gas-contacting electrode as described herein and in which a two-phase flow of reactant gas and liquid is fed to a fluid distribution space adjacent and parallel to the electrode.

In some aspects, the present invention provides a use of a gas-contacting electrode as claimed as described herein as a cathode in an electrochemical process for the reduction of carbon dioxide to carbon monoxide. In some embodiments the use of the gas contacting electrode may be as a cathode in an electrochemical process for the reduction of carbon dioxide gas to carbon monoxide in which the carbon dioxide gas is fed to a fluid distribution space in the electrochemical reactor adjacent and parallel to the cathode. In some embodiments the use of the gas contacting electrode may be as a

cathode in an electrochemical process for the reduction of carbon dioxide to formate salts. The carbon dioxide gas may be fed to a fluid distribution space in the electrochemical reactor adjacent and parallel to the cathode.

Brief Description of the Drawings

Fig. 1 is a flow diagram of an electrochemical reactor process according to the invention.

Fig. 2 shows an ERC reactor configuration.

Fig. 3 is a graph showing the data from Example 1.

Fig. 4 shows an electrode for use in an ERC reactor which includes electrode embellishments.

Fig. 5 shows the cross section of an experimental reactor used for electro-reduction of CO_2 to CO.

Fig. 6 a graph of data from example 2.

Fig. 7 a graph of data from example 3.

Fig. 8 a graph of data from example 4.

Fig. 9 a micro-graph of a hybrid diffusion electrode (HDE).

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

In aqueous solutions reaction 1 is usually accompanied by the parasitic reaction 2, which lowers the Faradaic efficiency of the process for CO_2 reduction.

$$2H^+ + 2e^- \rightarrow H_2 \qquad \text{Reaction 2}$$

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 of about 2 to 10 Volts/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 CO_2 containing gas **P** and a catholyte liquid solution **Q** in a volumetric flow ratio from about 1 to 1000, measured at 1 bar(abs), 273 K. In a conventional GDE the gas and liquid would be kept separate by the hydrophobic electrode, while in other cases the gas **P** and liquid **Q** may be introduced separately 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 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 comprise 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 in 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 3 to 11 listed below.

		Product
$4OH^- \rightarrow O_2 + 2H_2O + 4e^-$	Reaction 3	oxygen
$2Cl^- \rightarrow Cl_2 + 2e^-$	Reaction 4	chlorine
$2SO_4^{2-} \rightarrow S_2O_8^{2-} + 2e^-$	Reaction 5	persulphate
$2CO_3^{2-} \rightarrow C_2O_6^{2-} + 2e^-$	Reaction 6	percarbonate
$2H_2O \rightarrow O_2 + 4H^+ + 4e^-$	Reaction 7	oxygen
$C_6H_6 + 2H_2O \rightarrow C_6H_4O_2 + 2H^+ + 2e^-$	Reaction 8	benzoquinone
$C_8H_{10}O + H_2O \rightarrow C_8H_8O_2 + 4H^+ + 4e^-$	Reaction 9	methoxybenzaldehyde
$H_2 \rightarrow 2H^+ + 2e^-$	Reaction 10	proton
$CH_4 + H_2O \rightarrow CH_4O + 2H^+ + 2e^-$	Reaction 11	methanol

The primary reactants at the anode may be soluble ionic species as in reactions 3 to 6, neutral species as in reactions 7 to 11, “immiscible” organic liquids as in reactions 8 and 9 or gases as in reactions 10 and 11. 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.

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 Walas S., Chemical Process Equipmnent, Butterworth, Boston 1990, page 114 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.

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	CO, $HCOO^-$

	formation of CO and 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 $Re(dmb)(CO)_3S$ (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 process of **Figure 1**, its main components and variants, are the basis for the present invention, which is described below.

In one embodiment the subject electrodes are made from a mixture an optional nano to micrometer sized and relatively non-electro-catalytic catalyst support, a wetting alcohol, a dispersion or solution of hydrophobic fluorinated polymer, an electro-catalyst powder, a pore former and an optional solution of solid electrolyte. The resulting paste is formed into a sheet under pressure and temperature and the pore former is removed to leave a solid macro-porous matrix of the support, electro-catalyst, hydrophobe and, if present, the solid electrolyte. For example the initial mixture may consist of Vulcan XC-72 carbon black as the catalyst support, isopropanol, PTFE dispersion, tin powder catalyst, potassium sulphate powder pore-former and, optionally, a Nafion-propanol solution. This mixture is then dried, molded to the desired thickness, hot pressed at the desired pressure and temperature and the potassium sulphate leached out to form the porous electrode, then an electronically conductive mesh, or the like, is embedded on one face of the electrode. Manipulating the composition of the initial mixture gives control of the catalyst type, content and particle size as well as the porosity, pore size, hydrophobicity, electrical conductivity and thickness of the electrode. Such an electrode can also be constructed with properties graded by thickness and/or length to match potential and/or concentration and/or temperature profiles in the reactor. The hydrophilic internal surfaces of the electrode may subsequently be embellished with a nano-structured electro-catalyst.

Pore forming materials and process.

The subject electrode matrix comprises micro-scale pores of equivalent diameter in the range about 0.01 to 1 millimeter. The pores are formed from a sacrificial pore-forming agent that is mixed with the matrix components in the early stage of the electrode preparation process outlined below. The pore forming agent may be any compatible solid that can be removed from the matrix by dissolution, decomposition, vaporization or reaction. In some manifestations a solution of a sacrificial agent may be used in place of the solid. Examples of pore forming agents are: water soluble salts such as potassium sulphate, potassium nitrate, sodium acetate sodium citrate & ammonium chloride, materials volatilised or decomposed by heat such as ammonium bicarbonate, aluminium chloride, naphthalene and urea and materials decomposed and solubilised by reaction, such as sodium carbonate (with acid), calcium carbonate (with acid) and aluminium (with acid or base). The pore former is preferably in solid particulate form characterised by a particle size range and distribution that correspond to the pore size(s) in the finished electrode. The optimal pore size range and distribution depend on the electro-synthesis process conditions and desired reaction product. For example, a product in the liquid phase (e.g. potassium formate) may require pore sizes in the range about 0.1 to 1 millimeter, whereas gas phase product (e.g. carbon monoxide) may need a pore size about 0.01 to 0.1 millimeter. The pore-former should not be soluble in the reagents (e.g. alcohol) used to prepare the electrode paste or ink.

The pore forming agent specifications are critical to the performance of the finished electrode. In particular, the density and particle size range of the pore former affect the uniformity of distribution of pore former particulates in the pre-electrode paste or ink and

hence the distribution of pores in the finished electrode. As a rule, larger particulates should have a lower density to suppress segregation by sedimentation in the electrode paste prior to compression of the paste and removal of the pore former. In some manifestations it may be desirable to manipulate the pore-former material, density and size distribution to tailor the pore size distribution through the electrode thickness and so optimize the performance of the three dimensional (3D) electrode. Further, the pore former specifications along with the proportions of electronic conductors and non-conductors in the matrix can be used to modify the electronic conductivity of the electrode, which in turn affects the performance of the electrode.

Process for porous electrode fabrication.

The subject electrode (e.g. cathode) is fabricated as follows:

1. List the finished electrode specifications (thickness, porosity, pore size range, catalyst load, hydrophobe, ionomer, carbon and other support content, etc.) and calculate the required amounts of each component.
2. Assemble and weigh the components (pore former, catalyst, hydrophobe, ionomer, carbon black, support, etc.) to match the specifications.
3. Mix components to a homogeneous paste or ink by addition of an alcohol.
4. Sonicate the mixture at ambient temperature.
5. Spread the paste (e.g. by brushing, printing, spraying, rolling or calendering) onto a restricted clean surface (e.g. a mold) or onto an electronically conductive mesh (e.g. stainless steel, nickel, copper or graphite) with mesh size in the range about 20 to 100 mesh/inch or onto an electronically conductive porous structure (e.g.

carbon paper, cloth or felt) or onto an electronically non-conductive porous structure (e.g. plastic mesh or glass fiber felt).

6. Optional. Compress the [paste+support] matrix to form a sheet at a selected pressure and ambient or super-ambient temperature (e.g. 1.5 tons/square inch at 20 °C to 250 °C).
7. Optional. Attach (e.g. by compression and/or heat) the electrode matrix onto the separator (e.g. ion exchange membrane or polypropylene diaphragm)
8. Remove the pore former by dissolution, decomposition, vaporization or reaction. For example a potassium sulphate pore former is removed by immersing the sheet in warm water (e.g. 60 °C) for several hours. An ammonium bicarbonate pore former may be removed by holding the sheet at a temperature in the range about 70 to 200 °C for at least 1 hour, a calcium carbonate pore former may be removed by immersing the sheet in a solution of an acid such as acetic, formic or hydrochloric and an aluminium pore former may be removed by immersion in a caustic solution such as potassium hydroxide.
9. Clean the sheet by immersion in water at 20 °C to 80 °C for at least 1 hour.

As compared to a gas-diffusion electrode (GDE) that depends on nano-scale pores for contacting gaseous reactants the above procedure results in an electrode with micrometer sized pores, suitable for electrode reactions involving gas and liquid reactants. This new electrode is differentiated from the GDE by an acronym “HDE” = hybrid diffusion electrode.

Figure 9 shows the pore structure of a HDE prepared by the above method.

Example 1.

A single cell parallel plate electrochemical reactor was assembled as shown in the vertical cross-section of **Figure 2**. In **Figure 2** the reactor **1** consists of the porous gas-contacting cathode **2** in electronic contact with a tin plated copper mesh **3** and graphite plate with integral ribbed channels machined into each on one side to carry fluids [flow field + current feeder] **4.** Adjacent the cathode **2** is an electronically non-conductive layer of 0.3 mm thick micro-porous hydrophilic cloth **5**, against a Nafion N117 membrane **6** bonded to a platinum catalysed hydrogen electrode **7** forming the anode and supported on electronically conductive graphite ribbed channel [flow field + current collector] **8.** A two-phase mixture of (CO_2 gas and liquid catholyte) **9** flows to the cathode chamber, which is occupied by the cathode **2** and tin plated copper mesh **3,** and leaves as catholyte product **11** while a flow of hydrogen gas **10** is delivered to the anode **7** and exits the anode as anode product **12.** The reactor is driven by the DC power supply **13**, with current and voltage measurements monitored respectively by ammeter **14** and voltmeter **15**.

Cathode **2** with dimensions 24 mm high by 24 mm wide was prepared according to the above method, including hot pressing at 150 °C, with 500 pound force per square inch for 5 minutes. The properties of the resulting cathode were as follows:

Thickness: about 1 mm
Catalyst: 10 micron tin powder
Catalyst loading: 20 mg/cm^2
PTFE content: about 28 wt%
Carbon black content: about 50 wt%

Nafion content: zero
Pore size: 0.84 – 0.29 mm (20-50 mesh)
Porosity: about 55 %

The two-phase mixture **9** was formed of 1.2 ml/minute 1.5 M sodium sulphate aqueous solution plus 20 Sml/minute 100 vol % CO_2 gas and was fed to the cathode **2** while hydrogen gas **10** was fed to the anode **7**. The cathode product stream **11** was sampled at three minute intervals and analysed for formate during continuous operation at 2 V, 0.19 A under 105 kPa(abs) pressure at 293 K. **Figure 3** shows the resulting current (Faradaic) efficiency for formate generation versus operating time.

Relative to **Figure 3** the current density and current efficiency for CO_2 reduction products (e.g. formate) may be changed by tailoring several properties of the cathode **2**. For example the catalyst support may constitute about 30 to 70 wt% of the electrode and be composed of various electronically conductive materials with a relatively low electro-chemical activity, such as carbon black. The catalyst may be selected from those known to the art, such as cadmium, lead, tin, indium, copper, silver, gold, platinum and their alloys, as well as organo-metal compounds such as cobalt tetra-3-aminophenylporhyrin and nickel tetramethyldinaphthotetraazo annulene, with particle size from about 1 to 100 micron. Further, the catalyst support may be activated by absorption of catalyst salts and their subsequent in-situ conversion to the active catalyst, for example by the thermal and/or chemical reductive conversion of absorbed nitrate salts to metals. The catalyst load may range from about 1 to 100 mg/cm^2 of electrode superficial area, with an electrode thickness from about 0.1 to 5 mm. The pore former may be one of many water soluble salts, such as sodium chloride and

potassium nitrate, reactive solids such as aluminium and sodium carbonate or thermally decomposable solids such as ammonium bicarbonate and urea, or other substances known to the art. The pore size and porosity may be respectively from about 0.01 to 1 mm and 20 to 95 %. The hydrophobic component may be one of several solid fluoropolymers such as PTFE and FEP and constitute about 5 to 50 wt%, along with a solid electrolyte (e.g. Nafion) content from zero to about 20 wt% of the electrode.

The activity of the electrode may also be enhanced by embellishing the hydrophilic internal surfaces with nano-structured electro-catalyst(s), as represented in **Figure 4.** All elements of the reactor shown in **Figure 4** that are the same as shown in **Figure 3** have been given identical reference numbers. In **Figure 4**, the cathode **2** also includes embellishment **16, as described below.**

Electrocatalytic embellishment.

The effectiveness of three-dimensional (3D) electrodes is largely dependent on the specific surface area of the electro-active component(s) (i.e. the catalyst(s)). In the present case the electro-active specific surface is initially fixed by the catalyst loading, the size and shape of the catalyst particles, the porosity and pore size distribution and the hydrophobe content. The specific surface may be enhanced in a second stage of the electrode fabrication that deposits nano-scale catalyst particles or structures on electronically conductive interior surfaces of the pores, as shown in Figure 4. Such nano-embellishments can both increase the specific surface and raise the kinetic activity of the catalyst for selected reactions.

Nano-embellishment of the electrode pores may be done by several methods. For example by electro, electro-phoretic or preferably electro-less deposition. In electro-deposition the electrode is made to function as the cathode of an electrochemical cell with an electrolyte solution containing the desired catalyst and suitable additives (e.g. surfactants) to promote the formation of nano-structured catalyst deposits. In electro-phoretic deposition the electrode is made to function as an anode or cathode in a suspension of charged catalyst particles, where the charge comes from the native double-layer of the catalyst or by adsorption suitable additives, such as those used as flotation agents in the mineral industry.

The preferred method of nano-embellishment is electro-less deposition, which may be as follows:

1. The porous electrode is immersed in a pre-treatment solution of stannous chloride, washed in water, immersed in a solution of palladium chloride and washed again in preparation for step 2.
2. The porous electrode is immersed in a plating solution containing a compound of the desired catalyst and a surfactant above its liquid crystalline or critical micelle concentration, along with the requisite complexing agents and pH buffers.
3. Optionally, in steps 1 and 2 the containment vessel is evacuated and/or heated and cooled to draw solution into the pores of the electrode.
4. A solution of a reducing agent is added stepwise to the plating solution, with mixing at a controlled temperature.
5. The resulting plated electrode is removed from the plating solution then washed successively in a water miscible solvent and water.

For example to obtain silver catalyst nano-structures the plating solution may be an aqueous mixture of silver nitrate, 30 wt% ammonia solution and water in the mass ratio about 1/1/10 with the addition of about 60 wt% Triton X-100 non-ionic surfactant. The reducing agent may be an aqueous solution of hydrazine sulphate and 30 wt% ammonia solution and water in the mass ratio about 1/1/10, with the plating at about 50 °C over a period up to about 1 hour. The final wash to remove residual surfactant may be in warm water, followed successively by methanol and water.

Similar methods but with different reagents (salts, complexants, buffers, etc.) may be used for the electro-less plating of other catalytic metals, such as copper, nickel, iron, cobalt, gold, palladium, platinum, tin, lead and their alloys.

Example 2.

The subject electrodes were made from a mixture of an electro-catalyst powder, a wetting alcohol, a dispersion of hydrophobic fluorinated polymer, a pore former, and optionally a solution of solid electrolyte. The resulting paste was formed into a sheet under pressure and the pore former removed to leave a solid macro-porous matrix of the electro-catalyst, hydrophobe, and if present the solid electrolyte.

A single cell parallel plate electrochemical reactor was assembled as shown in the vertical cross-section of Figure 5. In Figure 5 the reactor 1 consists of the porous gas-

contacting cathode 2 in electronic contact with a stainless steel current collector 4 and a plastic mesh distributor 3. Adjacent the cathode 2 is a Fumasep cation exchange membrane 5. The Fumasep CEM is separated by a thin mesh 6 from the stainless steel flow channel and anode current collector 7.

A two-phase mixture of CO_2 gas and liquid catholyte 8 flows to the cathode chamber and leaves as cathode product 10 while an anolyte 9 flows through the anode chamber and leaves as the anode product 11.

The reactor is driven by a potentiostat 12, with current and voltage measurements.

A cathode 2 of dimensions 20 mm by 20 mm was prepared according to the above method, including pressing at 25 °C, 1.5 tonnes force per square inch for 6 minutes. The properties of the resulting cathode were as follows:

Thickness: about 0.3 mm
Catalyst: silver nano-powder
Catalyst loading: 31 mg/cm^2
Fluorinated polymer (PTFE) content: 40% wt
Carbon black content: zero
Solid electrolyte (Nafion) content: zero
Porosity: about 50%

A mixture of 15 ml/minute 0.5 M potassium bicarbonate plus 50 sml/minute 100 vol% CO2 gas was fed to the cathode and 150 ml/minute 2.5 M potassium hydroxide was fed to the anode. Both anode and cathode contents were recirculated. The gas and liquid products were analysed respectively by a gas chromatograph and a UV-vis spectrophotometer. The reactor operation was galvanostatic under a pressure of 105

kPa(abs) at 293 K. Samples were taking at currents of 0.1, 0.2, 0.4, and 0.8 A, which correspond to superficial current densities of 250, 500, 1000, and 2000 A/m^2. Figure 6 shows the performance of this improved cathode structure compared to a commercial silver gas diffusion electrode (Gaskatel Biplex with about 100 mg/cm^2 Ag) and to a conventional gas diffusion electrode fabricated in house (60 wt% Ag which gave a loading of 31 mg/cm^2 + 40 wt% PTFE), all operating under similar conditions. These data include the Faradaic efficiency for CO, the reactor voltage and the ratio of hydrogen to carbon monoxide (H_2/CO) in the product gas as a function of the superficial current density. The H_2/CO ratio is important to applications of CO_2 electro-reduction., Relative to Figure 6 the current density and efficiency for CO_2 reduction products (e.g. CO) may be changed by tailoring several properties of the cathode. Different support material such as carbon black and can be used modify porosity while maintaining the electronic conductivity of the electrode matrix. Example 1 summarizes several other variations in the materials and method of fabrication that may be used to affect the reactivity and selectivity of the cathode.

Example 3.

The subject electrodes were made as in Example 2 with three different pore-forming agents and tested as cathodes in the reactor of Figure 5.

Particulate potassium sulphate, sodium acetate and sodium citrate in the size range 63-125 um were the pore-forming agents, with the properties of each cathode as follow:

Thickness: about 0.3 mm
Catalyst: silver nano-powder
Catalyst loading: 31 mg/cm^2
PTFE content: 40% wt

Carbon black content: zero
Nafion content: zero
Porosity: about 50%

The reactor was operated and tested as in Example 2, except with a cathode feed of 3 ml/minute 0.5 M potassium bicarbonate plus 25 sml/minute 100 vol% CO_2 gas, an anolyte flow of 30 ml/minute and superficial current density of 500 A/m2. Figure 7 shows the performance of this improved cathode structure using different pore forming agents, compared to the conventional gas diffusion electrode fabricated in house, all operating under similar conditions.

Example 4.

The subject electrodes were made as in Example 2 and tested as cathodes in the reactor of Figure 5. In this case a single pore-forming agent, potassium sulphate, was used with particle size ranges of 48-63, 63-125, 125-250, and 250-500 um, each in cathodes with the following properties:

Thickness: about 0.2-0.5 mm
Catalyst: silver nano-powder
Catalyst loading: 31 mg/cm^2
PTFE content: 40% wt
Carbon black content: zero
Nafion content: zero
Porosity: about 40-60%

The reactor was operated and tested as in Example 3 to give the results of Figure 8. Figure 8 compares the performance the four cathodes to the conventional gas diffusion electrode fabricated in house, all operating under similar conditions.

All examples 2-4 demonstrate the superiority of the subject hybrid diffusion electrode (HDE) over the gas diffusion electrode (GDE) for the electroreduction of carbon dioxide to carbon monoxide.

Based on this invention those skilled in the art will see that many levels and combinations of the properties of the subject electrode listed above can be employed to enhance the performance of reactors used in the electrochemical reduction of carbon dioxide.

While the invention has been particularly shown and described with reference to the preferred embodiments thereof, it will be understood by those skilled in the art that various changes in form and details may be made without departing from the scope of the invention.

WHAT IS CLAIMED IS:

1. A process for making a gas contacting electrode comprising the steps of:

(a) forming a porous matrix by applying a mixture comprising a catalyst, a hydrophobe and a micro-sized pore-former onto a substrate; and

(b) treating the matrix to remove the pore-former.

2. The process as claimed in claim 1, wherein the step of treating the matrix to remove the pore-former is by any one of the dissolution, decomposition and reaction of pore forming particulates.

3. The process as claimed in any one of claims 1 and 2, wherein the mixture is applied to the substrate by any one of rolling, calendering, hot pressing, cold pressing, printing, spraying, brushing and electrostatic spraying.

4. The process as claimed in any one of claims 1 - 3, wherein the pore-former comprises one or more of an inorganic and organic salt that is soluble in water but possess low solubility in alcohols.

5. The process as claimed in any one of claims 1 - 3, wherein the pore-former comprises material volatilised or decomposed by heat.

6. The process as claimed in claim 5 wherein the pore former comprises one or more of ammonium bicarbonate, aluminium chloride, naphthalene and urea.

7. The process as claimed in any one of claims 1 - 3, wherein the pore-former comprises material decomposed and solubilised by reaction.

8. The process as claimed in claim 7 wherein the pore former comprises one or more of sodium carbonate that may be removed with an acid, calcium carbonate that may be removed with an acid, and aluminium that may be removed with an acid or base.

9. The process as claimed in any one of claims 1 - 8, wherein the particle size of the pore-former in the mixture is between 1 micrometer to 1 millimeter.

10. The process as claimed in any one of claims 1 - 9, wherein the amount of the pore-former in the mixture is between about 10 and about 60% by weight.

11. The process as claimed in any one of claims 1 - 10, wherein the substrate comprises a porous structure of any one or more of a metal mesh, carbon cloth, carbon paper, porous carbon, porous metal, porous plastic and glass fiber.

12. A micro-porous gas-contacting electrode produced in accordance with the process as claimed in any one claims 1-11.

13. The micro-porous gas-contacting electrode as claimed in claim 12 having pore diameters in the range about 1 micrometer to 1000 micrometer.

14. The micro-porous gas-contacting electrode as claimed in any one of claims 12 and 13 in which the catalyst comprises a particulate in the size (equivalent diameter) range of 1 nanometer to 100 micrometer.

15. The micro-porous gas-contacting electrode as claimed in any one of claims 12 – 14, wherein the catalyst content is from 10 to 80 wt%.

16. The micro-porous gas-contacting electrode as claimed in any one of claims 12 – 15 further comprising carbon black.

17. The micro-porous gas-contacting electrode as claimed in claim 16 wherein carbon black is in an amount ranging from 0 to 70% by weight.

18. The micro-porous gas-contacting electrode as claimed in any one of claims 12 – 17 in which the pore surfaces are embellished by nano-structured catalyst.

19. The micro-porous gas-contacting electrode as claimed in claim 18 in which the embellishments are obtained by one or more of electro-phoretic deposition, micelle templated electro deposition and micelle template electro-less deposition.

20. The micro-porous gas-contacting electrode as claimed in claim 18 in which the embellishments comprise one or more of cadmium, lead, tin, indium, thallium, iron, nickel, copper, silver, gold, palladium and platinum.

21. The micro-porous gas-contacting electrode as claimed in any one of claims 12 – 20 in which the porosity ranges from 20 to 95 %.

22. The micro-porous gas-contacting electrode as claimed in any one of claims 12 – 21 having a thickness ranging from 0.1 to 5 millimeter.

23. The micro-porous gas-contacting electrode as claimed in any one of claims 12 – 22 having pore sizes ranging from 0.01 to 1 millimeter.

24. An electrochemical reactor comprising the gas-contacting electrode of any one of claims 12 - 23 in which a two-phase flow of reactant gas and liquid is fed to a fluid distribution space adjacent and parallel to the electrode.

25. A use of a gas-contacting electrode as claimed any one of claims 12 – 23 as a cathode in an electrochemical process for the reduction of carbon dioxide to carbon monoxide.

26. A use of a gas-contacting electrode as claimed any one of claims 12 – 23 as a cathode in an electrochemical process for the reduction of carbon dioxide gas to carbon monoxide in which the carbon dioxide gas is fed to a fluid distribution space in the electrochemical reactor adjacent and parallel to the cathode.

27. A use of a gas-contacting electrode as claimed any one of claims 12 – 23 as a cathode in an electrochemical process for the reduction of carbon dioxide to formate salts.

28. The use as claimed in claim 27 in which the carbon dioxide gas is fed to a fluid distribution space in the electrochemical reactor adjacent and parallel to the cathode.

29. The micro-porous gas-contacting electrode as claimed in any one of claims 12 – 23 further comprising a solid polymer electrolyte.

30. The micro-porous gas-contacting electrode as claimed in claim 29 in which the solid polymer electrolyte content is ≤ 50 wt%.

Figure 1 ERC process conceptual flowsheet

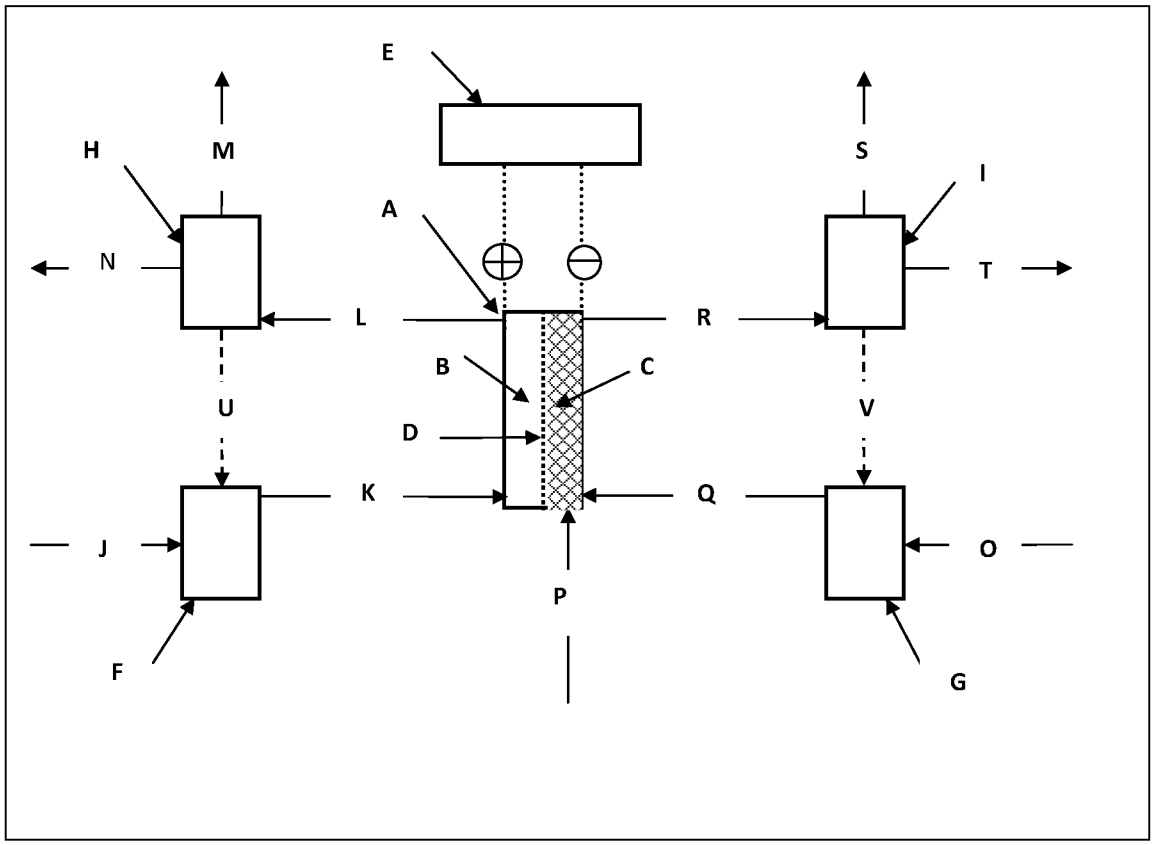


Figure 2 ERC reactor configuration

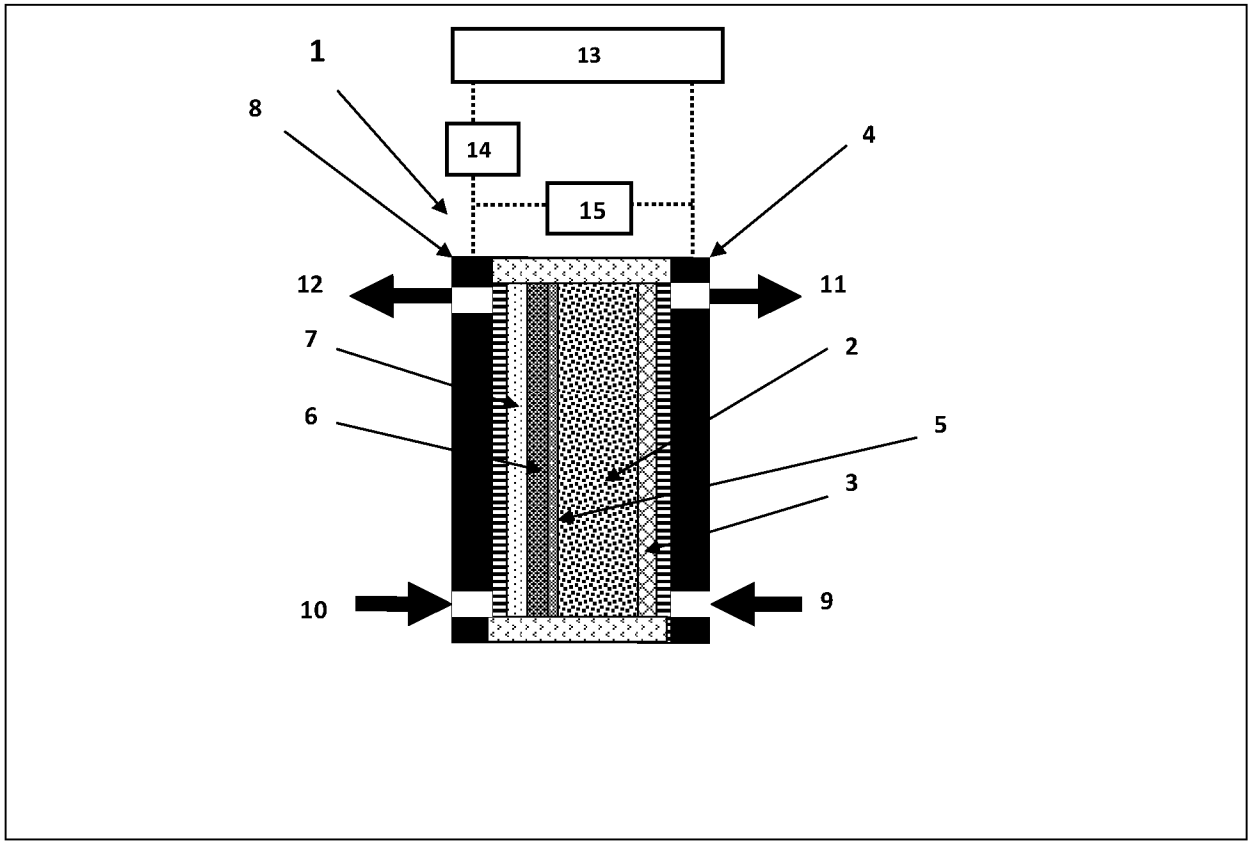


Figure 3 Example 1 data

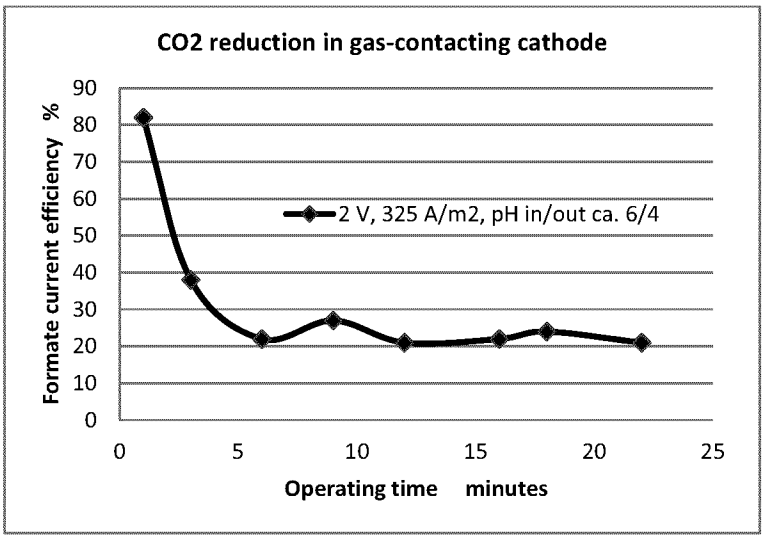


Figure 4 Electrode embellishments

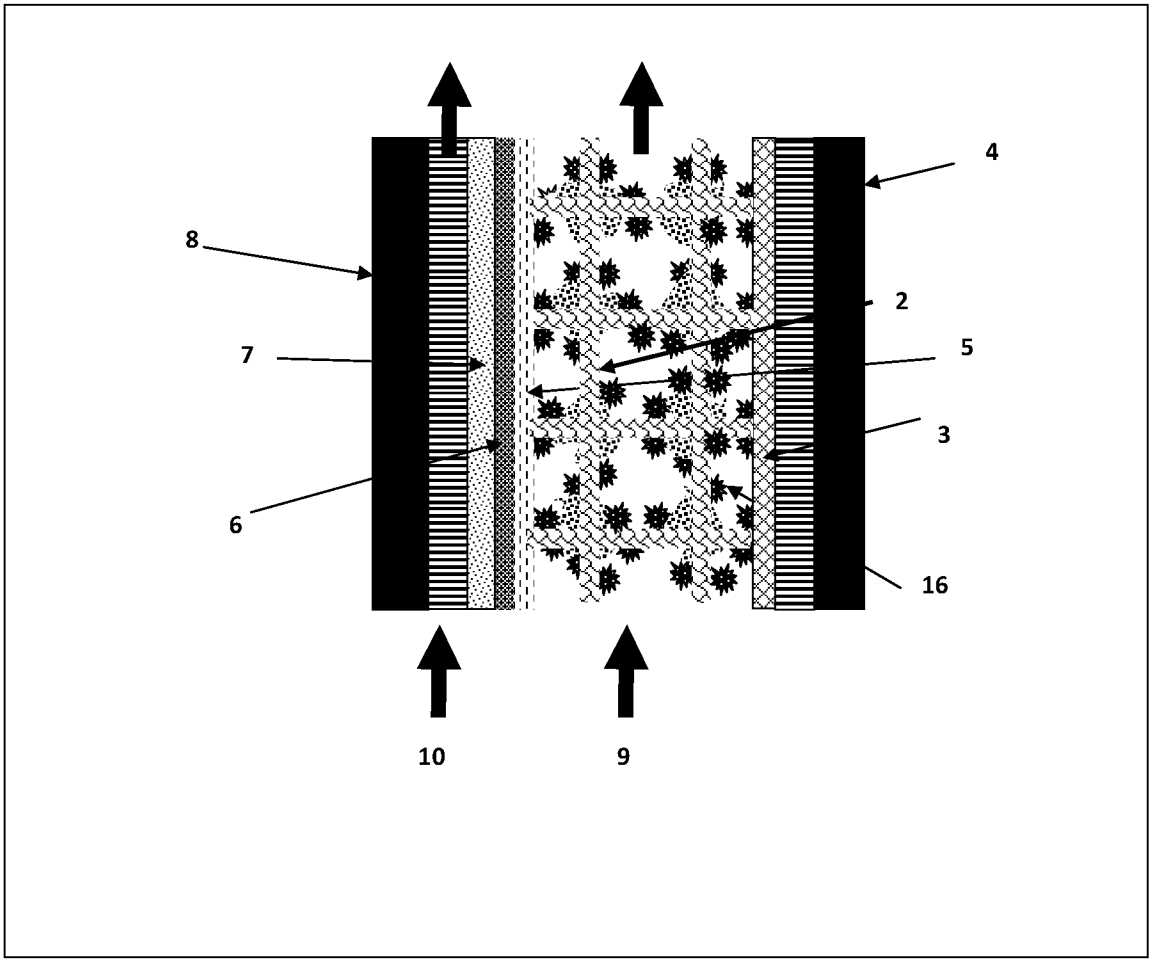


Figure 5. Reactor, Example 2.

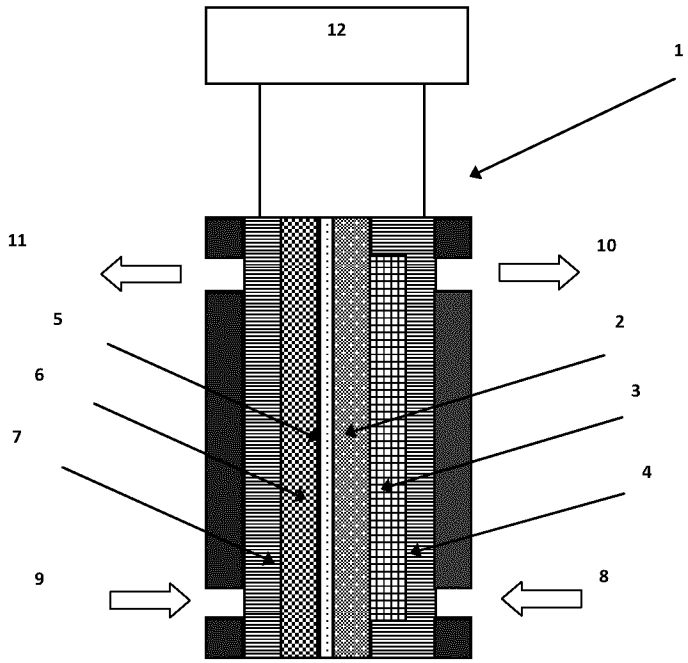


Figure 6. Example 2. Data.

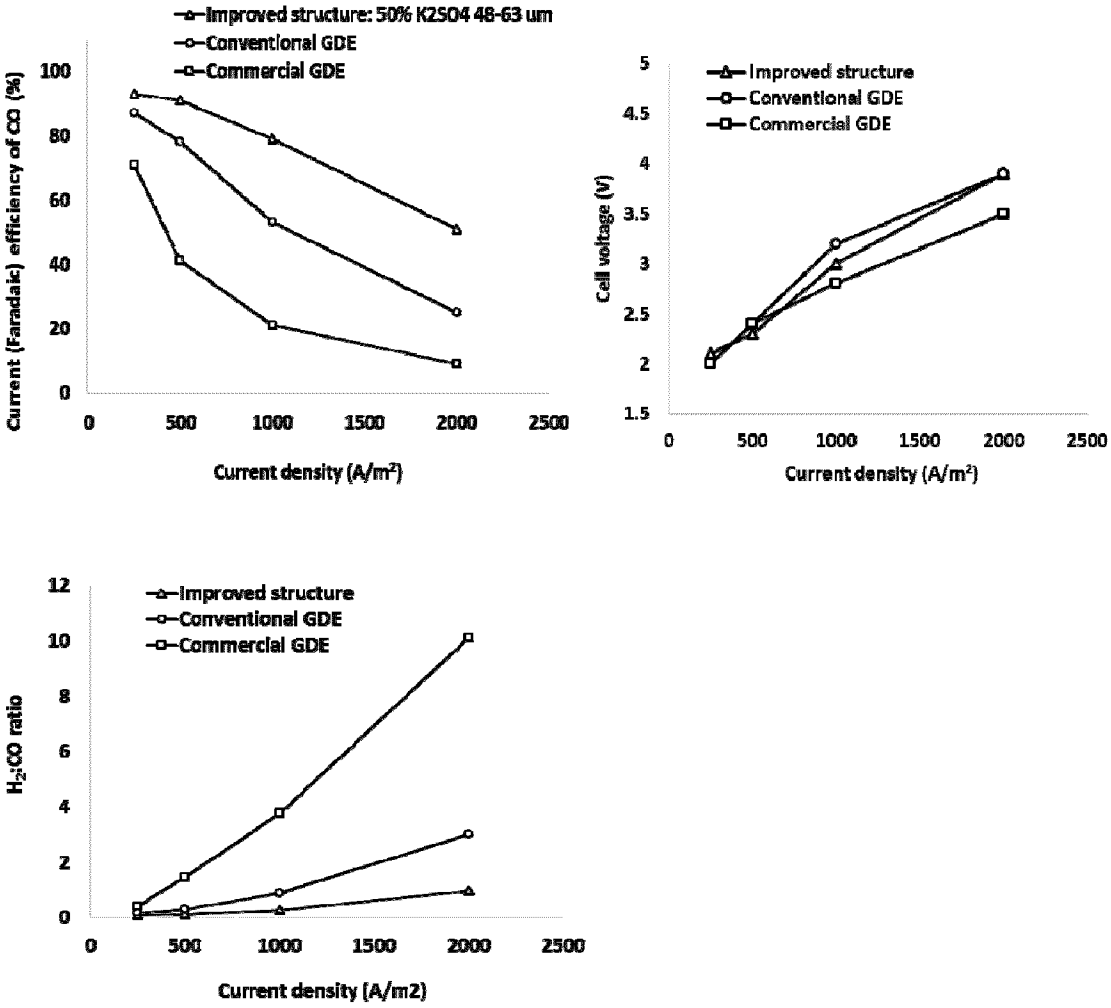


Figure 7. Example 3. Data

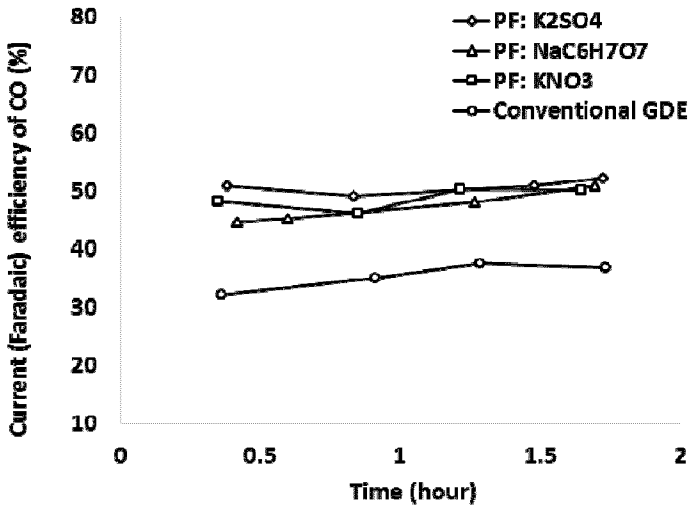


Figure 8. Example 4. Data

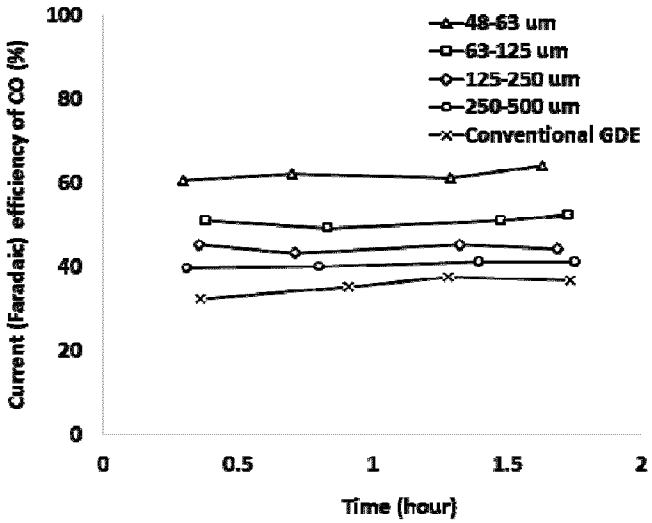
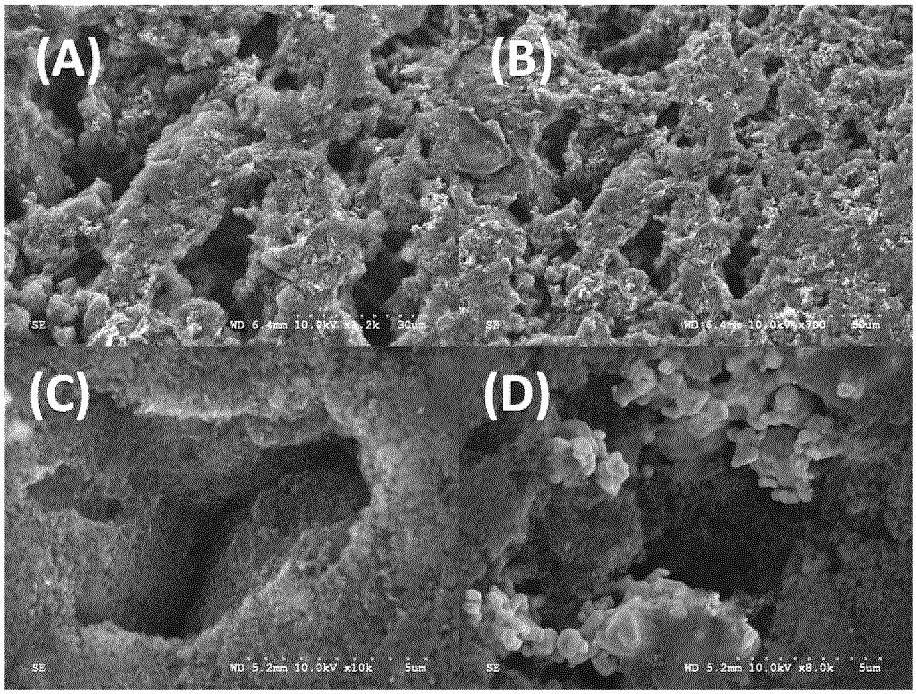


Figure 9. Microscopic image of micro-pores in a HDE



INTERNATIONAL SEARCH REPORT

International application No.
PCT/CA2015/050197

A. CLASSIFICATION OF SUBJECT MATTER
IPC: ***C25B 11/03*** (2006.01) , ***C25B 1/00*** (2006.01) , *C01B 31/18* (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 11/03*** (2006.01) , ***C25B 1/00*** (2006.01) , *C01B 31/18* (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)
Canadian Patent Database, Orbit, Academic Search R&D, Google Scholar
Catalyst or Pt or Pd or Ni, Teflon or PTFE, pore former, microporous, anode, cathode, salt, support, hydroph*, carbon dioxide, formate

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X Y	US 4,581,116 (PLOWMAN et al) 8 April 1986 (08-04-1986) (* columns 3-8 *)	1-8, 10-14, 16, 17, 21-23 24-30
X Y	US 5,584,977 (BACHOT et al) 17 December 1996 (17-12-1996) (* columns 4-5 *)	1, 2, 4, 9-11, 15 and 22 24-28
X Y	GB 2 181 115 (HARTY et al) 15 April 1987 (15-04-1987) (* abstract *)	24-28
Y	PEM Fuel Cell Electrodes, Lister et al, *Journal of Power Sources* Vol.130, pp 61-76, May 2004 (*Sections 2 and 3 *)	29, 30

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

☑ See patent family annex.

*	Special categories of cited documents:
"A"	document defining the general state of the art which is not considered to be of particular relevance
"E"	earlier application or patent but published on or after the international filing date
"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O"	document referring to an oral disclosure, use, exhibition or other means
"P"	document published prior to the international filing date but later than the priority date claimed
"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&"	document member of the same patent family

Date of the actual completion of the international search 3 June 2015 (03-06-2015)	Date of mailing of the international search report 17 June 2015 (17-06-2015)
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

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/CA2015/050197

Patent Document Cited in Search Report	Publication Date	Patent Family Member(s)	Publication Date
US4581116A	08 April 1986 (08-04-1986)	US4581116A	08 April 1986 (08-04-1986)
		US4659528A	21 April 1987 (21-04-1987)
US5584977A	17 December 1996 (17-12-1996)	US5584977A	17 December 1996 (17-12-1996)
		BG61617B1	30 January 1998 (30-01-1998)
		BG98876A	31 May 1995 (31-05-1995)
		CA2126653A1	26 December 1994 (26-12-1994)
		CN1122381A	15 May 1996 (15-05-1996)
		EP0630870A1	28 December 1994 (28-12-1994)
		FR2706912A1	30 December 1994 (30-12-1994)
		FR2706912B1	15 September 1995 (15-09-1995)
		JPH07166388A	27 June 1995 (27-06-1995)
		JP2651999B2	10 September 1997 (10-09-1997)
		KR0174280B1	01 April 1999 (01-04-1999)
		NO942391D0	23 June 1994 (23-06-1994)
		NO942391A	27 December 1994 (27-12-1994)
		PL303956A1	09 January 1995 (09-01-1995)
		RU94022259A	27 June 1996 (27-06-1996)
		US5626905A	06 May 1997 (06-05-1997)
GB2181115A	15 April 1987 (15-04-1987)	GB8616719D0	13 August 1986 (13-08-1986)
		GB2181115B	05 April 1989 (05-04-1989)
		AT49812T	15 February 1990 (15-02-1990)
		AU580354B2	12 January 1989 (12-01-1989)
		AU5069585A	03 June 1986 (03-06-1986)
		BR8507039A	10 March 1987 (10-03-1987)
		CA1255499A1	13 June 1989 (13-06-1989)
		DE3441463A1	25 September 1986 (25-09-1986)
		DE3575616D1	01 March 1990 (01-03-1990)
		DK331086A	11 July 1986 (11-07-1986)
		DK331086D0	11 July 1986 (11-07-1986)
		DK154460B	14 November 1988 (14-11-1988)
		DK154460C	24 April 1989 (24-04-1989)
		EP0201552A1	20 November 1986 (20-11-1986)
		EP0201552B1	24 January 1990 (24-01-1990)
		ES548830D0	01 December 1986 (01-12-1986)
		ES8701671A1	01 March 1987 (01-03-1987)
		JPS62501491A	18 June 1987 (18-06-1987)
		NO862812A	11 July 1986 (11-07-1986)
		NO862812D0	11 July 1986 (11-07-1986)
		NO166979B	10 June 1991 (10-06-1991)
		NO166979C	18 September 1991 (18-09-1991)
		US4784556A	15 November 1988 (15-11-1988)
		US4902193A	20 February 1990 (20-02-1990)
		WO8603030A1	22 May 1986 (22-05-1986)
		ZA8508713A	27 August 1986 (27-08-1986)