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(54) FUNCTIONNALISED COPPER ELECTROCHEMICAL CATALYSTS FOR CONVERSION OF CO2 TO SMALL MOLECULES

(57) The present invention belongs to the field of catalytic chemistry, and more specifically to catalysed reduction chemical reactions, preferably of CO_2 into small molecules.

The present invention relates to a new catalyst compound comprising at least a copper (Cu) layer, wherein the copper layer is functionalized with at least one aryl group and its use thereof in a reduction chemical reaction, preferably in reduction of CO_2 into CO, ethylene and other small molecules such as gaseous hydrocarbons (methane, propane) or liquid molecules (ethanol, formic acid, propanol). The invention relates to the process of manufacture of said catalyst compound and to a process electrochemical conversion of CO_2 to small molecules and in particular ethylene.

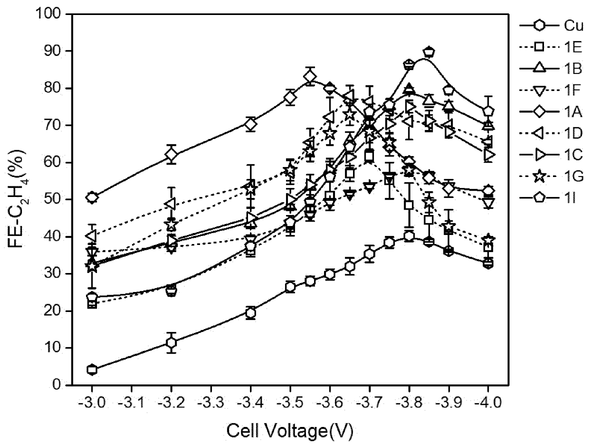

Figure 2

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Processed by Luminess, 75001 PARIS (FR)

Description

Technical field

[0001] The present invention belongs to the field of catalytic chemistry, and more specifically to catalysed reduction chemical reactions, preferably of CO_2 into small molecules.

[0002] The present invention relates to a new catalyst compound comprising at least a copper (Cu) layer, wherein the copper layer is functionalized with at least one aryl functional group and its use thereof in a reduction chemical reaction, preferably in reduction of CO_2 into CO, ethylene and other small molecules such as gaseous hydrocarbons (methane, propane) or liquid molecules (ethanol, formic acid, propanol). The invention relates to the process of manufacture of said catalyst compound and to a process electrochemical conversion of CO_2 to small molecules and in particular ethylene.

[0003] In the description below, references between [1-4] refer to the list of references at the end of the examples.

Technical background

[0004] The release of carbon dioxide (CO_2) is a major concern for the environment. Its capture and recycling into small organic bricks such as carbon monoxide (CO), formic acid (HCOOH), methane (CH_4) or methanol (CH_3OH), ethanol (C_2H_5OH) and ethylene (C_2H_4) could prove to be very advantageous.

[0005] Particularly, the electrochemical conversion of CO_2 into small molecules such as gaseous hydrocarbons (methane, ethylene) or liquid molecules (ethanol, formic acid) is an attractive method as these molecules can be used as fuels or organic bricks to produce longer hydrocarbon molecules [1-3]. Currently only copper-based catalysts (Cu) can convert CO_2 in small organic molecules, but their efficiency is still limited - preventing its use in industrial process **[4].**

[0006] Therefore, there is a critical necessity to explore for an easier and cheaper way to produce small molecules such as ethylene and gaseous hydrocarbons (methane, ethylene) or liquid molecules (ethanol, formic acid) from CO_2 in a cheap and environmentally friendly procedure.

Detailed description of the invention

[0007] Applicant has developed a new process and a new catalyst compound that solves all of the problems listed above.

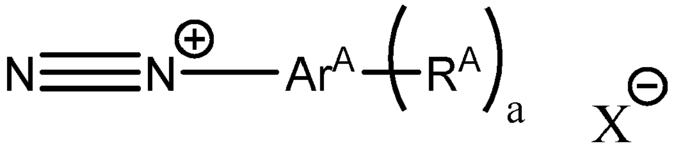
[0008] The present invention deals with a new process and a new catalyst compound, and its applications, such as a method to convert CO_2 into small molecules, more preferably ethylene, at room temperature and atmospheric pressure. Being able to produce such small molecules at room temperature and atmospheric pressure in large quantities is, to the knowledge of Applicant, something that was not observed in the art.

[0009] Applicant surprisingly found out that using a functionalized Cu catalyst made according to process of the invention gives very good yields in conversion of CO_2 into small molecules such as ethylene and gaseous hydrocarbons (methane, ethylene) or liquid molecules (ethanol, formic acid). Specifically, it was identified that the performance is considerably improved by grafting specific functional groups on the surface of inorganic electrocatalysts. These functional groups, substituted aryl groups, allow increasing the current density and improving the Faradaic efficiency of the reaction towards the production of ethylene up to about 83% at -3.55 V in a membrane-electrode-assembly cell (MEA).

[0010] The catalyst compound of the invention is based on copper (Cu) and optionally Ag, Bi, Zn and/or Sn crystal grown on a porous gas diffusion layer (typically a commercial carbon support such as a gas diffusion electrode or a porous polymer substrate such as PTFE, nylon or PVDF) via electrodeposition and then functionalization with various substituted aryl groups. The catalyst compound obtained by the process of the invention may present a raspberry-like morphology.

[0011] A first object of the invention is a process of manufacture of a catalyst compound comprising the steps of:

a) electrodepositing copper on a porous gas diffusion layer, the porous gas diffusion layer being optionally pre-treated;
b) functionalisation of the metal catalyst obtained in step a) by contacting with a diazonium salt of formula I:

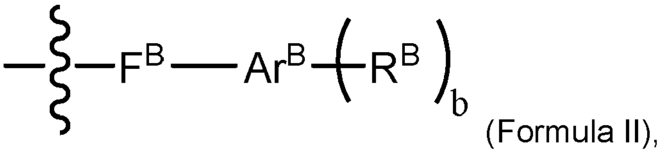


$$N\equiv N^{\oplus}-Ar^{A}\left(R^{A}\right)_{a} \quad X^{\ominus}$$

(Formula I)

wherein,

- X^- represents an anion,
- a is an integer from 1 to 3,
- Ar^A represents an aryl group, substituted by at least one $-R^A$ group,
- $-R^A$ represents at least one substituent chosen from a halo group, - R^1, $-NO_2$, $-OR^1$, $-NR^2R^3$ and a group of formula II:



$$-\!\!\wr\!\!-F^B-Ar^B\left(R^B\right)_b$$

(Formula II),

in which,

  - ◦ $-R^1$ represents a C_1 to C_3 alkyl group,
  - ◦ $-R^2$ and R^3 independently represent H or a C_1 to C_3 alkyl group,
  - ◦ b is an integer from 1 to 3,
  - ◦ F^B is a functional group chosen from -N=N- and -NH-,
  - ◦ Ar^B represents an aryl group, substituted by at least one $-R^B$ group,
  - ◦ $-R^B$ represents at least one substituent chosen from a halo group, $-R^1$, $-OR^1$ and $-NR^2R^3$,

〰

represent the point of attachment to Ar^A.

[0012] Advantageously, the diazonium salt may be chosen from diazonium salts of formula I, wherein X^- is chosen from BF_4^-, Cl^- and HSO_4^-.

[0013] It is meant by "aryl", a group derived from arenes by removal of a hydrogen atom from a ring carbon atom; arenes being monoyclic and polycyclic aromatic hydrocarbons (IUPAC). According to the invention aryl groups may comprise from 4 to 10 carbon atoms, preferably 6 carbon atoms. According to the invention, aryl groups Ar^A and Ar^B do not comprise, heteroatoms besides the heteroatoms comprised in R^A, F^B and R^B.

[0014] Advantageously, the diazonium salt may be chosen from diazonium salts of formula I, wherein Ar^A and/or Ar^B are aryl groups comprising 6 carbon atoms and are phenyl groups. Preferably, Ar^A and/or Ar^B are phenyl groups substituted by at least one $-R^A$ group in ortho, meta and/or para position.

[0015] Advantageously, when Ar^A is substituted by more than one R^A group (i.e, a = 2 or 3), the R^A groups may be identical or different from each other.

[0016] Advantageously, when Ar^B is substituted by more than one R^B group (i.e, b = 2 or 3), the R^B groups may be identical or different from each other.

[0017] In other terms, when there is more than one R^A substituent, the R^A substituents may be identical or different from each other and/or when there is more than one R^B substituent, the R^B substituents may be identical or different from each other. Also, when there is R^A and R^B groups, the R^A and R^B groups may be identical or different. For example, when there are two R^A, they may both be R^1, and yet be identical or different (e.g. one may be -Me and the other may be -Et or they may both be -Me). Also, for example, when one R^A substituent and one R^B substituent are both R^1, they may be identical or different (e.g. one may be -Me and the other may be -Et or they may both be -Me).

[0018] Advantageously, the diazonium salt may be chosen from diazonium salts of formula I, wherein a = 1 or 2.

[0019] Advantageously, the diazonium salt may be chosen from diazonium salts of formula I, wherein b = 1 or 2, more preferably 1.

[0020] Advantageously, the diazonium salt may be chosen from diazonium salts of formula I, wherein at least one R^A is a halo group, preferably chosen from Br, Cl and I.

[0021] Advantageously, the diazonium salt may be chosen from diazonium salts of formula I, wherein at least one R^A is $-NO_2$.

[0022] Advantageously, the diazonium salt may be chosen from diazonium salts of formula I, wherein at least one R^A is $-R^1$, preferably chosen from - Me, -Et and -Pr (Pr being either isopropyl or n-propyl).

[0023] Advantageously, the diazonium salt may be chosen from diazonium salts of formula I, wherein at least one R^A is $-OR^1$, preferably chosen from - OMe, -OEt and -OPr (Pr being either isopropyl or n-propyl).

[0024] Advantageously, the diazonium salt may be chosen from diazonium salts of formula I, wherein at least one R^A is $-NR^2R^3$, preferably chosen from $-NEt_2$, $-NMe_2$, $-NPr_2$, -NMeEt and -NMePr (Pr being either isopropyl or n-propyl).

Advantageously, the diazonium salt may be chosen from diazonium salt of formula I, wherein at least one R^A group is a group of formula II.

[0025] Advantageously, the diazonium salt may be chosen from diazonium salts of formula I, wherein at least one R^B is a halo group, preferably chosen from Br, Cl and I.

[0026] Advantageously, the diazonium salt may be chosen from diazonium salts of formula I, wherein at least one R^B is $-NO_2$.

[0027] Advantageously, the diazonium salt may be chosen from diazonium salts of formula I, wherein at least one R^B is $-R^1$, preferably chosen from - Me, -Et and -Pr (Pr being either isopropyl or n-propyl).

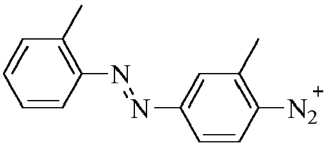
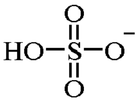
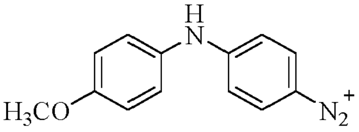
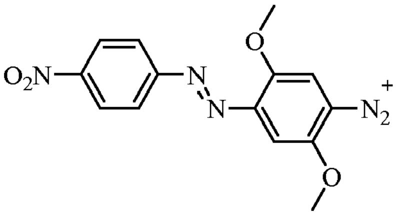
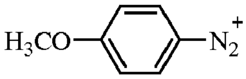
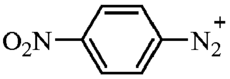
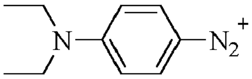
[0028] Advantageously, the diazonium salt may be chosen from diazonium salts of formula I, wherein at least one R^B is $-OR^1$, preferably chosen from - OMe, -OEt and -OPr (Pr being either isopropyl or n-propyl).

[0029] Advantageously, the diazonium salt may be chosen from diazonium salts of formula I, wherein at least one R^B is $-NR^2R^3$, preferably chosen from $-NEt_2$, $-NMe_2$, $-NPr_2$, -NMeEt and -NMePr (Pr being either isopropyl or n-propyl).

[0030] Advantageously, the diazonium salt may be chosen from diazonium salts of formula I, wherein at least one R^A group is a group of formula II and Ar^A and Ar^B are each substituted by one $-R^1$ group, preferably -Me. The diazonium salt may be chosen from diazonium salts of formula I, wherein at least one R^A group is a group of formula II and Ar^A is substituted by two - OR^1 groups, preferably -OMe and Ar^B is substituted by one $-NO_2$ group. The diazonium salt may be chosen from diazonium salts of formula I, wherein at least one R^A group is a group of formula II and Ar^B is substituted by one - OR^1 group, preferably -OMe.

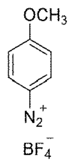
[0031] Advantageously, the diazonium salt may be chosen from the following salts:

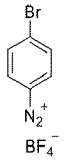
Table 1: example of salts

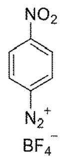
Salts names (IUPAC)	**Diazonium**	**X^-**
2-methyl-4-[(2-methylphenyl)diazenyl] benzenediazoniu m		 $HO-S(=O)_2-O^-$
4-[(4-methoxyphenyl)amino]benzene-1-diazonium chloride		Cl^-
dichlorozinc;2,5-dimethoxy-4-[(4-nitrophenyl) diazenyl]benzenediazonium; dichloride		Cl^-. ½ $ZnCl_2$
4-methoxybenzenediazonium;tetrafluorobo rate		BF_4^-
4-B romobenzenediazonium;tetrafluorobora te		BF_4^-
4-nitrobenzenediazonium; tetrafluoroborate		BF_4^-
4-(diethylamino)benzenediazonium;tetraflu oroborate		BF_4^-

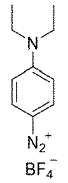
[0032] The different anions in the table above may be used independently to the nature of the cations. For example, "2-methyl-4-[(2-methylphenyl)diazenyl]benzenediazonium", "4-[(4-methoxyphenyl)amino]benzene-1-diazonium chloride" or "dichlorozinc;2,5-dimethoxy-4-[(4-nitrophenyl)diazenyl]benzenediazonium;dichloride" may have BF_4^- as counter anion.

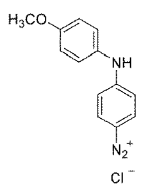
[0033] Advantageously, the diazonium salt of formula I may be chosen from the following salts:

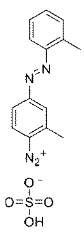

4-Methoxybenzenediazonium tetrafluoroborate

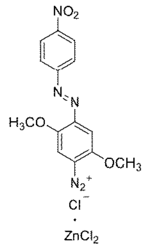

4-Bromobenzenediazonium tetrafluoroborate


4-Nitrobenzenediazonium tetrafluoroborate


4-Diazo-*N*,*N*-diethylaniline fluoroborate


4-Amino-4'-methoxydiphenylamine-diazonium chloride


4, 2-Methyl-4-([2-methylphenyl]azo)benzenediazonium salt


2,5-Dimethoxy-4-([4-nitrophenyl]azo)benzenediazonium chloride hemi(zinc chloride) salt

[0034] Advantageously, step a) and/or step b) of the process according to the invention may be conducted using a potentiostat.

[0035] Advantageously, the porous gas diffusion layer may be a commercial conducting carbon-based gas diffusion electrode or a porous polymer substrate such as (PTFE, nylon, PVDF).

[0036] Advantageously, step a) and/or step b) of the process according to the invention may be conducted under a current density from 5 $mA.cm^{-2}$ to 50 $mA.cm^{-2}$, preferably from 10 $mA.cm^{-2}$ to 20 $mA.cm^{-2}$, and more preferably at 15 $mA.cm^{-2}$.

[0037] Advantageously, in step a) of the process according to the invention, the quantity of deposited Cu may be from 0.5 $C.cm^{-2}$ to 50 $C.cm^{-2}$, preferably between 15 $C.cm^{-2}$ to 35 $C.cm^{-2}$, more preferably at 15 $mA.cm^{-2}$.

[0038] Advantageously, step a) and/or step b) of the process according to the invention may be done under pulse deposition or galvanostatic method. Preferably, the applied current density for electrodepositing copper is 15 $mA.cm^{-2}$, and the electrodepositing time is 5 minutes.

[0039] Advantageously, in the step a) of the process according to the invention, the source of copper (Cu) may be chosen in the group comprising $CuBr_2$, $CuCl_2$ and $CuSO_4$. The source of copper may be an electrolyte comprising $CuBr_2$, sodium tartrate dibasic dihydrate and KOH.

[0040] Advantageously, in the step a) of the process according to the invention, the electrodeposition of copper may be done using a carbon based-gas diffusion layer (GDL), a Pt plate, and Ag/AgCl (saturated with KCl) respectively as the working, counter, and reference electrodes, respectively. Alternatively, the process can be done using a 2-electrode configuration using a carbon based-gas diffusion layer (GDL) and a Pt plate respectively as the working and counter electrodes, respectively.

[0041] Advantageously, in step a) of the process according to the invention, the copper may be electrodeposited in a raspberry-like morphology.

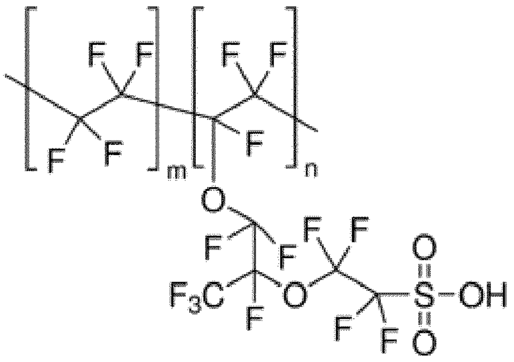
[0042] Advantageously, the process according to the invention may further comprise a pre-treatment step a') (prior to step a)) of electrodepositing Ag, Bi, Zn and/or Sn on the porous gas diffusion layer. In the pre-treatment step a') of the process according to the invention, the source of Ag, Bi, Zn and/or Sn may be chosen in the group comprising $-NO_3$, CH_3COO-, and/or -Cl. The source of Ag, Bi, Zn and/or Sn may be an electrolyte comprising $AgNO_3$, CH_3COOAg, $Bi(NO_3)_3{\cdot}5H_2O$, $ZnCl_2$ and/or $SnCl_4$, sodium tartrate dibasic dihydrate and KOH. The pre-treatment step a') may be done under the same conditions as step a) in terms of current density, quantity of deposited metal and pulse deposition or galvanostatic method.

[0043] Advantageously, the step b) of the process according to the invention may be performed in water, organic solvent(s) and mixtures thereof. The organic solvents may be chosen from ethanol, acetonitrile, methanol, acetone, propanol, tetrahydrofuran and mixtures thereof. The concentration of the diazonium salt of formula I in the water and/or an organic solvent may be from 1 to 100 mM, preferably from 2 to 10 mM. For example, when the diazonium salt is 4, 2-methyl-4-([2-methylphenyl]azo)benzenediazonium salt, the preferred concentration is 3 mM.

[0044] Advantageously, the step b) of the process according to the invention may be done under galvanostatic method with a current density from 0.1 to 5 mA.cm^{-2}, preferably from 0.2 to 2.5 mA.cm^{-2} , and more preferably at 0.75 mA.cm^{-2}.

[0045] Advantageously, the step b) of the process according to the invention may have a duration from 5 seconds to 30 minutes, preferably from 30 seconds to 10 minutes and more preferably 100 seconds. Step b) may be performed at a temperature from 5°C to 80 °C, preferably at room temperature (i.e., from 15 to 30 °C).

[0046] Advantageously, the process according to the invention may further comprise a step c) of spray coating an ionomer of formula III:



(Formula III)

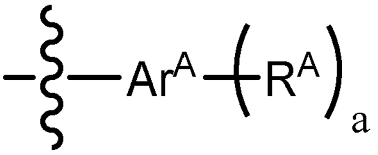
wherein,

m and n are integers from 1 to 50,000.

[0047] Advantageously, the process according to the invention may further comprise a step d) of washing the obtained catalyst compound with deionized water.

[0048] The invention also relates to a catalyst compound obtained by the process according to the invention.

[0049] The invention relates to a catalyst compound comprising a porous gas diffusion layer, said porous gas diffusion layer being at least partially coated by copper atoms, wherein at least one copper atom is functionalised by a substituent of formula I':

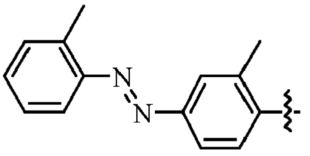
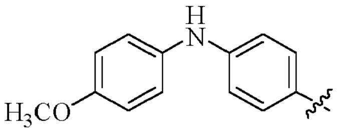


(Formula I')

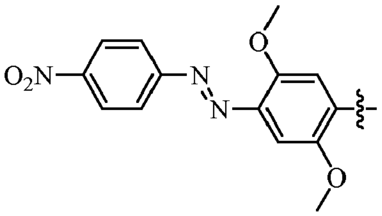
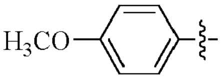
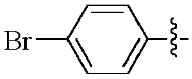
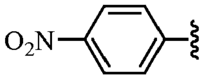
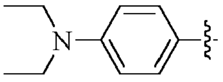
wherein Ar^A, R^A and a are defined as above and 〰 represents the point of attachment to copper.

[0050] Advantageously, the compound according to the invention may be chosen from catalyst compounds comprising a porous gas diffusion layer, said porous support being at least partially coated by copper atoms, wherein at least one copper atom is functionalised by a substituent of one or more of the following formulas:

Table 2: example of substituents

Substituents names	**Cation ions**
2-methyl-4-[(2-methylphenyl)diazenyl]phenyl	
4-[(4-methoxyphenyl)amino]phenyl	

(continued)

Substituents names	Cation ions
2,5-dimethoxy-4-[(4-nitrophenyl)diazenyl]phenyl	
4-methoxyphenyl	
4-Bromophenyl	
4-nitrophenyl	
4-(diethylamino)phenyl	

wherein 〰 represents the point of attachment to copper.

[0051] Advantageously, the compound according to the invention may further comprise a Ag, Bi, Zn and/or Sn atom layer in between the porous gas diffusion layer and the copper layer.

[0052] Advantageously, in the compound according to the invention, the copper may be in a raspberry-like morphology, while higher deposition currents will form dendritic fern-like structure.

[0053] Advantageously, the compound according to the invention, may comprise from 70 to 100 at.% of copper atoms, preferably 85 at.%, with regards to the total number of metal atoms in the compound.

[0054] Advantageously, the compound according to the invention, may have an Ar^A/Cu atomic surface ratio from 1 to 3, preferably from 1 and 2. The Ar^A/Cu atomic surface ratio, in number of atoms, is estimated from the top 5 nm of the surface of the compound and measured by X-ray photoelectron spectroscopy.

[0055] Advantageously, the compound according to the invention, may comprise from 0.5 to 50 at.% of Ag, Bi, Zn and/or Sn atoms, preferably 6 at.%, with regards to the total number of metal atoms in the compound.

[0056] Advantageously, the compound according to the invention, may have an Ar^A/(Ag, Bi, Zn and/or Sn) atomic surface ratio from 1 to 3, preferably from 1 and 2. The Ar^A/(Ag, Bi, Zn and/or Sn) atomic surface ratio, in number of atoms, is estimated from the top 5 nm of the surface of the compound and measured by X-ray photoelectron spectroscopy.

[0057] Advantageously, the compound according to the invention, may comprise a porous gas diffusion layer, preferably a commercial carbon-based gas diffusion electrode. The structure of the catalyst compound according to the invention is such as the porous gas diffusion layer is coated by a functionalized copper layer and may optionally comprise an in-between layer of Ag, Bi, Zn and/or Sn atom layer in between the porous gas diffusion layer and the copper layer.

[0058] Some advantages of the catalyst compound according to the invention are listed below:

- the catalyst compound according to the invention has an increased current density and an improved selectivity of the reaction towards the production of C_2 molecules (mainly ethylene) up to -213 mA.cm^{-2} and a Faradaic efficiency > 80 % at a full cell potential ($V_{cathode}$-V_{anode}) of -3.55 V compared to -122 mA.cm^{-2} and ~40 % for pristine non-functionalized Cu-based electrocatalyst at -3.80 V when measured in a 2-electrode configuration;
- the catalyst compound according to the invention can be easily obtained by electrodepositing Cu and optionally Ag, Bi, Zn and/or Sn metals in the form of a flower structure for larger active surface;
- the functionalization step b) is easy and cheap as the molecules needed are very common and easily obtainable;
- the catalyst compound according to the invention allows the production of high concentrated gaseous product, notably C_2 products and more specifically ethylene molecule with high added values
- the catalyst compound according to the invention have a total current density over 683 mA m^{-2} at -3.9 V in a 2-electrode configuration;

- the catalyst compound according to the invention have a specific current density over 536 mA m^{-2} for ethylene for CO_2RR at -3.9 V, which means 461 g $m^{-2}h^{-1}$ of ethylene.

[0059] The invention further relates to the use of the catalyst compound according to the invention as a catalyst, preferably to convert CO_2 into small molecules. It is meant by small molecules, molecules such as gaseous hydrocarbons (methane, ethylene) or liquid molecules (ethanol, formic acid). H_2 may be formed from the electrolysis of water (side-reaction). According to the invention, the conversion of CO_2 mainly leads to C_2H_4. Ethylene may represent up to ~82.4 % (volume ratio) of the gas products (the normalized concentration of CO and ethylene are 5.1 and 24 in GC) of the conversion of CO_2.

[0060] The invention further relates to a process of conversion of CO_2 into small molecules comprising a step of contacting CO_2 (gas) with a catalyst compound according to the invention. The conversion reaction of CO_2 may be done under atmospheric pressure and at room temperature (i.e., from 15 to 30°C). According to invention, the conversion reaction of CO_2 mainly leads to C_2H_4. Ethylene may represent up to ~82.4 % (volume ratio) of the gas products (the normalized concentration of CO and ethylene are 5.081 and 23.959 in GC) of the conversion of CO_2.

[0061] The conversion of CO_2 to products (mainly gas products, CO and ethylene) is conducted at room temperature and (25°C, 1 atm) with the periodic electrolyte of 0.5 M $KHCO_3$. The reactant of CO_2 is continuously flow into the membrane electrode assembly cell with the flow rate of 10 sccm.

Brief description of the figures

[0062]

Figure 1. Low-magnification scanning electron microscopy (SEM) images for the pristine and functionalized Cu catalysts. (a) Precursor 1 (Cu), (b_1) 1A and (b_2) the cross-section of 1A.

Figure 2. Comparison of FEs for ethylene on different Cu electrodes measured at full-cell potentials ranging from -3.0 to -4.0 V and measured in 0.5 M $KHCO_3$. Cu refers to Precursor 1, unfunctionalized Cu catalyst; 1A, 1B, 1C, 1D, 1E, 1F and 1G respectively refer to Cu modified with 2-methyl-4-[(2-methylphenyl)diazenyl]benzenediazonium; 4-[(4-methoxyphenyl)amino]benzene-1-diazonium chloride; dichlorozinc;2,5-dimethoxy-4-[(4-nitrophenyl)diazenyl]benzenediazonium; dichloride; 4-methoxybenzenediazonium;tetrafluoroborate; 4-Bromobenzenediazonium;tetrafluoroborate; 4-nitrobenzenediazonium;tetrafluoroborate and 4-(diethylamino)benzenediazonium;tetrafluoroborate; and 1I refers to Cu modified with 2-methyl-4-[(2-methylphenyl)diazenyl]benzenediazonium and the ionomer.

Figure 3. The total current density from different functionalized electrodes in membrane-electrode-assembly reactor (MEA). Cu refers to Precursor 1, unfunctionalized Cu catalyst; 1A, 1B, 1C, 1D, 1E, 1F and 1G respectively refer to Cu modified with 2-methyl-4-[(2-methylphenyl)diazenyl]benzenediazonium; 4-[(4-methoxyphenyl)amino]benzene-1-diazonium chloride; dichlorozinc;2,5-dimethoxy-4-[(4-nitrophenyl)diazenyl]benzenediazonium; dichloride; 4-methoxybenzenediazonium;tetrafluoroborate; 4-Bromobenzenediazonium;tetrafluoroborate; 4-nitrobenzenediazonium;tetrafluoroborate and 4-(diethylamino)benzenediazonium;tetrafluoroborate; and 1I refers to Cu modified with 2-methyl-4-[(2-methylphenyl)diazenyl]benzenediazonium and the ionomer.

Figure 4. The C_2H_4 specific current density from different functionalized electrodes in membrane-electrode-assembly reactor (MEA). Cu refers to Precursor 1, unfunctionalized Cu catalyst; 1A, 1B, 1C, 1D, 1E, 1F and 1G respectively refer to Cu modified with 2-methyl-4-[(2-methylphenyl)diazenyl]benzenediazonium; 4-[(4-methoxyphenyl)amino]benzene-1-diazonium chloride; dichlorozinc;2,5-dimethoxy-4-[(4-nitrophenyl)diazenyl]benzenediazonium; dichloride; 4-methoxybenzenediazonium;tetrafluoroborate; 4-Bromobenzenediazonium;tetrafluoroborate; 4-nitrobenzenediazonium;tetrafluoroborate and 4-(diethylamino)benzenediazonium;tetrafluoroborate; and 1I refers to Cu modified with 2-methyl-4-[(2-methylphenyl)diazenyl]benzenediazonium and the ionomer.

EXAMPLES

Example 1: Preparation of a catalyst compound precursor 1

[0063] The electrodeposition of Cu was conducted on a potentiostat. Firstly, to electrodeposit Cu, an electrolyte composed of 0.1 M copper bromide (98%, Sigma-Aldrich), 0.2 M sodium tartrate dibasic dihydrate (purum pro analysis ≥ 98.0% non-aqueous titration (NT), Sigma-Aldrich), and 1 M KOH was prepared. Acid-treated gas diffusion layer (GDL), Pt plate, and Ag/AgCl (saturated with KCl) were used as the working, counter, and reference electrodes, respectively. The Cu was electrodeposited galvanostatically on the GDL at a constant current density of 15 mA cm^{-2}. The loading amount of Cu is 4.5 C cm^{-2} with electrodepositing time of 300 seconds.

[0064] Firstly, Cu is successively electrodeposited on the support by controlling the voltage or the current density in order to control the morphology of the deposited. Cu was successively electrodeposited using a current density of 15 mA cm^{-2}. The loading of Cu is comprised 4.5 C cm^{-2}.

[0065] The best performance is obtained when the copper is grown in the form of a raspberry structure using a galvanostatic deposition method where the applied current density is 15 mA cm^{-2} (Figure. 1). The source of Cu used for the electrodeposition at $CuBr_2$ (CAS: 7789-45-9).

[0066] The catalyst compound precursor 1 was obtained.

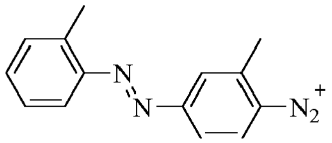
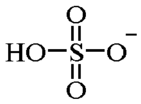
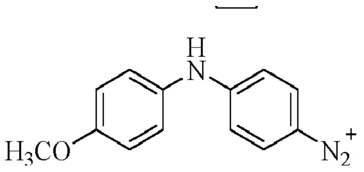
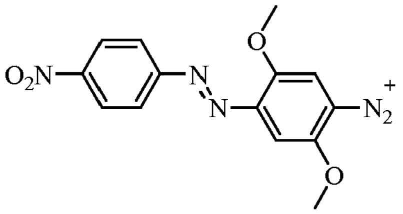
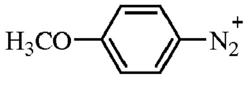
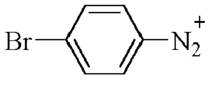
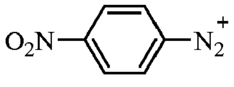
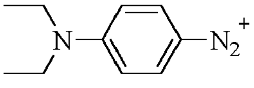
Example 2: Synthesis of the catalyst compounds 1A-1G according to the invention

[0067] The raspberry structured copper gave the performance in term of Faradaic efficiency (FE) towards C_2H_4 of 40% at -3.8 V in a MEA electrolyzer (Table 1).

[0068] Different diazonium salts functional groups of formula I were attached on the catalyst compound precursor 1 by an electroreduction method. The different diazonium salts molecules that have been tested are shown in Figures 2, 3 and 4. The functionalization of the catalyst compound precursor 1 was performed in water. The concentration of the diazonium salt of formula I, and reaction conditions are detailed in table 3 below. The electrodes were functionalized using the same optimized conditions in order to compare the performance of the different functional groups and the performances were recorded under the exact same conditions (electrolyte, temperature, time). The obtained electrodes (catalyst compounds 1A-1G) were washed with water and dried with Ar.

[0069] The catalyst compounds 1A-1G were obtained.

Table 3: reaction conditions

C. No	Reagents / concentration / solvent	Cation ions	Anion ions
1A	4, 2-Methyl-4-([2-methylphenyl] azo) benzenediazonium salt 3 mM in water		 $HO-S(=O)_2-O^-$
1B	4-Amino-4'-methoxydiphenylamine-diazonium chloride 3 mM in water		Cl^-
1C	dichlorozinc;2,5-dimethoxy-4-[(4-nitrophenyl) diazenyl] benzenediazonium; dichloride 3 mM in water		Cl^-. ½ $ZnCl_2$
1D	4-Methoxybenzenediazonium tetrafluoroborate 3 mM in water		BF_4^-
1E	4-Bromobenzenediazonium tetrafluoroborate 3 mM in water		BF_4^-
IF	4-Nitrobenzenediazonium tetrafluoroborate 3 mM in water		BF_4^-
1G	4-Diazo-*N*,*N*-Diethylaniline fluoroborate 3 mM in water		BF_4^-

Example 3: Performances of the catalyst compounds 1A-1G according to the invention

[0070] The catalytic performance of compounds 1A to 1G is presented in table 4 below:

Table 4: Summary of the electrocatalytic performance for pristine and functionalized Cu electrodes.

Electrode	**Cell voltages (V)**	**Faradaic efficiency (FE, %)**				
		H_2	**CO**	**HCOOH**	**C_2H_4**	**C_2H_5OH**
Precursor 1 (Cu)	-3.0	64.2±1.0	31.9±1.0	0	4.1±0.9	0
	-3.2	57.4±2.3	29.8±0.9	0	11.4±2.7	0
	-3.4	47.9±2.5	27.9±0.7	1.8±0.6	19.4±1.7	0
	-3.5	41.7±0.9	26.6±0.8	2.2±0.6	26.5±1.6	1.8±0.5
	-3.55	40.8±1.6	25.3±0.9	2.8±0.6	28.0±1.3	3.6±1.1
	-3.6	37.1±1.2	24.3±1.2	3.2±0.7	29.8±1.4	4.2±0.9
	-3.65	36.9±1.9	22.2±1.4	5.1±0.6	31.9±2.3	5.7±1.1
	-3.7	35.9±1.5	21.7±0.7	4.5±0.8	35.3±2.3	7.1±2.0
	-3.75	32.8±0.4	19.6±0.7	3.2±0.8	38.4±1.5	8.1±2.1
	-3.8	32.8±0.4	18.4±0.5	2.1±0.7	40.2±1.4	11.9±3.0
	-3.85	37.9±0.8	17.5±0.5	1.4±0.5	38.6±0.8	10.6±1.0
	-3.9	43.9±1.1	16.4±0.6	1.5±0.5	36.2±0.4	8.7±2.0
	-4.0	48.5±1.7	14.1±1.0	1.0±0.6	32.7±0.4	4.9±0.357.7
1G	-3.0	47.3±1.1	12.3±0.8	0	32.0±5.9	0
	-3.2	42.9±1.3	10.6±1.1	0	43.2±1.6	0
	-3.4	38.1±1.2	8.7±1.1	0.9±0.2	52.7±2.6	0.6±0
	-3.5	32.1±0.2	9.1±1.2	1.0±0.5	57.9±2.9	0.6±0.3
	-3.55	28.4±0.7	7.9+1.5	1.2±0.5	63.0±2.7	0.9±0.5
	-3.6	24.6±0.9	6.2±1.3	1.4±0.4	67.8±3.1	1.4±0.3
	-3.65	21.7±1.2	5.3±0.5	1.5±0.8	72.9±2.9	1.9±0.5
	-3.7	23.7±0.7	4.6±0.6	1.1±0.4	68.3±3.1	2.3±1.1
	-3.75	26.6±0.5	4.1±0.6	0.7±0.5	65.4±2.3	3.2±1.3
	-3.8	37.6±1.0	3.3±0.6	0.7±0.4	57.9±1.7	2.5±1.4
	-3.85	47.9±0.8	2.2±0.5	0.6±0.4	49.3±2.7	2.0±0.8
	-3.9	53.3±0.8	1.8±0.5	0.6±0.4	42.7±1.5	1.6±0.4
	-4.0	57.7±0.6	1.8±0.1	0.5±0.2	39.0±0.8	1.5±0.7

(continued)

Electrode	Cell voltages (V)	Faradaic efficiency (FE, %)				
1D	-3.0	33.0±7.7	22.8±1.1	0	40.2±3.1	0
	-3.2	26.2±2.1	24.3±1.9	0	48.9±4.3	0
	-3.4	23.6±2.7	20.1±2.1	0.9±0.3	53.6±5.6	1.0±1.9
	-3.5	23.2±3.4	15.4±1.7	0.9±0.8	57.3±3.2	1.5±2.7
	-3.55	18.7±2.9	10.3±1.6	1.3±0.6	65.4±3.7	2.9±4.2
	-3.6	16.4±3.2	9.0±4.7	1.4±0.8	72.2±5.3	3.1±3.3
	-3.65	15.3±3.4	6.7±1.6	1.5±0.8	78.0±2.7	3.8±4.5
	-3.7	14.3±3.5	5.3±2.3	1.3±0.8	76.4±4.1	5.1±4.6
	-3.75	16.9±4.2	3.6±1.0	1.2±0.7	74.3±2.7	3.8±3.0
	-3.8	19.5±5.4	3.2±1.9	1.4±0.6	71.1±4.9	3.3±3.1
	-3.85	22.8±7.1	2.7±1.9	0.8±0.7	70.6±2.2	2.3±3.1
	-3.9	24.1±8.4	2.4±0.8	1.1±0.8	70.0±3.3	1.9±2.9
	-4.0	29.3±0.9	2.5±0.3	0.8±0.2	65.6±0.6	1.2±0.4
1B	-3.0	47.3±2.5	35.4±3.0	0	15.5±2.0	0
	-3.2	37.2±2.5	34.1+1.7	0.3±0.1	22.5±1.7	0
	-3.4	25.9±1.4	31.8±1.4	0.4±0.1	36.6±1.4	1.1±0.1
	-3.5	22.0±1.0	24.6±0.5	0.5±0.1	43.7±0.6	1.3±0.4
	-3.55	20.8±1.3	19.5±1.4	0.7±0.2	51.7±0.9	1.3±0.6
	-3.6	19.1±1.2	14.2±0.1	1.1±0.7	61.7±2.3	2.3±0.8
	-3.65	17.8±1.0	11.0±1.1	1.2±0.8	68.6±2.5	2.5±0.7
	-3.7	16.3±0.6	9.3±0.4	1.2±0.4	72.7±2.0	2.6±1.0
	-3.75	15.3±0.4	7.1±0.7	1.8±0.8	76.8±1.1	2.7±1.1
	-3.8	14.2±0.2	5.5±0.8	1.2±0.8	79.9+0.5	3.3±0.6
	-3.85	15.5±0.4	5.1±0.9	0.9±0.9	78.1±1.7	3.1±1.1
	-3.9	16.5±1.0	4.7±1.2	0.8±0.8	75.3±1.3	3.1±1.2
	-4.0	20.7±0.5	3.4±0.9	0.5±0.6	72.0±0.9	2.3±0.8

(continued)

Electrode	Cell voltages (V)	Faradaic efficiency (FE, %)				
1A	-3.0	34.0±2.1	8.0±1.6	0	50.6±1.2	0
	-3.2	25.2±1.4	9.5±1.8	0.2±1.4	62.2±2.5	1.9±1.1
	-3.4	15.4±0.5	10.0±0.4	0.2±1.1	70.3±1.9	2.3±1.0
	-3.5	10.0±1.2	8.5±2.2	2.5±0.8	77.5±2.1	2.3±2.0
	-3.55	8.3±2.8	6.3±1.1	2.3±0.9	83.2±2.4	2.5±1.0
	-3.6	12.3±2.3	5.6±3.0	1.4±0.8	80.0±0.8	2.5±2.0
	-3.65	15.8±3.1	5.4±2.0	1.2±1.0	76.6±0.6	2.6±1.0
	-3.7	19.2±1.2	4.9±2.0	1.3±0.9	71.1±1.8	4.0±1.0
	-3.75	22.1±3.2	4.8±1.1	1.3±1.1	64.1±2.4	4.5±0.8
	-3.8	26.4±4.1	4.4±2.0	1.1±0.9	60.2±1.3	4.4±0.9
	-3.85	30.2±3.3	4.4±3.1	0.9±1.1	55.9±1.6	4.8±1.0
	-3.9	34.8±2.4	4.0±1.2	0.8±1.0	53.0±2.4	3.9±1.1
	-4.0	38.4±3.1	3.9±0.9	0.7±1.3	52.3±1.1	3.6±0.8
1C	-3.0	54.3±1.1	4.4±0.9	0	32.1±6.0	0
	-3.2	49.5±1.3	4.4±1.1	0	38.9±1.7	0
	-3.4	42.8±1.2	5.2±1.1	1.1±0.4	45.1±2.6	1.4±0.4
	-3.5	38.4±0.2	6.1±1.2	2.1±0.2	49.9±2.9	1.3±0.8
	-3.55	34.9±0.7	6.4±1.5	2.6±0.2	53.9±2.7	1.4±0.7
	-3.6	32.3±0.9	7.3±1.3	3.5±0.3	57.9±3.1	1.7±0.8
	-3.65	26.7±1.2	6.3±0.5	3.8±1.0	61.5±2.9	2.4±0.8
	-3.7	23.4±0.7	5.8±0.6	3.2±0.9	66.6±3.1	3.8±0.9
	-3.75	19.5±0.5	4.9±0.6	3.3±0.3	70.4±2.3	4.6±1.2
	-3.8	16.2±1.0	4.2±0.6	2.3±0.4	75.1±1.7	5.1±1.2
	-3.85	19.2±0.8	3.7±0.5	1.2±0.5	71.2±2.7	4.9±1.3
	-3.9	23.3±0.8	3.4±0.5	1.5±0.4	68.2±1.5	3.8±1.1
	-4.0	27.2±2.0	2.5±1.0	1.1±1.0	61.3±2.9	2.7±1.5

(continued)

Electrode	Cell voltages (V)	Faradaic efficiency (FE, %)				
1E	-3.0	48.5±3.7	25.0±0.5	0	21.9±0.5	0
	-3.2	43.9±4.7	27.7±1.0	0	25.9±1.0	0
	-3.4	38.2±7 .5	23.1±2.5	0.7±0.9	36.3±1.7	0.7±0.4
	-3.5	34.2±5.3	20.6±3.2	1.5±0.9	42.5±2.2	2.0±0.7
	-3.55	31.5±4.2	15.9±4.0	2.4±1.2	47.0±2.8	2.9±1.2
	-3.6	29.2±2.0	13.4±5.1	3.4±1.1	51.1±3.9	3.5±1.3
	-3.65	26.7±6.4	9.7+6.3	2.3±0.9	57.0±2.1	5.1±1.5
	-3.7	25.8±5.4	7.0±2.9	1.9±0.7	61.7±1.6	6.0±2.6
	-3.75	34.7±5.3	5.9±5.3	1.5±0.6	55.1±4.9	5.5±2.0
	-3.8	42.0±4.1	4.2±2.9	1.2±0.9	48.5±5.9	5.2±2.2
	-3.85	48.9±3.1	2.9±7.9	1.1±0.8	44.5±5.4	4.1±1.1
	-3.9	50.5±3.1	2.6±5.2	0.9±0.7	41.7±5.5	3.1±2.1
	-4.0	56.6±2.1	2.6±3.5	0.8±1.0	37.1±2.8	2.8±1.9
1F	-3.0	48.9±1.2	9.8+1.1	0	35.9±0.9	0
	-3.2	47.3±1.3	12.5±0.4	0	37.2±1.1	0
	-3.4	44.6±1.2	12.6±0.6	0.7±0.3	39.3±1.1	0
	-3.5	43.2±0.8	14.4±0.3	1.2±0.2	43.4±0.8	0.8±0.5
	-3.55	37.4±0.5	10.9±0.6	1.7±0.2	45.9±0.6	1.4±0.4
	-3.6	34.7±0.5	9.7+0.5	1.9±0.0	49.2±0.7	1.9±0.4
	-3.65	33.5±0.3	8.9+0.1	2.9±0.4	51.6±0.5	3.2±0.5
	-3.7	33.5±0.4	7.8±0.1	3.5±0.4	53.5±0.6	4.6±0.4
	-3.75	28.6±0.2	7.0±0.5	2.3±0.3	56.3±0.4	5.6±0.4
	-3.8	32.3±0.4	6.0±0.1	1.1±0.2	57.9±0.8	6.8±0.3
	-3.85	38.9±0.9	5.9±0.2	1.1±0.6	56.3±1.2	4.8±0.3
	-3.9	40.7±0.7	5.4±0.1	1.3±0.1	53.6±0.9	3.7±0.3
	-4.0	45.7±1.3	4.2±0.3	0.7±1.1	49.2±1.4	2.0±1.5

(continued)

Electrode	Cell voltages (V)	Faradaic efficiency (FE, %)				
1I	-3.0	66.9±3.5	4.6±0.2	0	23.7±1.0	0
	-3.2	58.9±1.5	5.1±0.3	0	25.3±0.6	0
	-3.4	53.7±1.8	7.1±0.2	1.0±0.5	37.4±1.1	0.6±0.4
	-3.5	47.9±1.1	7.1±0.3	1.4±0.5	43.9±1.8	1.0±0.5
	-3.55	44.9±1.5	5.3±0.1	1.5±0.5	49.4±0.8	1.0±1.1
	-3.6	40.4±1.0	4.8±0.1	1.7±0.4	56.1+1.3	1.2±0.6
	-3.65	34.1±0.9	4.7±0.2	2.0±0.5	64.2±1.8	1.7±1.0
	-3.7	28.9±0.6	4.2±0.1	1.5±0.4	73.6±2.0	2.1±0.5
	-3.75	24.4±0.5	4.2±0.1	1.1±0.5	75.5±1.7	2.5±1.1
	-3.8	17.8±0.1	3.6±0.3	1.1±0.4	86.3±0.5	2.8±1.5
	-3.85	10.2±0.3	4.0±0.1	1.1±0.6	89.7+0.9	2.3±1.0
	-3.9	27.6±0.4	3.2±0.4	1.1±0.4	79.5±1.0	2.3±0.9
	-4.0	33.2±2.2	3.6±1.3	0.6±0.9	73.8±2.1	1.7±1.5

[0071] The results shown in table 4 demonstrate that both the current density and the Faradaic efficiency are both strongly improved after functionalization. Compounds 1A and 1I groups gave the best results and the Faradaic efficiency towards the formation of C_2H_4 can reach 83% at - 3.55 V and 89% at -3.9 V compared to 40% for Precursor 1 (Fig. 2). By taking into account the current density, the results show that the specific current density for ethylene can be as high as 212 mA cm^{-2} and 536 mA cm^{-2} respectively from 1A and 1I (Figure. 4). These values correspond to a production of ~ 147.84 L and 369.6 L of ethylene per m^2 per hour of electrode for their applied potentials of -3.55 V and -3.9 V, respectively.

[0072] Importantly the functionalization of Cu to obtain compounds according to the invention translates into 1) high activity (higher current density), 2) higher efficiency towards the conversion of CO_2, 2) High activity towards the production of C_2H_4 product (Table 1).

[0073] The catalysts according to the invention prepared and tested in the example allowed improving the performance towards the production of C_2H_4 molecule at room temperature and atmospheric pressure. Compared to traditional Cu electrocatalyst, the Faradaic efficiency towards ethylene are increased by 43% and 49% for 1A and 1I groups modified Cu.

[0074] The new electrocatalysts according to the invention are more energy efficient.

List of references

[0075]

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[3]. Jouny, M., Luc, W. & Jiao, F. General techno-economic analysis of CO2 electrolysis systems. Industrial & Engineering Chemistry Research 57, 2165-2177 (2018).
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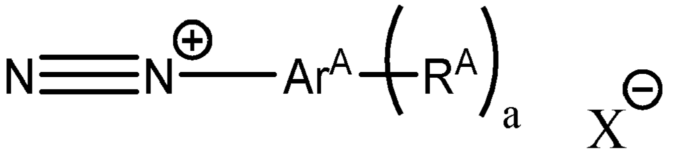
Claims

1. A process of manufacture of a catalyst compound comprising the steps of:

a) electrodepositing copper on a porous gas diffusion layer, the porous gas diffusion layer being optionally pretreated;
b) functionalization of the metal catalyst obtained in step a) by contacting with a diazonium salt of formula I:

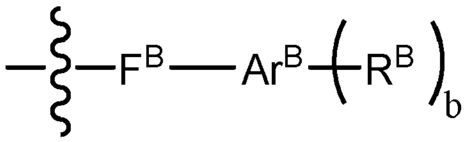


$$N\equiv N^{\oplus}-Ar^{A}\left(R^{A}\right)_{a}\quad X^{\ominus}$$

(Formula I)

wherein,

- X^- represents an anion,
- a is an integer from 1 to 3,
- Ar^A represents an aryl group, substituted by at least one $-R^A$ group,
- $-R^A$ represents at least one substituent chosen from a halo group, $-R^1$, $-NO_2$, $-OR^1$, $-NR^2R^3$ and a group of formula II:



$$-F^{B}-Ar^{B}\left(R^{B}\right)_{b}$$

(Formula II),

in which,

- ◦ $-R^1$ represents a C_1 to C_3 alkyl group,
- ◦ $-R^2$ and R^3 independently represent H or a C_1 to C_3 alkyl group,
- ◦ b is an integer from 1 to 3,
- ◦ F^B is a functional group chosen from -N=N- and -NH-,
- ◦ Ar^B represents an aryl group, substituted by at least one $-R^B$ group,
- ◦ $-R^B$ represents at least one substituent chosen from a halo group, $-R^1$, $-OR^1$ and $-NR^2R^3$,
- ◦ 〰 represent the point of attachment to Ar^A.

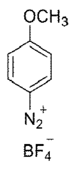
2. The process according to claim 1, wherein the copper is electrodeposited in a raspberry-like morphology.

3. The process according to any of preceding claims, further comprising a pre-treatment step a') of electrodepositing Ag, Bi, Zn and/or Sn on the porous gas diffusion layer.

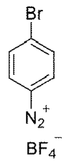
4. The process according to any of preceding claims, wherein X^- is chosen from BF_4^-, Cl^- and HSO_4^-.

5. The process according to any of preceding claims, wherein Ar^A and/or Ar^B are phenyl groups.

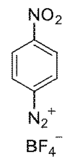
6. The process according to any of preceding claims, wherein the diazonium salt of formula I is chosen from the following salts:



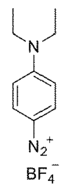
4-Methoxybenzenediazonium tetrafluoroborate



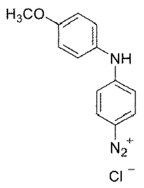
4-Bromobenzenediazonium tetrafluoroborate

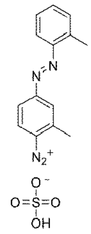


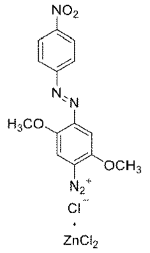
4-Nitrobenzenediazonium tetrafluoroborate



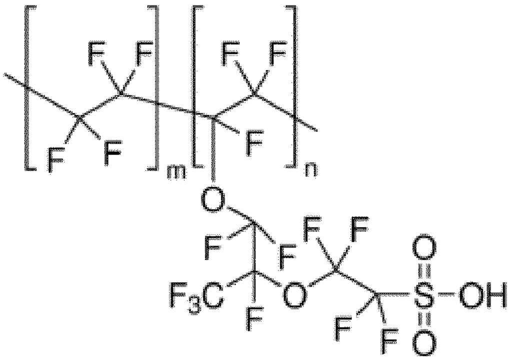
4-Diazo-*N*,*N*-diethylaniline fluoroborate


4-Amino-4'-methoxydiphenylamine-diazonium chloride


4, 2-Methyl-4-([2-methylphenyl]azo)benzenediazonium salt


2,5-Dimethoxy-4-([4-nitrophenyl]azo)benzenediazonium chloride hemi(zinc chloride) salt

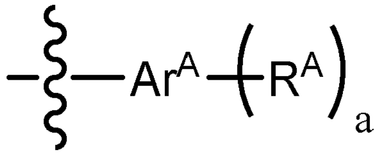
7. The process according to any of preceding claims, further comprising a step c) of spray coating an ionomer of formula III:


(Formula III)

wherein,
m and n are integers from 1 to 50,000.

8. A catalyst compound obtained by the process according to any of the preceding claims.

9. A catalyst compound comprising a porous gas diffusion layer, said porous gas diffusion layer being at least partially coated by copper atoms, wherein at least one copper atom is functionalised by a substituent of formula I':


$$-Ar^{A}\left(R^{A}\right)_{a}$$
(Formula I')

wherein Ar^A, R^A and a are defined as in previous claims and 〰 represents the point of attachment to copper.

10. The compound according to the preceding claim, further comprising a Ag, Bi, Zn and/or Sn atom layer in between the porous gas diffusion layer and the copper layer.

11. The compound according to any of claims 8 to 10, wherein the copper is in a raspberry-like morphology.

12. The compound according to any of claims 8 to 11, wherein the porous gas diffusion layer is a commercial conducting carbon-based gas diffusion electrode or a porous polymer substrate such as PTFE, nylon or PVDF.

13. Use of the compound according to any of claims 8 to 12 as a catalyst, preferably to convert CO_2 into small molecules, preferably C_2H_4, C_2H_5OH, CO, formic acid, as well as small amount of H_2.

14. A process of conversion of CO_2 into small molecules comprising a step of contacting CO_2 with a catalyst compound according to any of claims 8 to 12.

15. The process according to the preceding claim, wherein the conversion reaction of CO_2 is done under atmospheric pressure and at room temperature.

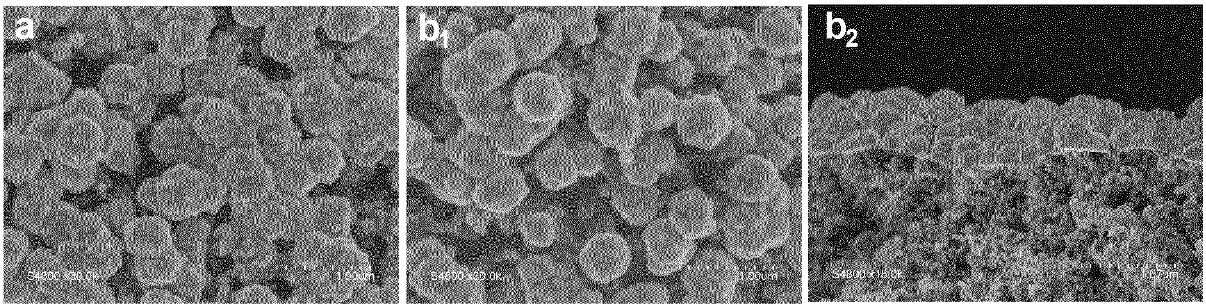


Figure 1

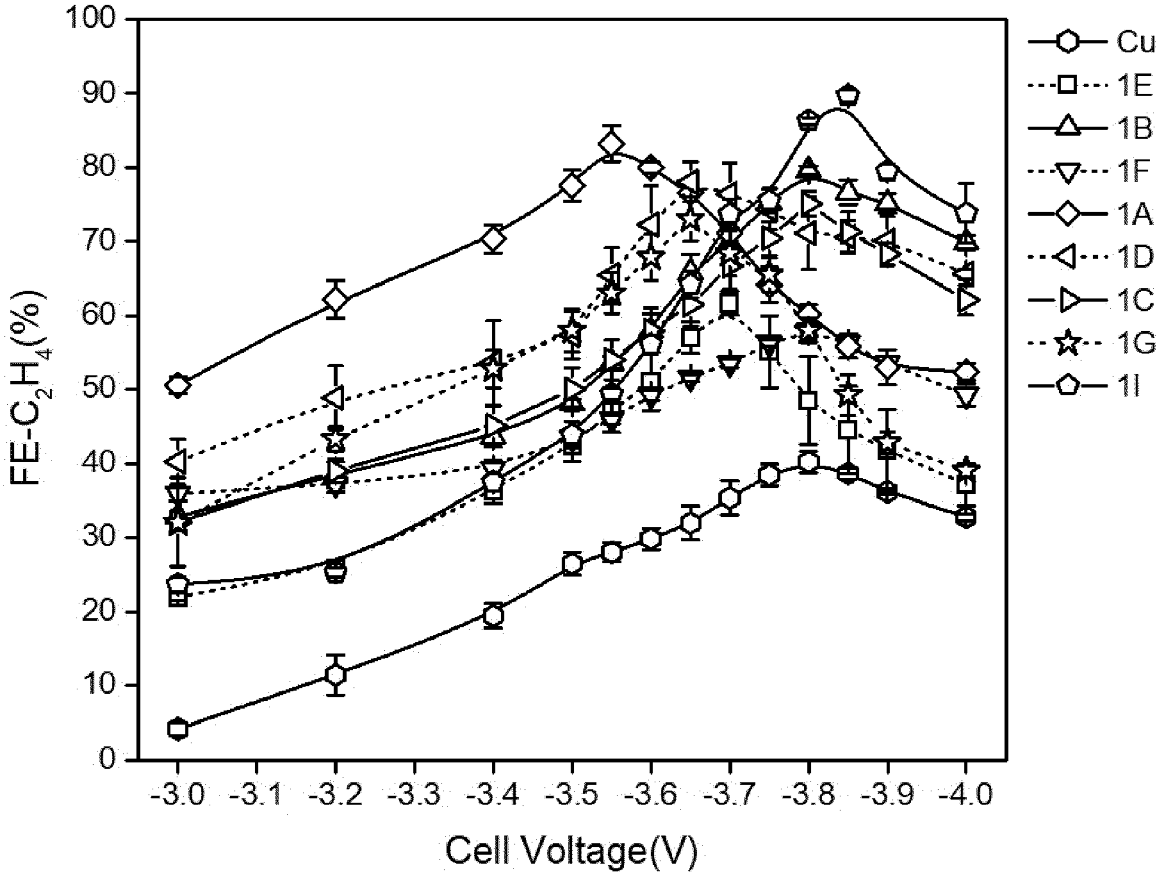


Figure 2

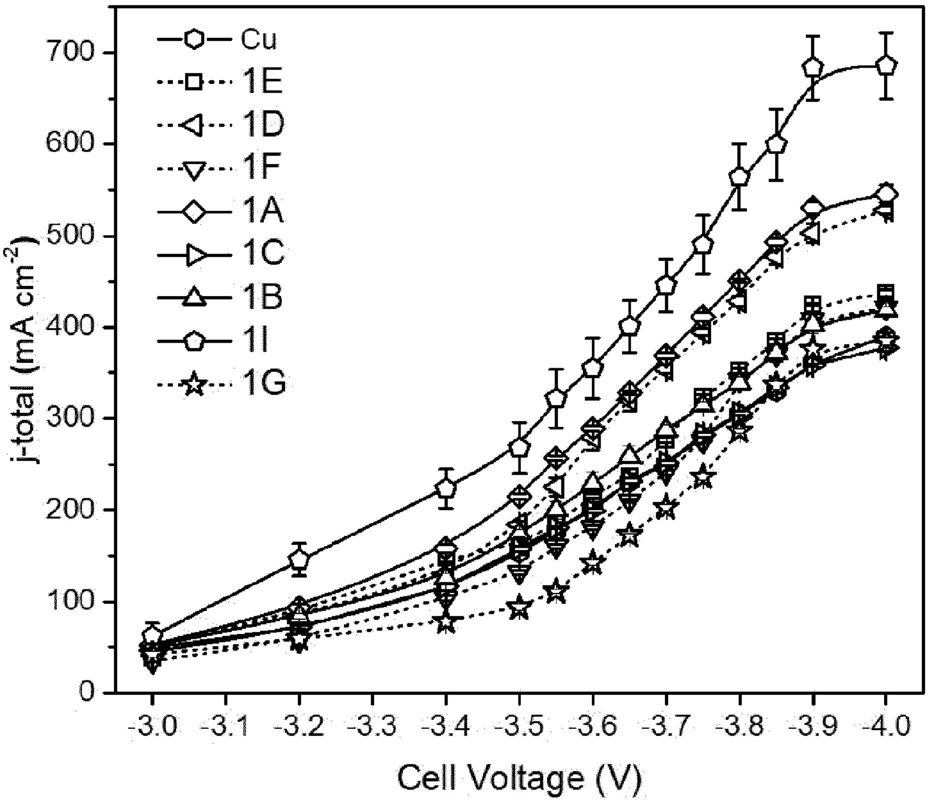


Figure 3

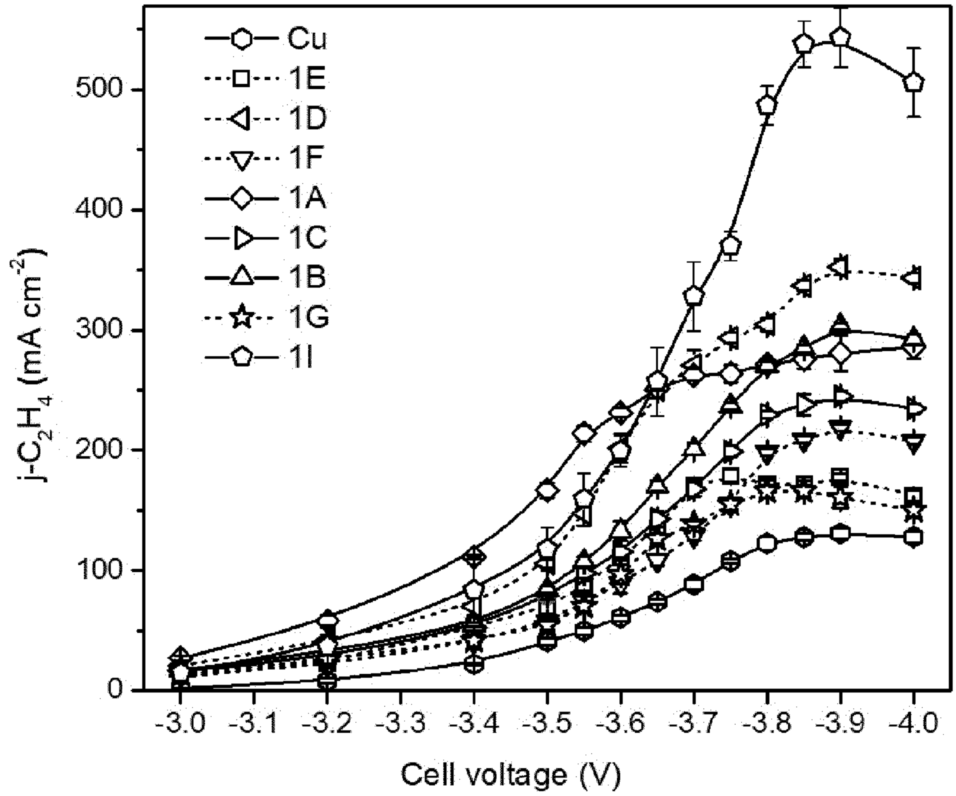


Figure 4

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EUROPEAN SEARCH REPORT

Application Number
EP 22 30 5716

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
X	FAN LEI, XIA CHUAN, YANG FANGQI, WANG JUN, WANG HAOTIAN, LU YINGYING: "strategies in catalyst and electrolyzer design for electrochemical CO2 reduction toward C2+ productsproducts", SCIENCE ADVANCES, vol. 6, 21 February 2020 (2020-02-21), pages 1-17, XP009541564, DOI: 10.1126/sciadv.aay3111 * pages 7, 11-13; figure 5e * -----	1,3,5, 8-10, 12-15	INV. C25B1/23 C25B3/09 C25B3/26 C25B11/032 C25B11/052 C25B11/085 C25D3/38 C25D5/10 C25D5/34 C25D5/48
A	Koval 'chuk Eugen P ET AL: "Products of the interaction of copper and benzenediazonium tetrafluoroborate in acetonitrile medium", Chem. Met. Alloys, 1 January 2009 (2009-01-01), XP093011503, Retrieved from the Internet: URL:http://www.chemetal-journal.org/ejournal5/CMA0099.pdf [retrieved on 2023-01-04] * the whole document * -----	1-15	
A	CHIRA ANA ET AL: "Electrodeposited Organic Layers Formed from Aryl Diazonium Salts for Inhibition of Copper Corrosion", MATERIALS, vol. 10, no. 3, 1 January 2017 (2017-01-01), page 235, XP093011401, CH ISSN: 1996-1944, DOI: 10.3390/ma10030235 * the whole document * -----	1-15	**TECHNICAL FIELDS SEARCHED (IPC)** C25B C23C C25D
A	US 2006/226021 A1 (BRUNNER HEIKO [DE] ET AL) 12 October 2006 (2006-10-12) * claims 1-22 * ----- -/--	1-15	

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
Munich	4 January 2023	Teppo, Kirsi-Marja

1

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Application Number
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DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
A	US 2006/141156 A1 (VIEL PASCAL [FR] ET AL) 29 June 2006 (2006-06-29) * claims 1-28 * -----	1-15	
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The present search report has been drawn up for all claims

1

Place of search	Date of completion of the search	Examiner
Munich	4 January 2023	Teppo, Kirsi-Marja

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For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

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- **AGER, J. W. ; LAPKIN, A. A.** Chemical storage of renewable energy. *Science,* 2018, vol. 360, 707-708 **[0075]**
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