



(11) **EP 4 136 277 B1**

(12) **EUROPEAN PATENT SPECIFICATION**

(45) Date of publication and mention  
of the grant of the patent:  
**22.05.2024 Bulletin 2024/21**

(21) Application number: **21724756.8**

(22) Date of filing: **14.04.2021**

(51) International Patent Classification (IPC):  
**C25B 1/23** <sup>(2021.01)</sup> **C25B 11/02** <sup>(2021.01)</sup>  
**C25B 11/043** <sup>(2021.01)</sup> **C25B 11/065** <sup>(2021.01)</sup>  
**C25B 11/091** <sup>(2021.01)</sup>

(52) Cooperative Patent Classification (CPC):  
**C25B 11/02; C25B 1/23; C25B 11/043;**  
**C25B 11/065; C25B 11/091**

(86) International application number:  
**PCT/IB2021/053074**

(87) International publication number:  
**WO 2021/209920 (21.10.2021 Gazette 2021/42)**

(54) **COPPER AND ANTIMONY BASED MATERIAL AND ELECTRODE FOR THE SELECTIVE  
CONVERSION OF CARBON DIOXIDE TO CARBON MONOXIDE**

MATERIAL AUF KUPFER- UND ANTIMONBASIS UND ELEKTRODE ZUR SELEKTIVEN  
UMWANDLUNG VON KOHLENDIOXID IN KOHLENMONOXID

MATÉRIAU À BASE DE CUIVRE ET D'ANTIMOINE ET ÉLECTRODE POUR LA CONVERSION  
SÉLECTIVE DE DIOXYDE DE CARBONE EN MONOXYDE DE CARBONE

(84) Designated Contracting States:  
**AL AT BE BG CH CY CZ DE DK EE ES FI FR GB  
GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO  
PL PT RO RS SE SI SK SM TR**

(30) Priority: **15.04.2020 IT 202000007948**

(43) Date of publication of application:  
**22.02.2023 Bulletin 2023/08**

(73) Proprietor: **Fondazione Istituto Italiano di  
Tecnologia  
16163 Genova (IT)**

(72) Inventors:  
• **ZENG, Juqin  
10144 Torino (IT)**  
• **CHIODONI, Angelica Monica  
10144 Torino (IT)**  
• **RINO, Telemaco  
10141 Torino (IT)**

(74) Representative: **Palladino, Saverio Massimo et al  
Notarbartolo & Gervasi S.p.A.  
Viale Achille Papa, 30  
20149 Milano (IT)**

(56) References cited:  
**US-A1- 2018 119 296**

- **YOUNG DAE YUN ET AL: "Optimal synthesis of antimony-doped cuprous oxides for photoelectrochemical applications", THIN SOLID FILMS, vol. 671, 1 February 2019 (2019-02-01), pages 120-126, XP055762036, AMSTERDAM, NL ISSN: 0040-6090, DOI: 10.1016/j.tsf.2018.12.037**
- **LILY MANDAL ET AL: "Investigating the Role of Copper Oxide in Electrochemical CO<sub>2</sub> Reduction in Real Time", ACS APPLIED MATERIALS & INTERFACES, vol. 10, no. 10, 13 February 2018 (2018-02-13), pages 8574-8584, XP055636493, US ISSN: 1944-8244, DOI: 10.1021/acsami.7b15418**
- **IRFAN MALIK M ET AL: "Electrochemical reduction of CO<sub>2</sub> to methanol over MWCNTs impregnated with Cu<sub>2</sub>O", CHEMICAL ENGINEERING SCIENCE, OXFORD, GB, vol. 152, 17 June 2016 (2016-06-17), pages 468-477, XP029667794, ISSN: 0009-2509, DOI: 10.1016/J.CES.2016.06.035**
- **IN-YUP JEON ET AL: "Antimony-doped graphene nanoplatelets", NATURE COMMUNICATIONS, vol. 6, 22 May 2015 (2015-05-22), page 7123, XP055353208, DOI: 10.1038/ncomms8123**

Note: Within nine months of the publication of the mention of the grant of the European patent in the European Patent Bulletin, any person may give notice to the European Patent Office of opposition to that patent, in accordance with the Implementing Regulations. Notice of opposition shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European Patent Convention).

**EP 4 136 277 B1**

## Description

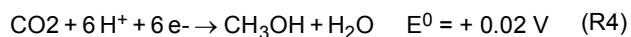
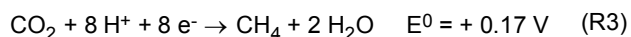
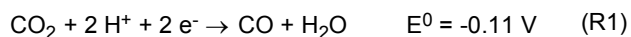
## FIELD OF THE INVENTION

**[0001]** The present invention relates to a copper and antimony based material, and an electrode obtained from this material, useful for the electrochemical reduction of carbon dioxide to carbon monoxide with high efficiency and selectivity.

## STATE OF THE ART

**[0002]** Massive emissions of carbon dioxide (CO<sub>2</sub>), also known as carbonic anhydride, due to the burning of fossil fuels, have been recognized as responsible for global climate change. To tackle this problem, strategies such as CO<sub>2</sub> capture and storage are being studied, with the aim of slowing or even stopping the accumulation of CO<sub>2</sub> in the atmosphere. The transformation of captured CO<sub>2</sub> into additional chemicals, fuels or other products is of paramount importance to achieve a sustainable carbon cycle and to store energy in the long term. Among the different technologies for CO<sub>2</sub> transformation, electrochemical conversion is considered particularly interesting since it can use energy obtained from renewable sources. This technology, although very promising, is of non-immediate applicability due to the high stability of the CO<sub>2</sub> molecule, the slow kinetics and the complex mechanisms of the CO<sub>2</sub> reduction reaction.

**[0003]** CO<sub>2</sub> reduction can occur according to several proton-coupled electron transfer processes. CO<sub>2</sub> reduction reactions for the production of compounds containing a single carbon atom and the electrochemical evolution of H<sub>2</sub> are reported below as R1-R5, together with their standard potentials:



**[0004]** Values of E<sup>0</sup> are reported under standard conditions (1 atm and 25 °C) with respect to the reversible hydrogen electrode (RHE) in aqueous media. Unless otherwise stated, all potentials in this description refer to the RHE.

**[0005]** Among the numerous products of CO<sub>2</sub> reduction, formic acid (HCOOH) and carbon monoxide (CO) are the only economically viable products that have been obtained so far with relevant productivity. CO is highly desired in the industrial sector, since its mixture with hydrogen (H<sub>2</sub>), i.e., synthetic gas or syngas, can be converted into hydrocarbons through the Fischer-Tropsch process.

**[0006]** Since, however, the values of the standard potentials of the above reactions are similar, the result of the process is usually a mixture of products, which is difficult or not easy to use industrially. In addition, the parasitic reaction of hydrogen evolution usually occurs in higher yield than the reduction of CO<sub>2</sub> in aqueous electrolyte.

**[0007]** Therefore, electrode materials are required that can provide high CO<sub>2</sub> conversion efficiency and at the same time high selectivity towards a specific reaction product, in particular towards CO; materials of this kind are generally known in electrochemistry as electrocatalysts.

**[0008]** According to experimental and theoretical studies, gold (Au), silver (Ag) and palladium (Pd) are considered the best metal electrocatalysts to convert CO<sub>2</sub> into CO; however, these metals cannot be used on an industrial scale for this purpose due to their high cost and low availability.

**[0009]** In addition to the previous materials, the electrocatalytic properties, in CO<sub>2</sub> reduction, of metals such as copper (Cu), zinc (Zn), tin (Sn), indium (In) and bismuth (Bi) have been studied. Cu alone has no good selectivity for any product; Zn has sufficient, but not optimal, selectivity for CO production; Sn, In and Bi are selective for HCOOH production.

**[0010]** In some papers, the properties as electrocatalysts of compositions other than single metals are discussed.

**[0011]** Patent application US 2019/0127866 A1 describes an electrocatalyst material for converting CO<sub>2</sub> to ethanol, comprising nanoparticles of copper or alloys thereof supported by nanometer-sized tips ("nanospikes") of carbon doped with nitrogen, boron or phosphorus. Copper alloys indicated as useful by this document are all those of the element with one or more elements selected from those in the Groups 3-15 of the periodic table. Alloys indicated as preferred are those between copper and an element selected from Ni, Co, Zn, In, Ag and Sn. The electrocatalysts of this document exhibit higher selectivity for CO<sub>2</sub> electroreduction than H<sub>2</sub> evolution with high faradic efficiency in ethanol production, with a yield in this compound of at least 60% of the mixture; other species, such as carbon monoxide, are thus produced with yields not exceeding 40%. In addition to the fact that a mixture of products is produced, the preparation of the doped carbon nanospikes makes the process not straightforward.

**[0012]** The article "Achieving highly selective electrocatalytic CO<sub>2</sub> reduction by tuning CuO-Sb<sub>2</sub>O<sub>3</sub> nanocomposites",

Y. Li et al., ACS Sustainable Chem. Eng. 2020, 8, 12, 4948-4954, describes an electrocatalyst material comprising a mixture of carbon in a finely divided form ("carbon black") and powders of a mixed oxide of copper(II) (CuO) and antimony(III) (Sb<sub>2</sub>O<sub>3</sub>). The purpose of this study is to identify the best conditions for converting CO<sub>2</sub> to CO. The materials in this paper are produced by dissolving soluble Cu(II) and Sb(III) salts in a suspension of carbon black in ethanol, adding a base (KOH) to the suspension and allowing the system to react for 6 hours at a temperature of 80 °C obtained with an oil bath; the precipitate obtained is then washed with water and ethanol and finally dried. The mixture of powders thus obtained is then distributed on a carbon paper obtaining electrodes. In the section "Results and discussion" of the article, it is confirmed that copper oxide is in the form of CuO (i.e., copper is in oxidation state (II)) and that antimony oxide is in the form of Sb<sub>2</sub>O<sub>3</sub> (i.e., antimony is in oxidation state (III)), by X-ray diffraction analysis (XRD, Fig. 1.a of the article) showing the presence of the characteristic peaks of CuO and Sb<sub>2</sub>O<sub>3</sub>, by X-ray photoelectron spectroscopy (XPS, Fig. 1.b) and by Raman spectroscopy (Fig. 1.c). As shown in the article (see Figure 3.b), the best results are obtained with the molar ratio Cu:Sb 10: 1, with which faradic yields of approximately 10% for HCOOH, 10% for H<sub>2</sub> and 80% for CO are obtained, while the authors report that as the Sb content increases, the CO yield drops rapidly. The results obtained with the best material of this article are already interesting, but still not optimal both as CO yield and as selectivity towards this compound (a mixture of three products is obtained).

**[0013]** The object of the present invention is to overcome the problems of the prior art, and in particular to provide an electrocatalyst material which allows to obtain in the electrochemical reduction reaction of CO<sub>2</sub> a CO yield and a selectivity towards this compound higher than with the electrocatalysts of the prior art. Another object of the invention is to make available a cost-effective process for large-scale production of this electrocatalyst.

## SUMMARY OF THE INVENTION

**[0014]** These objects are achieved with the present invention, which in a first aspect relates to an electrocatalyst material comprising copper(I) oxide (Cu<sub>2</sub>O) containing antimony, wherein the amount of antimony is between 5% to 30% by weight.

**[0015]** This material is used in a finely divided form to produce electrodes for the electrochemical reduction of CO<sub>2</sub>, wherein said material is combined with an electroconductive material.

**[0016]** In a second aspect thereof, the invention relates to a process for the production of the electrocatalyst material, comprising the following steps:

- a) dissolving a copper(II) salt and an antimony(III) salt in a solvent selected from ethanol, ethylene glycol, acetylacetone, diethylamine, ethylenediamine, oleylamine, N,N-dimethylformamide, mixtures of these solvents with each other, with water or with aqueous solutions of D-glucose, hydrazine hydrate, amino acids or sodium carboxymethylcellulose, obtaining a solution;
- b) heating the solution in a microwave oven at a temperature between 180 and 230 °C for a time between 1 and 10 minutes;
- c) separating the precipitate from the solution and its drying.

## BRIEF DESCRIPTION OF THE DRAWINGS

**[0017]** The invention will be described in detail in the following with reference to the figures, in which:

- Fig. 1 shows photomicrographs obtained by field effect scanning electron microscope (FESEM) of various materials of the invention and three comparison materials;
- Fig. 2 shows results of X-ray diffraction (XRD) of powder samples of materials of the invention having different compositions and three comparison materials;
- Fig. 3 shows spectra obtained by X-ray photoelectron spectroscopy (XPS) for Cu and Sb on a sample of the invention;
- Fig. 4 represents in a schematic form an electrolytic cell used to carry out the CO<sub>2</sub> reduction tests reported in the Examples section;
- Fig. 5 shows graphs representative of the faradic efficiency in the conversion of CO<sub>2</sub> to CO obtained with a material of the invention.

## DETAILED DESCRIPTION OF THE INVENTION

**[0018]** The inventors have found that copper(I) oxide (Cu<sub>2</sub>O, cuprous oxide) containing antimony in an amount between 5 and 30% by weight, when used to produce an electrode, enables the electrochemical reduction of CO<sub>2</sub> to CO to be achieved with higher values of faradic efficiency and selectivity than known materials. The compounds of the invention enable these results to be obtained by employing copper and antimony, which are inexpensive and widely available

components.

**[0019]** A material similar to that of the present invention has been described in the paper "Optimal synthesis of antimony-doped cuprous oxides for photoelectrochemical applications", Dae Yun et al., Thin Solid Films 671 (2019) 120-126. However, this paper is directed to the study of the influence of Sb concentration on the structural, electrical and photoelectrochemical properties of cuprous oxide thin films for the purpose of photoelectrochemical water splitting; besides, this study reports materials in which the amount of Sb reaches at most up to 1% in moles, and indicates as a preferred material for the mentioned purpose Cu<sub>2</sub>O doped with 0.75% molar Sb.

**[0020]** The materials of the invention will generally be referred to in the following by the notation Cu<sub>2</sub>O/Sb, regardless of the specific composition.

**[0021]** The Cu<sub>2</sub>O/Sb materials of the invention have a Sb content between 5 and 30% by weight; preferred are the materials having a Sb content between 17.2 and 23.9% by weight.

**[0022]** The materials of the invention are obtained and used in powder form. The morphology of these powders is uniform and homogeneous at least up to the Sb concentration of 26.4%. Fig. 1 shows images obtained by field effect scanning electron microscope (FESEM) of samples of the invention with increasing Sb content (Figs. 1(b) to 1(i)) and, for comparison, of three samples produced following the same method as the samples of the invention but containing only copper (Fig. 1(a)), only antimony (Fig. 1(k)), and a sample not of the invention containing an amount of antimony of 36% (Fig. 1(j)); in particular, the weight percentage amount of Sb in the samples of the invention prepared as described in Example 1, determined by chemical analysis, is as follows:

- Fig. 1(b):	5.2;
- Fig. 1(c):	9.4;
- Fig. 1(d):	13.6;
- Fig. 1(e):	17.2;
- Fig. 1(f):	20.1;
- Fig. 1(g):	23.9;
- Fig. 1(h):	25.2
- Fig. 1(i):	26.4.

**[0023]** As can be seen in the images, the materials of the invention with a Sb content of up to 26.4% by weight have a similar morphology to one another, and comprise powders in the form of essentially spherical particles with very narrow size distribution (all particles have a size of about 5 μm), composed of tightly packed nanoparticles. For concentrations higher than 26.4%, Sb-rich particles and the formation of an isolated phase consisting of crystalline Sb<sub>2</sub>O<sub>3</sub> are observed (octahedral particles in Fig. 1(j)), to be compared with the image of pure antimony oxide in Fig. 1(k)). Energy dispersive X-ray spectroscopy (EDX) analysis indicates that Sb is uniformly distributed in the samples of the invention.

**[0024]** XRD analysis confirms that the material is essentially copper oxide. In Fig. 2 are shown, from top to bottom, the diffractograms for the sample containing only copper (diffractogram indicated with (Cu)), of the samples of the invention with increasing concentration of antimony (diffractograms from A to H), and of the sample containing 36% by weight of antimony (diffractogram indicated with (NI), which stands for "not of the invention"), respectively. As can be seen in the figure, in the samples of the invention up to a Sb content of 26.4% by weight, only peaks attributable to the Cu<sub>2</sub>O phase are present (with decreasing intensity as the Sb content increases); in the sample with a Sb content of 36.0% by weight, peaks attributable to the Sb<sub>2</sub>O<sub>3</sub> phase appear instead, although with low intensity.

**[0025]** The composition is also confirmed by high-resolution (HR) XPS spectroscopy. Figure 3 shows the typical spectra of the sample containing 17.2% by weight of Sb. From the XPS measurement (Fig. 3a) it appears that antimony is present in the sample in the form of Sb<sup>3+</sup> ions, as highlighted by the intense peaks relative to Sb 3d<sub>5/2</sub> and Sb 3d<sub>3/2</sub> centred at 530.06 eV and 539.45 eV, respectively. Fig. 3b shows instead the region of the XPS spectrum corresponding to the Cu 2p doublet; since the Cu 2p peak is difficult to deconvolve due to the overlap of numerous peaks, the Auger CuLMM region is also acquired (inset in Figure 3b). The kinetic energy of the peak is 916.8 eV, which corresponds to Cu<sup>+</sup>. The modified Auger parameter is about 1848.8 eV, which correlates with an average oxidation state of Cu(I). It is therefore evident that copper is present in the samples in the form of Cu<sup>+</sup> ion.

**[0026]** Since the electrocatalyst materials of the invention are poor electrical conductors *per se*, they are used in combination with conductive materials for the production of electrodes for CO<sub>2</sub> reduction. Preferably, the conductive material is in turn in the form of powders or other finely divided form. A carbon-based material is generally used for this purpose, thanks to its low catalytic activity, for example carbon black, graphite, graphene, carbon nanotubes or mixtures thereof; the preferred conductive material is carbon black. The electrocatalyst material of the invention and the conductive material are used in weight ratios between 9:1 and 19:1. For the production of the electrode, the mixture between the electrocatalyst material of the invention and the conductive material is distributed on a support, which may in turn be

conductive or non-conductive. Examples of preferred supports are conductive carbon paper, conductive carbon cloth and metal mesh. Stabilization of the powder mixture on the support can be achieved with ionomers, i.e., ion conductive polymers, which form a containing and conductive film on the powders.

[0027] In a second aspect thereof, the invention relates to a process for the production of the electrocatalyst material, which consists of steps a) to c) above.

[0028] Step a) consists in dissolving a copper(II) salt and an antimony(III) salt in a solvent selected from ethanol, ethylene glycol, acetylacetone, diethylamine, ethylenediamine, oleylamine, N,N-dimethylformamide, mixtures of these solvents with each other, with water or with aqueous solutions of D-glucose, hydrazine hydrate, amino acids and sodium carboxymethylcellulose. The most suitable salts for the purposes of the invention are acetates, sulfates and nitrates of both metals. The starting salts are weighed to obtain the desired weight ratio of Cu:Sb, and thus the desired weight ratio of Cu<sub>2</sub>O to Sb; the calculations necessary to determine the quantities to be used of the starting salts, given a desired final composition, are of simple executability for the average chemist.

[0029] The solution thus formed is heated in a microwave oven, within a sealed container of suitable material (e.g., Teflon) at a temperature between 180 and 230 °C for a time between 1 and 10 minutes. In addition to causing the metal salts to react to form the final material, microwave heating in the presence of the aforementioned solvents results in the reduction of the Cu<sup>2+</sup> ion of the starting copper salt to Cu<sup>+</sup> ion present in the Cu<sub>2</sub>O oxide. In the case of ethylene glycol, glycol functions as both a solvent and a reducing agent, and increasing temperature can increase its reducing capacity. Normally a temperature between 180 °C and 230 °C is suitable for the formation of Cu<sup>+</sup> from Cu<sup>2+</sup> in the given solution.

[0030] Finally, the precipitate formed in the microwave heating is separated from the liquid phase, e.g., by filtration or centrifugation, washed with ethanol, and dried, e.g., by treatment in an oven at a temperature between 50 and 100 °C under vacuum or in an inert atmosphere.

[0031] The process of the invention differs from that of the article by Li *et al.* cited above in that microwave heating is used instead of conventional heating, that as said results in the reduction of the Cu<sup>2+</sup> ion of the starting copper salt and the formation of the Cu<sub>2</sub>O phase.

[0032] The invention will be further described in the experimental section below.

#### **Materials, instrumentation and methods**

[0033] The following precursors were used in the preparation of the samples:

- copper(II) acetate, Cu(OAc)<sub>2</sub>·xH<sub>2</sub>O (Sigma-Aldrich, catalogue No. 66923-66-8 degree of hydration, ~1), 98% purity;
- antimony(III) acetate, Sb(OAc)<sub>3</sub>, (Sigma-Aldrich, catalogue No. 6923-52-0), 99.99% purity;
- ethylene glycol (Sigma-Aldrich, catalogue No. 107-21-1), 99.8% purity;
- Nafion® 117 solution (Sigma-Aldrich, catalogue no. 31175-20-9; Nafion is a registered trademark of E. I. du Pont de Nemours and Company), purity: ~ 5% in a mixture of lower aliphatic alcohols and water.

[0034] Chemical composition analyses of the samples were performed by inductively coupled plasma optical emission spectroscopy (ICP-OES, iCAP 7600 DUO instrument, Thermo Fisher Scientific); each analysis was performed by dissolving 5.0 mg of the sample in 10.0 ml of an aqueous solution with 10% aqua regia.

[0035] Electron microscope images and energy dispersive X-ray spectroscopy (EDX) analyses were obtained with a FESEM Supra 40 (Zeiss) equipped with a detector (Oxford Instruments Si(Li)) for energy dispersive X-ray spectroscopy (EDX) analyses.

[0036] The phase composition of each sample was determined by X-ray diffraction (XRD) with a diffractometer (PAN-alytical X'Pert Pro equipped with an X'Celerator detector) that uses Cu K $\alpha$  radiation ( $\lambda$  = 1.54178 Å) generated at 40 kV and 30 mA. XRD diffractograms were recorded in the 2 $\theta$  25-80° range with a step (2 $\theta$ ) of 0.017° and a counting time of 0.45 seconds.

[0037] High-resolution (HR) XPS analyses were performed with a PHI 5000 VersaProbe instrument (Physical Electronics) using monochromatic Al K $\alpha$  (1486.6 eV) radiation.

[0038] Analyses of gaseous products derived from CO<sub>2</sub> electroreduction were performed in real time with an INFICON Fusion® microgas chromatograph ( $\mu$ GC) equipped with two channels with a 10 m Rt-Molsieve 5A column and an 8 m Rt-Q-Bond column, respectively, and thermal conductivity microdetectors (micro-TCD).

#### **EXAMPLE 1**

[0039] This example relates to the synthesis of the materials of the invention.

[0040] Seven samples of materials of the invention with different Sb contents were prepared using copper acetate and antimony acetate as precursors, used in the amounts shown in Table 1. The samples of the invention are indicated as A-H. For comparison, a sample from copper acetate alone (sample referred to as "Cu" in the table), a sample from

antimony acetate alone (sample "Sb"), and a sample of mixed Cu/Sb composition not of the invention (sample "NI") were also produced in the identical manner described below. The last column of the table shows the values of Sb content in each of the samples of the invention, obtained by ICP-OES analysis (the data for the Cu and Sb samples are not shown because naturally in these two cases the analysis for the determination of the percentage content of Sb was not carried out).

Table 1

Sample	Amount of precursor (mg)		Sb content (% by weight)
	$\text{Cu}(\text{OAc})_2 \cdot x\text{H}_2\text{O}$	$\text{Sb}(\text{OAc})_3$	
Cu	900	0	/
A	900	164	5.2
B	900	246	9.4
C	900	295	13.6
D	900	328	17.2
E	900	410	20.1
F	900	470	23.9
G	900	492	25.2
H	900	600	26.4
NI	900	820	36.0
Sb	0	900	/

**[0041]** The indicated amounts of precursors were dissolved in 40 ml of ethylene glycol and 5 ml of double distilled  $\text{H}_2\text{O}$  (resistivity about  $18 \text{ M}\Omega \cdot \text{cm}$ ). Each solution was then transferred to a Teflon container (volume 100 mL). The Teflon container was sealed, placed in a microwave oven (Milestone, STARTSynth, HPR-1000-10S segment with temperature and pressure control), heated to  $220^\circ \text{C}$  and then maintained at this temperature by powering the oven with a maximum power of 900 W for a total irradiation time of 2 minutes. After cooling to room temperature, the suspended product in each container was separated by centrifugation and washed twice with double-distilled  $\text{H}_2\text{O}$  and subsequently once with ethanol. Each powder sample was finally dried under vacuum at  $60^\circ \text{C}$  overnight.

**[0042]** In addition to ICP-OES analysis, the samples of the invention were examined by scanning electron microscopy and EDX analysis to determine the morphology (also for Cu and Sb samples) and the antimony distribution, by X-ray diffraction to determine the crystal structure (also for Cu and Sb samples) and by XPS to determine the oxidation state of Cu and Sb; the results of the three analyses have been discussed above with reference to Figures 1, 2 and 3 respectively.

## EXAMPLE 2

**[0043]** This example relates to the production of electrodes for electrochemical  $\text{CO}_2$  reduction using the materials of the invention (samples A-H) and the three comparison materials (samples Cu, Sb and NI).

**[0044]** Each electrode was prepared by mixing 10 mg of sample A-H, Cu, Sb or NI, 1 mg of carbon black from acetylene,  $90 \mu\text{l}$  of Nafion® 117 solution and  $320 \mu\text{l}$  of isopropanol. Each mixture was sonicated for 30 minutes until a uniform suspension was obtained. Each suspension was then used to coat a carbon paper covered with a gas permeable layer (GDL; SIGRACET 28BC, SGL Technologies); the geometric area of each electrode was  $1.5 \text{ cm}^2$ . The obtained electrode was dried at  $60^\circ \text{C}$  overnight to evaporate the solvents. The electrocatalyst loading on each electrode was approximately  $3.0 \text{ mg cm}^{-2}$ . The electrodes thus obtained are referred to in the following by the abbreviations  $\text{E}_x$ , where the subscript x corresponds to the sample A-H, Cu, Sb or NI used for its production.

## EXAMPLE 3

**[0045]** This example refers to the measurement of the  $\text{CO}_2$  reduction efficiency of the electrodes prepared in the previous Example.

**[0046]** Electrochemical measurements were performed with a cell having the configuration schematically shown in Fig. 4; the cell as a whole, 10, is shown in the figure enclosed by a discontinuous line. As shown in the figure, the cell

has two compartments separated by an ion exchange membrane 11 (Nafion® N117 membrane, Sigma-Aldrich), and adopts a three-electrode configuration. Each compartment has a total volume of 10 ml and contains 7 ml of electrolyte, and thus 3 ml of headspace. The reference electrode, 12, is an Ag/AgCl electrode (1 mm, lossless LF-1) that is inserted into the cathode compartment. The counter electrode, 13, is a Pt foil (Goodfellow, 99.95%). The working electrode, i.e., the electrode of the invention, is shown in the figure as element 14. An aqueous solution of 0.1 M KHCO<sub>3</sub> was used as the electrolyte solution. In this configuration, gaseous CO<sub>2</sub> is fed into both half-cells from the lower part of the two compartments, while the mixture of products on which the results are evaluated is extracted from the cathode compartment (on the right in the figure); most of this mixture is sent to the separation and purification stage (performed with methods known in the field and not described in this text), while a fraction of the mixture is sent to the analysis. Chronoamperometric measurements were performed using a CHI760D electrochemical workstation (CH Instruments, Inc., USA). Gas phase products were analysed in real time with a microgas chromatograph ( $\mu$ GC). The inlet of the  $\mu$ GC instrument was connected to the cathode side of the electrochemical cell through a GENIE filter, to remove humidity from the gas before it entered the analysis instrument ( $\mu$ GC). During the chronoamperometric measurements, the electrolytes on both sides of the anode and cathode were static, while a constant CO<sub>2</sub> flow rate of 15 ml/min was maintained to saturate the cathode electrolyte and to bring the gaseous products to the  $\mu$ GC. The tests were performed at different potentials between -0.79 V and -0.99 V. The potential was corrected by compensating for the ohmic potential drop, 85% of which was from the instrument (iR compensation).

**[0047]** Selectivity is described by the faradic efficiency (FE), which is the ratio of the amount of charge (coulomb, C) required to produce a certain amount of a product to the total charge consumed over the reaction time, and is expressed by the following equation:

$$FE (\%) = nNF/Q \times 100$$

where n is the number of electrons transferred in the faradic process (for the reduction of CO<sub>2</sub> to CO and to H<sub>2</sub>, n is 2 as shown in the reactions R1 and R5 above), N is the moles of a product generated in a specific reaction period, F is the faradic constant (96485.33 C/mol), and Q is the total charge in a specific reaction period.

**[0048]** The results of the tests at two potential values are shown in Table 2.

**Table 2**

Electrode	Potential -0.79 V		Potential -0.99 V	
	FE <sub>CO</sub> (%)	FE <sub>H<sub>2</sub></sub> (%)	FE <sub>CO</sub> (%)	FE <sub>H<sub>2</sub></sub> (%)
E <sub>Cu</sub>	9.5	90	8.5	85
E <sub>A</sub>	87	14	73	26
E <sub>B</sub>	85	13	84	15
E <sub>C</sub>	90	8.5	81	18
E <sub>D</sub>	90	8	92	7
E <sub>E</sub>	91	8.5	90	8
E <sub>F</sub>	90	10.5	89	9.5
E <sub>G</sub>	89	10	85	14
E <sub>H</sub>	83.8	16.5	68.5	33
E <sub>NI</sub>	55	43	62	37
E <sub>Sb</sub>	0	63	0	83

**[0049]** As can be seen from the test results, the E<sub>Sb</sub> electrode does not produce CO at either test potential. The Cu electrode has poor selectivity for CO, with FE<sub>CO</sub> values below 10%. The comparison E<sub>NI</sub> electrode shows poor selectivity values towards CO, probably because it is formed by a mixture containing only a small amount of active material together with a completely inactive material (antimony oxide). In contrast, the E<sub>A</sub>-E<sub>H</sub> electrodes of the invention exhibit high selectivity towards CO, with FE<sub>CO</sub> above 80% for all A-H materials at -0.79 V. Among these materials, in particular, D

and E show excellent selectivity values for CO, of at least 90% at both potentials.

#### EXAMPLE 4

**[0050]** This example relates to the measurement of CO<sub>2</sub> reduction with an electrode of the invention at various potentials.

**[0051]** The E<sub>D</sub> electrode, which gave the best results in Example 3, was tested at five different potential values ranging from -0.69 V to -1.09 V. In each test, the evolution of CO and H<sub>2</sub> over time was evaluated during tests lasting between one and two hours.

**[0052]** The results of these tests are shown graphically in Fig. 5. In detail, Figures 5(a) to 5(e) report tests performed at the following potentials: 5(a) -0.69 V; 5(b) -0.79 V; 5(c) -0.89 V; 5(d) -0.99 V; 5(e) -1.09 V. The tests at -0.79 V and -0.99 V are the same as those whose results have already been reported in the previous example. The results of these tests are provided in summary form in the graph in Fig. 5(f), in which the faradic efficiency values for CO and H<sub>2</sub>, taken when the reduction process has reached steady state, are reported at all evaluated potentials.

**[0053]** As can be seen in the graphs (Figs. 5(a)-(e)), in each test there is an initial settling time between about 10 minutes (test at -0.99 V) and 20 minutes; this is attributed to stabilization of the electrode and filling of the headspace of the electrochemical cell and of tubes between the cell and the  $\mu$ GC. Then, the FE values stabilize, indicating the stable performance of the electrode. The E<sub>D</sub> electrode shows very good performance in the conversion of CO<sub>2</sub> to CO (FE<sub>CO</sub> > 80%) over the whole range of potentials explored, with values up to 90-92% at potentials from -0.79 V to -1.09 V. At more negative potentials (< -1.09 V), FE<sub>CO</sub> falls below 90%. FE<sub>H2</sub> values remain low ( $\leq$  9%) from -0.69 V to -1.09 V. No other gas phase products other than CO and H<sub>2</sub> were detected. Liquid products (e.g., HCOOH) were not quantified, but can be assumed to be present in very small or negligible amounts, since the total faradic efficiency for CO and H<sub>2</sub> measured in all tests is around 100%.

#### COMMENTARY ON THE RESULTS

**[0054]** As demonstrated in the tests described above, the electrocatalyst materials of the invention catalyze the electrochemical reduction of CO<sub>2</sub> with high selectivity toward CO. The materials of the invention then offer further advantages.

**[0055]** Firstly, antimony and copper, and the compounds thereof used as precursors in the process of the invention, are inexpensive materials; moreover, the production of these materials is simple and easily scalable at an industrial level, also because it does not employ toxic or harmful products; the invention therefore offers a technically viable and competitive alternative to the use of metals such as Au, Ag and Pd.

**[0056]** Since the materials of the invention are in powder form, they can be used in reactors with various configurations as a gas diffusion electrode (GDE) and different sizes.

#### Claims

1. Electrocatalyst material consisting of copper(I) oxide (Cu<sub>2</sub>O) containing antimony, wherein the amount of antimony is between 5% to 30% by weight.
2. Electrocatalyst material according to claim 1, wherein the amount of antimony is between 5.2% and 26.4% by weight.
3. Electrocatalyst material according to claim 2, wherein the amount of antimony is between 17.2% and 23.9% by weight.
4. Electrode comprising powder of an electrocatalyst material of any one of claims 1 to 3 and a conductive material deposited on a support, in a weight ratio between electrocatalyst material and conductive material between 9:1 and 19:1.
5. Electrode according to claim 4, wherein the conductive material is in the form of powder.
6. Electrode according to any one of claims 4 or 5 wherein the conductive material is carbon based.
7. Electrode according to claim 6, wherein the conductive material is chosen from carbon black, graphite, graphene, carbon nanotubes and mixtures thereof.
8. Electrode according to any one of claims 4 to 7 wherein the support is selected from conductive carbon paper, conductive carbon cloth and metal mesh.



9. Electrode according to any one of claims 4 to 8 wherein the powder of the electrocatalyst material and possibly of the conductive material are stabilized on the support with an ionomer.

10. Process for the production of the electrocatalyst material of any one of claims 1 to 3, comprising the following steps:

- a) dissolving a copper(II) salt and an antimony(III) salt in a solvent selected from ethanol, ethylene glycol, acetylacetone, diethylamine, ethylenediamine, oleylamine, N,N-dimethylformamide, mixtures of these solvents with each other, with water or with aqueous solutions of D-glucose, hydrazine hydrate, amino acids or sodium carboxymethylcellulose, obtaining a solution;
- b) heating the solution in a microwave oven at a temperature between 180 and 230 °C for a time between 1 and 10 minutes;
- c) separating the precipitate from the solution and its drying.

11. Process according to claim 10, wherein the copper(II) salt is selected from acetate, sulfate and nitrate, and the antimony(III) salt is selected from acetate, sulfate and nitrate.

12. Method for the selective electrochemical reduction of CO<sub>2</sub> to CO, comprising the use of an electrode of any one of claims 4 to 9 at a potential between -0.69 V to -1.09 V.

## Patentansprüche

1. Elektrokatalysatormaterial, bestehend aus Kupfer(I)-oxid (Cu<sub>2</sub>O), das Antimon enthält, wobei die Antimonmenge zwischen 5 und 30 Gew.-% liegt.

2. Elektrokatalysatormaterial nach Anspruch 1, wobei die Antimonmenge zwischen 5,2 und 26,4 Gew.-% liegt.

3. Elektrokatalysatormaterial nach Anspruch 2, wobei die Antimonmenge zwischen 17,2 und 23,9 Gew.-% liegt.

4. Elektrode, aufweisend ein Pulver aus einem Elektrokatalysatormaterial nach einem der Ansprüche 1 bis 3 und ein auf einem Träger abgeschiedenes leitfähiges Material in einem Gewichtsverhältnis zwischen Elektrokatalysatormaterial und leitfähigem Material zwischen 9:1 und 19:1

5. Elektrode nach Anspruch 4, wobei das leitfähige Material in Form eines Pulvers vorliegt.

6. Elektrode nach einem der Ansprüche 4 oder 5, wobei das leitfähige Material auf Kohlenstoffbasis ist.

7. Elektrode nach Anspruch 6, wobei das leitfähige Material ausgewählt ist aus Ruß, Graphit, Graphen, Kohlenstoff-Nanoröhren und Mischungen davon.

8. Elektrode nach einem der Ansprüche 4 bis 7, wobei der Träger aus leitfähigem Kohlenstoffpapier, leitfähigem Kohlenstoffgewebe und Metallgeflecht ausgewählt ist.

9. Elektrode nach einem der Ansprüche 4 bis 8, wobei das Pulver des Elektrokatalysatormaterials und gegebenenfalls des leitfähigen Materials auf dem Träger mit einem Ionomer stabilisiert ist.

10. Verfahren zur Herstellung des Elektrokatalysatormaterials nach einem der Ansprüche 1 bis 3, das die folgenden Schritte aufweist:

- a) Lösen eines Kupfer(II)-Salzes und eines Antimon(III)-Salzes in einem Lösungsmittel, ausgewählt aus Ethanol, Ethylen, Glykol, Acetylaceton, Diethylamin, Ethylendiamin, Oleylamin, N,N-Dimethylformamid, Gemischen dieser Lösungsmittel untereinander, mit Wasser oder mit wässrigen Lösungen von D-Glucose, Hydrazinhydrat, Aminosäuren oder Natriumcarboxymethylcellulose, wobei man eine Lösung erhält;
- b) Erhitzen der Lösung in einem Mikrowellenofen bei einer Temperatur zwischen 180 und 230 °C für eine Dauer zwischen 1 und 10 Minuten;
- c) Abtrennung des Niederschlags von der Lösung und dessen Trocknung.

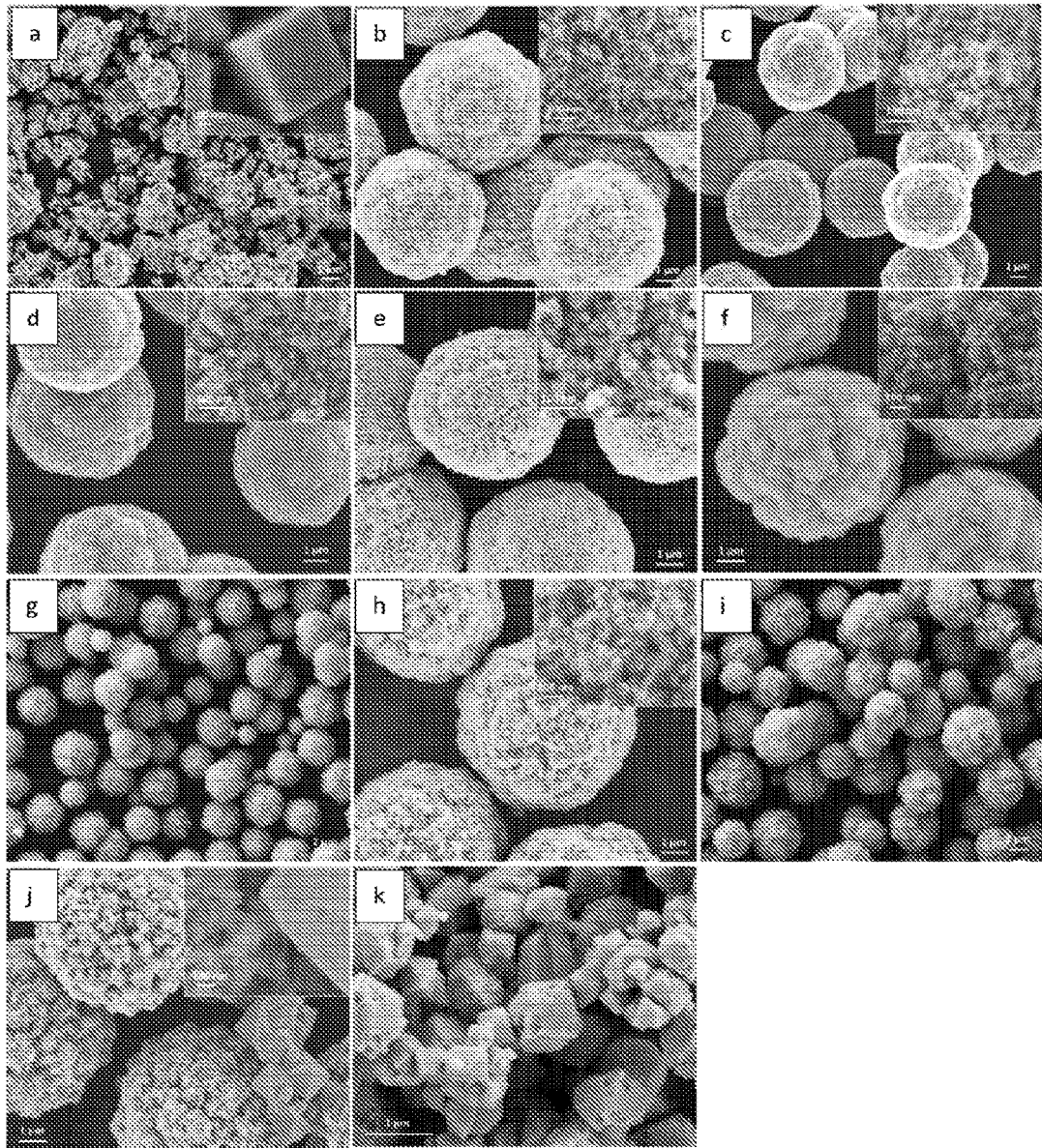
11. Verfahren nach Anspruch 10, wobei das Kupfer(II)-Salz ausgewählt ist aus Acetat, Sulfat und Nitrat und das Anti-

mon(III)-Salz ausgewählt ist aus Acetat, Sulfat und Nitrat.

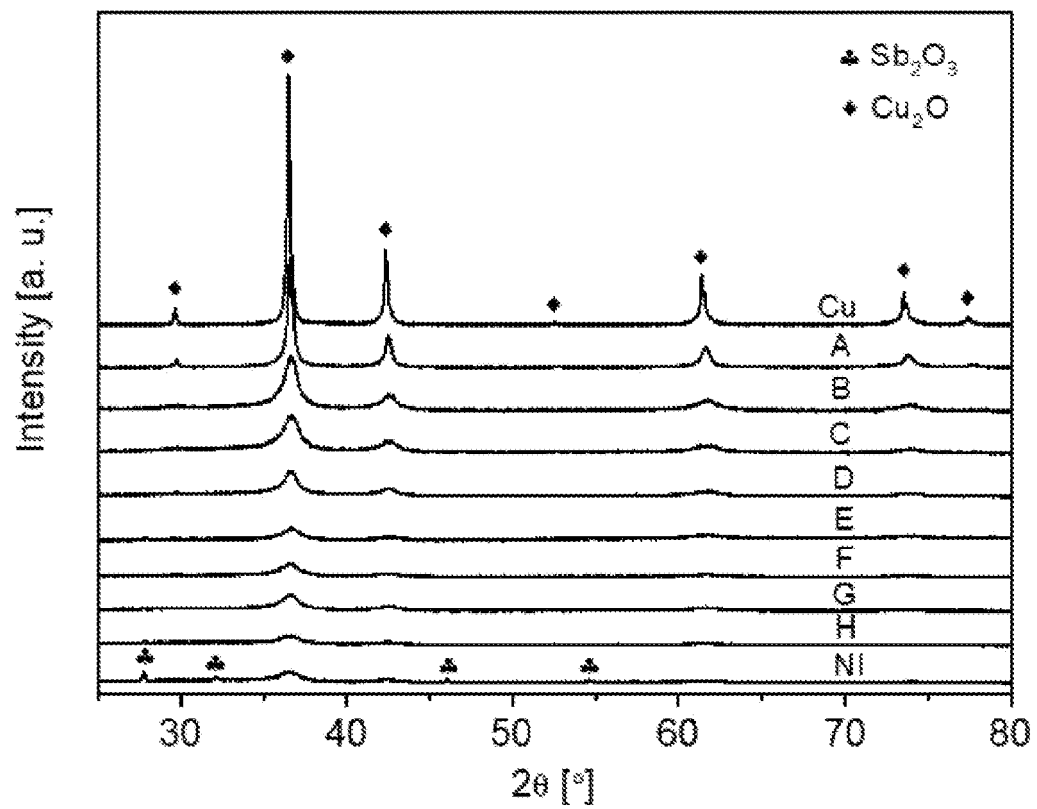
12. Verfahren zur selektiven elektrochemischen Reduktion von  $\text{CO}_2$  zu CO, das die Verwendung einer Elektrode nach einem der Ansprüche 4 bis 9 bei einem Potential zwischen -0,69 V und -1,09 V aufweist.

## Revendications

1. Matériau d'électrocatalyseur constitué d'oxyde de cuivre(I) ( $\text{Cu}_2\text{O}$ ) contenant de l'antimoine, dans lequel la quantité d'antimoine est entre 5 % et 30 % en poids.
2. Matériau d'électrocatalyseur selon la revendication 1, dans lequel la quantité d'antimoine est entre 5,2 % et 26,4 % en poids.
3. Matériau d'électrocatalyseur selon la revendication 2, dans lequel la quantité d'antimoine est entre 17,2 % et 23,9 % en poids.
4. Électrode comprenant une poudre d'un matériau d'électrocatalyseur selon l'une quelconque des revendications 1 à 3 et un matériau conducteur déposé sur un support, dans un rapport en poids entre le matériau d'électrocatalyseur et le matériau conducteur d'entre 9:1 et 19:1.
5. Électrode selon la revendication 4, dans laquelle le matériau conducteur se présente sous la forme d'une poudre.
6. Électrode selon l'une quelconque des revendications 4 ou 5 dans laquelle le matériau conducteur est à base de carbone.
7. Électrode selon la revendication 6, dans laquelle le matériau conducteur est choisi parmi le noir de carbone, le graphite, le graphène, les nanotubes de carbone et les mélanges de ceux-ci.
8. Électrode selon l'une quelconque des revendications 4 à 7 dans laquelle le support est sélectionné parmi un papier de carbone conducteur, un tissu de carbone conducteur et un treillis métallique.
9. Électrode selon l'une quelconque des revendications 4 à 8 dans laquelle la poudre du matériau d'électrocatalyseur et éventuellement du matériau conducteur sont stabilisées sur le support avec un ionomère.
10. Processus pour la production du matériau d'électrocatalyseur selon l'une quelconque des revendications 1 à 3, comprenant les étapes suivantes :
  - a) la dissolution d'un sel de cuivre(II) et d'un sel d'antimoine(III) dans un solvant sélectionné parmi l'éthanol, l'éthylène glycol, l'acétylacétone, la diéthylamine, l'éthylènediamine, l'oléylamine, le N,N-diméthylformamide, les mélanges de ces solvants les uns avec les autres, avec de l'eau ou avec des solutions aqueuses de D-glucose, d'hydrate d'hydrazine, d'acides aminés ou de carboxyméthylcellulose sodique, en obtenant une solution ;
  - b) le chauffage de la solution dans un four à micro-ondes à une température entre 180 et 230 °C pendant une durée entre 1 et 10 minutes ;
  - c) la séparation du précipité à partir de la solution et son séchage.
11. Processus selon la revendication 10, dans lequel le sel de cuivre(II) est sélectionné parmi l'acétate, le sulfate et le nitrate, et le sel d'antimoine(III) est sélectionné parmi l'acétate, le sulfate et le nitrate.
12. Procédé pour la réduction électrochimique sélective de  $\text{CO}_2$  en CO, comprenant l'utilisation d'une électrode selon l'une quelconque des revendications 4 à 9 à un potentiel entre -0,69 V et -1,09 V.



*Fig. 1*

*Fig. 2*

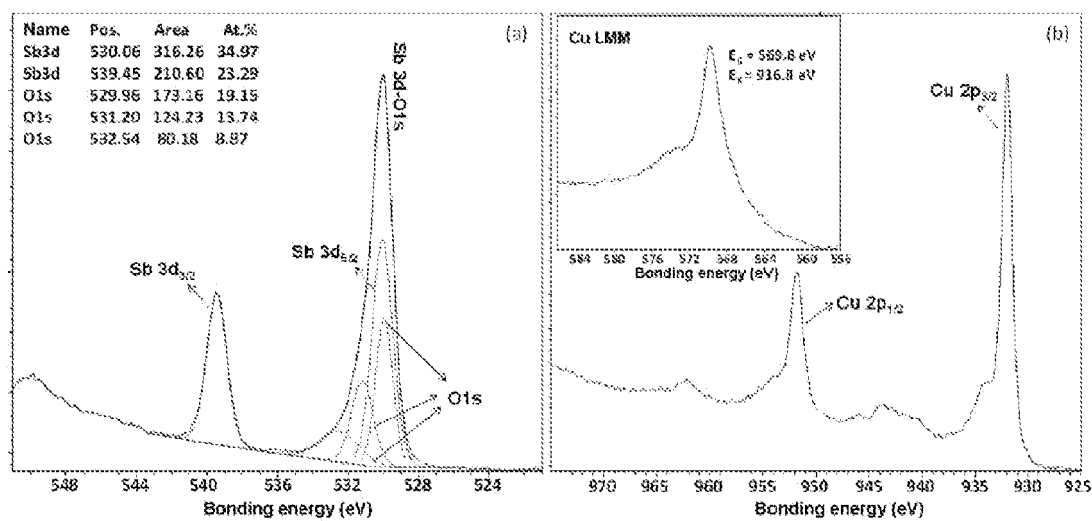


Fig. 3

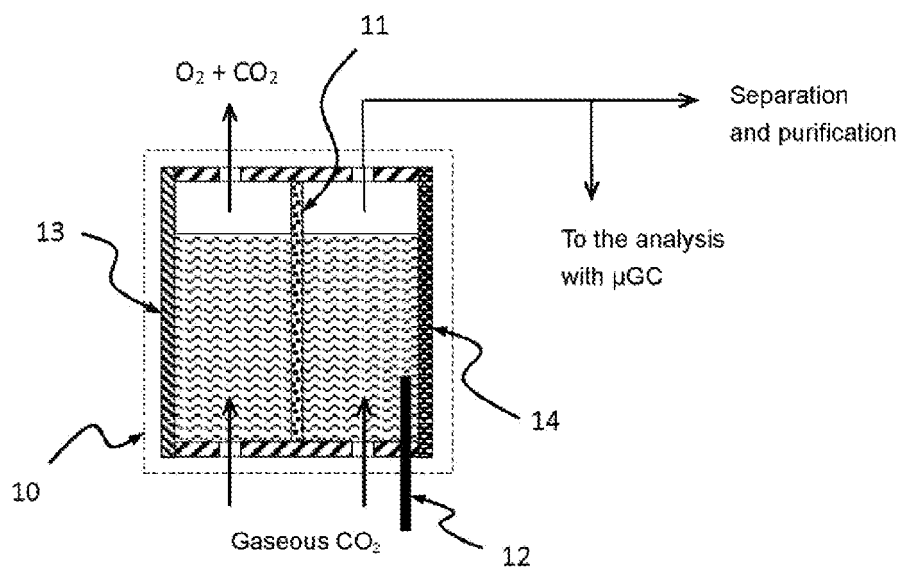


Fig. 4

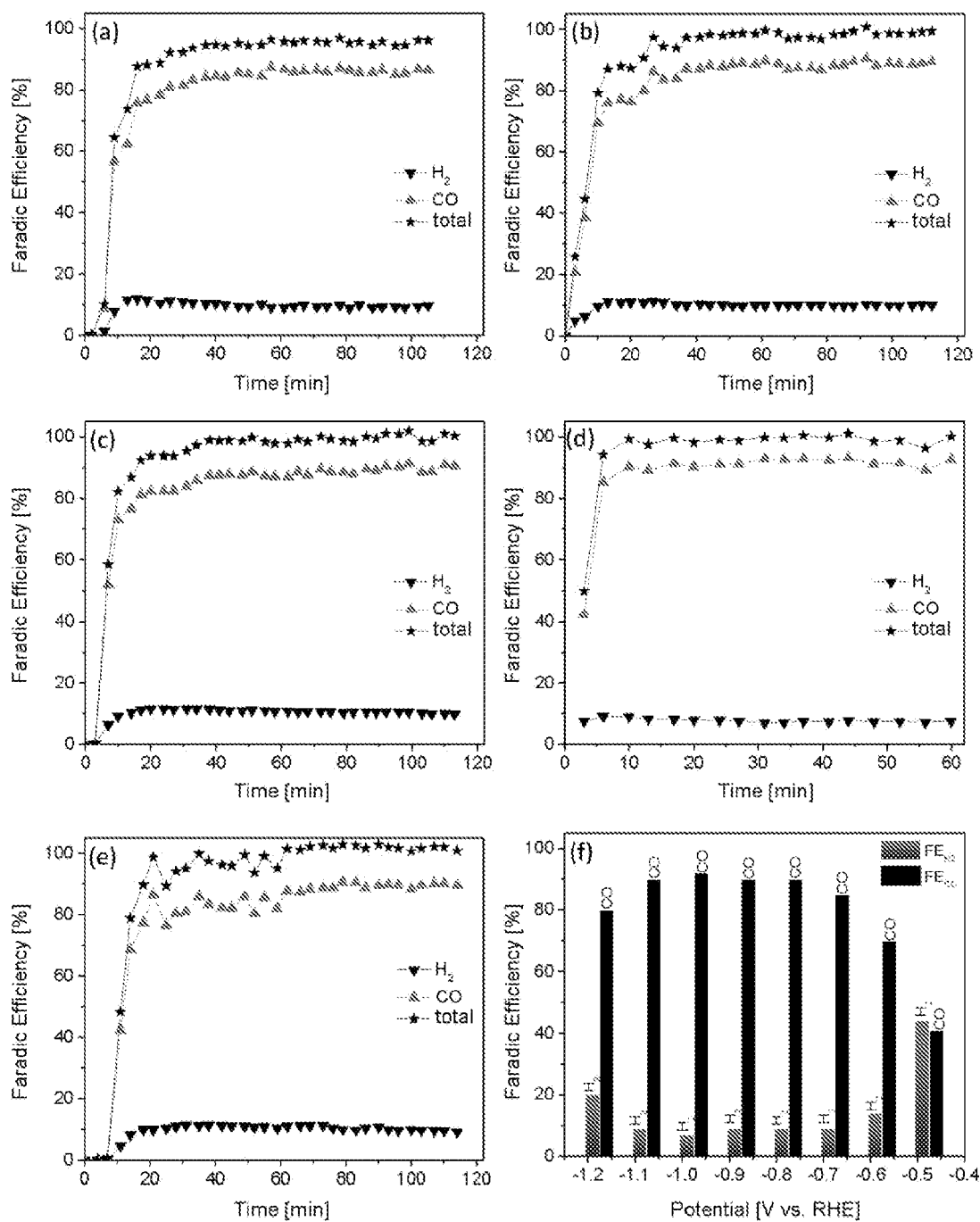


Fig. 5

## REFERENCES CITED IN THE DESCRIPTION

*This list of references cited by the applicant is for the reader's convenience only. It does not form part of the European patent document. Even though great care has been taken in compiling the references, errors or omissions cannot be excluded and the EPO disclaims all liability in this regard.*

### Patent documents cited in the description

- US 20190127866 A1 [0011]

### Non-patent literature cited in the description

- **Y. LI et al.** Achieving highly selective electrocatalytic CO<sub>2</sub> reduction by tuning CuO-Sb<sub>2</sub>O<sub>3</sub> nanocomposites. *ACS Sustainable Chem. Eng.*, 2020, vol. 8 (12), 4948-4954 [0012]
- **DAEYUN et al.** Optimal synthesis of antimony-doped cuprous oxides for photoelectrochemical applications. *Thin Solid Films*, 2019, vol. 671, 120-126 [0019]