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(54) **PROCESS AND USE OF COPPER BASED ELECTROCATALYST MATERIAL IN SUPERSATURATED ELECTROLYTE**

(57) The present invention belongs to the field of catalytic chemistry, and more specifically to catalyzed reduction chemical reactions, preferably the reduction of CO₂ into small molecules.

The present invention relates to a new copper based electrocatalyst material and its method of preparation comprising a step of in-situ electrodeposition or co-electrodeposition, in an electrolyte solution, of at least one catalytic metal in the presence of a gas comprising CO₂ under electroreduction conditions onto a conductive support, wherein the at least one catalytic metal comprises

copper (Cu) and is electrodeposited onto the conductive support and wherein the gas is supersaturated (*i.e.* with CO₂ concentrations above the saturation limit) in the electrolyte solution and its use thereof in a reduction chemical reaction, preferably in the reduction of CO₂ into CO or other small molecules such as gaseous hydrocarbons (methane, ethylene) or liquid molecules (ethanol, formic acid). The invention also relates to the process of manufacture of said catalyst compound. The invention thus also relates to a process electrochemical conversion of CO₂ to small molecules.

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Description**Technical field**

[0001] The present invention belongs to the field of catalytic chemistry, and more specifically to catalyzed reduction chemical reactions, preferably the reduction of CO₂ into small molecules.

[0002] The present invention relates to a new copper based electrocatalyst material and its method of preparation comprising a step of in-situ electrodeposition or co-electrodeposition, in an electrolyte solution, of at least one catalytic metal in the presence of a gas comprising CO₂ under electroreduction conditions onto a conductive support, wherein the at least one catalytic metal comprises copper (Cu) and is electrodeposited onto the conductive support and wherein the gas is supersaturated (*i.e.* with CO₂ concentrations above the saturation limit) in the electrolyte solution and its use thereof in a reduction chemical reaction, preferably in the reduction of CO₂ into CO or other small molecules such as gaseous hydrocarbons (methane, ethylene) or liquid molecules (ethanol, formic acid). The invention also relates to the process of manufacture of said catalyst compound. The invention thus also relates to a process electrochemical conversion of CO₂ to small molecules.

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

Technical background

[0004] The release of carbon dioxide (CO₂) is a major concern for the environment. Its capture and recycling into small organic bricks such as carbon monoxide (CO), formic acid, methane or methanol could prove to be very advantageous.

[0005] Particularly, the conversion of CO₂ into small molecules such as gaseous hydrocarbons (methane, ethylene) or liquid molecules (methanol, ethanol, formic acid) is an attractive method as these molecules can be used as fuels or organic bricks for the production of longer hydrocarbon molecules **[1-3]**. Currently, copper-based catalysts (Cu) can convert CO₂ in small multicarbon organic molecules but their efficiency is still limited - preventing its use in industrial process **[4,5]**.

[0006] While active and selective catalysts for CO₂ reduction to the C₁ product have achieved significant progress towards industrial developments over the past recent years, the formation of multicarbon molecules with superior energy density and higher commercial values is more desirable but remains a challenge. To date, only handful of systems have demonstrated the direct conversion of CO₂ to the hydrocarbons and oxygenates with 3 or more carbons (C₃₊) and the corresponding Faradaic efficiency typically remains below 20 %. Previous reports have pointed out that modulating local CO₂ concentration can enhance the C-C coupling in CO₂RR. The moderate coverage of *CO on the surface of catalyst was also found to be beneficial for the CO₂RR into C₃₊ products. Cu-based alloys have been identified to enhance the selectivity towards C₃₊ products by modulating the adsorption of *CO intermediates on the catalyst surface. Cavities on the catalyst surface have also demonstrated larger selectivity for the formation of propanol thanks to the confinement of the intermediates. These examples however rely on the use of CO instead on CO₂ that are involved in the C-C dimerization step associated with the formation of multicarbon molecules.

[0007] Usually, for the CO₂ reduction reaction (CO₂RR), CO₂ feeds from highly concentrated sources or special CO₂-capturing devices are required, because the low concentration of CO₂ makes it very difficult to be effectively adsorbed and activated on the surface of most catalysts, and the anaerobic atmosphere is requisite to prevent the adverse oxidation reaction from happening.

Detailed description of the invention

[0008] The Applicant has developed a new method to produce a copper based electrocatalyst compound that solves all the problems listed above.

[0009] The present invention deals with a new copper based electrocatalyst material, its manufacturing process and its applications, such as a method to convert CO₂ into small molecules (such as ethylene, ethanol and isopropanol) at room temperature and atmospheric pressure or higher. 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.

[0010] The applicant surprisingly found out that using a copper (Cu) based electrocatalyst material prepared according to the method of the invention gives very good yields in the conversion of CO₂ into small molecules under CO₂ supersaturated conditions. It is meant by "supersaturated conditions", conditions where the CO₂ concentrations is above the solubility limit of CO₂ in the electrolyte at a defined pressure. Supersaturation may be up to 6 times larger than the solubility limit of CO₂ in the electrolyte at atmospheric pressure and up to 120 times at a pressure of 20 bar. Specifically, it was identified that the performance of the copper based electrocatalyst material of the invention is considerably improved by combining two parameters:

- 1) manufacturing the catalyst in a CO₂ supersaturated electrolyte; and then
- 2) performing the conversion reaction (reduction) of CO₂ in CO₂-supersaturated electrolyte.

[0011] The electrocatalyst material of the invention is therefore both prepared and used in CO₂ supersaturated electrolyte.

[0012] These two conditions allow increasing the current density and improving the selectivity of the reaction towards the production of C₃₊ molecules (typically isopropanol). The Faradaic efficiency reaches a maximum of 59 % at -0.73 V versus RHE for CO₂ concentration of 3 mol L⁻¹ under a CO₂ pressure of 10 bar.

[0013] The copper based electrocatalyst material of the invention is based on monometallic (Cu) crystals or dendritic alloy (Ag-Cu) on a conducting support (typically a commercial carbon support such as a gas diffusion layer or a graphite foil electrode) according to the method of the invention. The copper based electrocatalyst material of the invention may present a dendritic morphology.

[0014] A first object of the invention is a method of preparing an copper based electrocatalyst material, comprising a step of in-situ electrodeposition or co-electrodeposition, in an electrolyte solution, of at least one catalytic metal in the presence of a gas comprising CO₂ under electroreduction conditions onto a conductive support, wherein

- the at least one catalytic metal comprises copper (Cu) and is electrodeposited or co-electrodeposited onto the conductive support and,
- the gas is supersaturated in the electrolyte solution.

[0015] Advantageously, in the method according to the invention, the at least one catalytic metal may further comprise silver (Ag). The at least one catalytic metal may consist of copper and silver. The atomic ratio Cu:Ag may be from 1:9 to 9.9:0.1, preferably from 7:3 to 9.8:0.2, more preferably from 8.5:1.5 to 9.5:0.5 or even preferably 9:1. The atomic ratio Cu:Ag may be tuned by adjusting the ratio of Cu and Ag precursors respectively.

[0016] Advantageously, in the method according to the invention, the electrolyte solution may be a carbonated water-based electrolyte solution. The carbonated water-based electrolyte is preferably chosen from CsHCO₃, KHCO₃ and K₂SO₄, preferably CsHCO₃. The concentration of carbonated water-based electrolyte may be from 0.5 mol L⁻¹ to 5.0 mol L⁻¹, preferably from 0.5 mol L⁻¹ to 1.5 mol L⁻¹, more preferably 1 mol L⁻¹.

[0017] Advantageously, in the method according to the invention, the gas may comprise from 0.04 wt.% to 100 wt.% of CO₂. Preferably, the gas is CO₂.

[0018] Advantageously, in the method according to the invention, the electrolyte solution is an aqueous solution. The electrolyte may be supersaturated in gas. The concentration of the gas, in the electrolyte solution, may be from 0.05 to 7.5 mol L⁻¹, while gas pressure may be up to 25 bar in the reactor. The gas concentration may depend on the pressure and the temperature applied to the electrolyte solution. The concentration may thus be from 0.05 to 0.3 mol L⁻¹, at atmospheric pressure (1 ATM), at a temperature from 15 to 25°C. The concentration may be from > 0.3 to 7.5 mol L⁻¹, at a pressure from > 1 bar to 25 bar, at a temperature from 15 to 25°C.

[0019] Advantageously, in the method according to the invention, the concentration of the gas is preferably maintained constant by continuous gas injection in the electrolyte during the step of in-situ electrodeposition or co-electrodeposition.

[0020] Advantageously, the conductive support may be a carbon based conductive support. Preferably, the conductive support may be a gas diffusion layer (GDL) or a graphite foil electrode. The conductive support may be hydrophilic. The method according to the invention may thus further comprise a step of hydrophilic pre-treatment of the conductive support followed by the step of in-situ electrodeposition or co-electrodeposition.

[0021] Advantageously, in the method according to the invention, the electrodeposition or co-electrodeposition is provided under a voltage of -0.80 to -2.20 V vs. Ag / AgCl (KCl saturated).

[0022] Advantageously, in the method according to the invention, the electrodeposition or co-electrodeposition may be provided under a current density from 1 mA cm⁻² to 50 mA cm⁻², preferably from 10 mA cm⁻² to 20 mA cm⁻², for total charge of 30 C corresponding to a loading amount of 5 mg cm⁻². Preferably, in the method according to the invention, the electrodeposition or co-electrodeposition may be provided under a current density of from 1.0 to 20.0 mA cm⁻². Copper (Cu) and the optional at least one further catalytic metal (Ag) may be electrodeposited (or co-electrodeposited) using a current density from 1.0 mA cm⁻² to 20 mA cm⁻², preferably from 5 mA cm⁻² to 15 mA cm⁻², preferably 10 mA cm⁻².

[0023] Advantageously, in the method according to the invention, the quantity of deposited silver and optional at least one further catalytic metal (Cu) may be from 0.5 C cm⁻² to 50 C cm⁻², preferably from 15 C cm⁻² to 35 C cm⁻². Preferably, the quantity of deposited Cu and optional Ag may be comprised from 15 C cm⁻² to 35 C cm⁻², and more preferably from 20 C cm⁻² to 30 C cm⁻².

[0024] Advantageously, in the method according to the invention, the source of silver (Ag) may be AgNO₃ or CH₃COOAg, preferably AgNO₃.

[0025] Advantageously, in the method according to the invention, the source of copper (Cu) may be CuSO₄ and Cu(NO₃)₂, preferably CuSO₄.

[0026] Advantageously, in the method according to the invention, the electrodeposition or co-electrodeposition of copper and the optional at least one further catalytic metal (Ag) 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.

[0027] The invention also relates to a copper based electrocatalyst material obtained according to the method of the invention. The copper based electrocatalyst material may comprise at least one catalytic material and a conductive support. The at least one catalytic metal may be in the form of a monometallic crystal or dendritic alloy. The at least one catalytic metal may be in the form of a metallic layer. The layer of monometallic crystal or dendritic alloy on the conductive support may have a thickness from 5.0 to 15.0 μm . The thickness may depend on the loading amount of the catalyst and the skilled person may adapt depending on the application.

[0028] The invention also relates to a process of conversion of CO_2 into small molecules, such as ethylene, ethanol and isopropanol, comprising a step of contacting CO_2 (gas) with a copper based electrocatalyst material according to the invention. The conversion reaction of CO_2 may be done in a supersaturated electrolyte by the use of an applied CO_2 pressure ranging from 1.0 bar to 25.0 bar and at a temperature from 15 to 40°C, with CO_2 (gas) at a concentration from 0.05 to 7.5 mol L^{-1} . The CO_2 concentration may depend on the pressure and the temperature applied to the electrolyte solution. Under atmospheric pressure, the concentration may thus be from 0.05 to 0.3 mol L^{-1} , at a temperature from 15 to 25°C. The concentration may be from > 0.3 to 7.5 mol L^{-1} , at a pressure from > 1 bar to 25 bar, at a temperature from 15 to 25°C.

[0029] Advantageously, in the process according to the invention, the concentration of the CO_2 is preferably maintained constant by continuous gas injection in the electrolyte during the step of in-situ electrodeposition or co-electrodeposition.

[0030] Advantageously, in the process according to the invention, the electrolyte is a carbonated water-based electrolyte. The carbonated water-based electrolyte is preferably chosen from CsHCO_3 , KHCO_3 and K_2SO_4 , preferably CsHCO_3 . The concentration of the carbonated water-based electrolyte may be from 0.5 mol L^{-1} to 5.0 mol L^{-1} , preferably from 0.5 mol L^{-1} to 1.5 mol L^{-1} , more preferably 1 mol L^{-1} .

[0031] The invention further relates to the use of the copper based electrocatalyst material according to the invention as a catalyst, preferably to convert CO_2 into small molecules. It is meant by small molecules, molecules such as CO , CH_4 , C_2H_4 , $\text{C}_2\text{H}_5\text{OH}$ and isopropanol.

[0032] In particular, some advantages of the copper based electrocatalyst material according to the invention are listed below:

- the electrocatalyst material according to the invention can be easily obtained by electrodepositing Cu or co-electrodepositing an Ag-Cu alloy;
- using an supersaturated carbonated water-based electrolyte greatly improves the selectivity of the reaction on the catalyst toward the reduction of CO_2 into molecules with two or more carbons.
- the gas (i.e. air or CO_2) oversaturation allow increasing the current density and improving the selectivity of the reaction towards the production of C_2+ molecules (such as ethylene, ethanol and isopropanol) ;
- the electrocatalyst material according to the invention achieved increased current density and improved selectivity of the reaction towards the production of C_3 molecules (mainly isopropanol) up to -60 mA cm^{-2} and 58 % at -0.73 V vs. RHE using the high-pressure reactor configuration with 10 bar of CO_2 , corresponding to a CO_2 concentration of 3 mol L^{-1} . For comparison, current density and Faradaic efficiency of -17.5 mA cm^{-2} and $\sim 39.6 \%$ for isopropanol were achieved when using a carbonated electrolyte at atmospheric pressure.
- the electrocatalyst material according to the invention allows the production of both the liquid and the gaseous product, notably C_{2+} molecules with high added values
- the electrocatalyst material according to the invention have a total current density over 36.5 mA cm^{-2} at -0.73 V vs. RHE in a three-electrode configuration at 1 ATM;
- the electrocatalyst material according to the invention has a specific current density over 17.5 mA cm^{-2} for isopropanol for CO_2 at -0.73 V vs. RHE at atmospheric pressure.

Brief description of the figures

[0033]

Figure 1 represents the characterization of the CuAg alloy decorated electrodes. (a) Electrochemical deposition curve for the CuAg alloy electrode at different deposition current with the total loading amount of 10 mg. (b) As prepared electrode with the geometric area of 2 cm^2 . (c-d) SEM images of CuAg sample synthesized under CO_2 supersaturated with (c) low and (d) high deposition current. (e) XRD spectrum of the Cu, Ag, CuAg without supersaturated (CE1) and CuAg with supersaturated samples (EM1).

Figure 2 represents the Faradaic efficiencies for each CO₂RR product and H₂ on CuAg alloy catalyst (A) electrodeposition (E-deposition) without CO₂ supersaturated (CE1), CO₂RR without CO₂ supersaturated; (B) E-deposition with CO₂ supersaturated (EM1), CO₂RR without CO₂ supersaturated; (C) E-deposition without CO₂ supersaturated (CE1), CO₂RR without CO₂ supersaturated; (D) E-deposition with CO₂ supersaturated (EM1), CO₂RR with CO₂ supersaturated at various potentials ranging from -0.4 to -1.2 V vs. RHE in 0.5 mol L⁻¹ CsHCO₃.

Figure 3 represents the evolution of the (a) specific current density of each product and (b) the specific current density of each CO₂ reduction product.

Figure 4 represents the Faradaic efficiencies for each CO₂RR product and H₂ on CuAg alloy catalyst (A) E-deposition without CO₂ supersaturated (CE1), CO₂RR without CO₂ supersaturated; (B) E-deposition with CO₂ supersaturated (EM1), CO₂RR without CO₂ supersaturated; (C) E-deposition without CO₂ supersaturated (CE1), CO₂RR without CO₂ supersaturated; (D) E-deposition with CO₂ supersaturated (EM1), CO₂RR with CO₂ supersaturated at various potentials ranging from -0.4 to -1.2 V vs. RHE in 1.0 mol L⁻¹ CsHCO₃.

Figure 5 represents the Faradaic efficiencies for each CO₂RR product and H₂ on CuAg alloy catalyst E-deposition with CO₂ supersaturated, CO₂ RR with CO₂ supersaturated at various potentials ranging from -0.4 to -1.2 V vs. RHE in different concentration of CsHCO₃. (A) 0.1 mol L⁻¹; (B) 0.5 mol L⁻¹; (C) 1.0 mol L⁻¹; (D) 2.0 mol L⁻¹ and (E) 5.0 mol L⁻¹.

Figure 6 represents the Faradaic efficiencies for the CO₂RR product of isopropanol on CuAg alloy catalyst EM1 at various potentials ranging from -0.4 to -1.0 V vs. RHE in 1.0 mol L⁻¹ KHCO₃ in high-pressure CO₂ electrolyzer with different CO₂ solubility.

Figure 7 represents the long-term stability measurement of CuAg alloy catalyst EM1 in CO₂-supersaturated 1.0 mol L⁻¹ CsHCO₃ aqueous electrolyte under a 10 bar CO₂ and room temperature (25 °C) at -0.80 V vs. RHE for 200 hours.

EXAMPLES

Example 1: Preparation of an electrocatalyst material 1 (EM1) according to the invention

[0034] The CuAg bimetallic electrode (Cu_xAg_{1-x}, with x = 0.9, 0.7, 0.5, 0.3, 0.1) was obtained through a chronoamperometry two-electrode co-electrodeposition approach with hydrophilic pre-treated gas diffusion layer (GDL) as working electrode and Pt foil as the counter electrode, respectively. A 0.2 mol L⁻¹ CuSO₄·5H₂O and 2 mmol L⁻¹ AgNO₃ mixture saturated with CO₂ was applied as the electrolyte. The conditions of pressure and temperature are the following:

- Pressure: 1 ATM,
- Temperature: room temperature (25 degree),
- CO₂ (gas) concentration: 0.3 mol L⁻¹ (supersaturated concentration : 0.05 mol L⁻¹).

[0035] The electrolyte was supersaturated with CO₂ during the deposition with a CO₂ concentration of 0.3 mol L⁻¹. The electrodeposition on GDL was performed at a current density of 1.0 and 10 mA cm⁻² at room temperature for the total charge of 30 C corresponding to a loading amount of 5 mg cm⁻² (Figure 1a,b). After the deposition, the electrolyte was rinsed with deionized water three times immediately to avoid the further galvanic reaction. The prepared electrode was dried under Ar at room temperature and store for further measurement. As shown from Figure 1c, the structure of CuAg alloy is cubic-like when CO₂ oversaturate is applied during the deposition with a deposition current density of 1.0 mA cm⁻². With a deposition current density 10.0 mA cm⁻², the structure of CuAg alloy is dendritic (Figure 1d).

[0036] From the XRD pattern of the metal crystals, the ratio of {100}:{111} peaks (seen at 52° and 44° respectively) of CuAg CO₂ saturated is increased compared to the same, but with no CO₂ saturation (Figure 1e).

Example 2: Preparation of an electrocatalyst material CE1 (not according to the invention)

[0037] The CuAg bimetallic electrode (Cu_xAg_{1-x}, with x = 0.9, 0.7, 0.5, 0.3, 0.1) was obtained through a chronoamperometry two-electrode co-electrodeposition approach with hydrophilic pre-treated GDL as working electrode and Pt foil as the counter electrode, respectively. As in example 1, a 0.2 M CuSO₄·5H₂O and 2 mM AgNO₃ mixture but saturated with Ar (instead of CO₂) was applied as the electrolyte. The conditions of pressure and temperature are the following:

- Pressure: 1 ATM,
- Temperature: room temperature (25 degree),
- Ar (gas) : purity 99.999%.

[0038] The electrodeposited on GDL was applied at a current density of 10 mA cm⁻² for the total charge of 30 C corresponding to a loading amount of 5 mg cm⁻². After the deposition, the redundant electrolyte was rinsed with deionized

water three times immediately to avoid the further galvanic reaction. The prepared electrode was dried under Ar flow at room temperature for further measurement.

Example 3: Comparison of the performances of the electrocatalyst materials 1 (EM1) and counter-example 1 (CE1)

[0039] The electrocatalyst materials EM1 and CE1 (where $x = 0.9$) were then tested in a CO_2 -supersaturated electrolyte solution comprising of 1 mol L^{-1} CsHCO_3 as the electrolyte at 25°C and atmospheric pressure. The electrolyte solution was supersaturated with CO_2 gas to reach a concentration of 0.3 mol L^{-1} .

[0040] Results of the selectivity of EM1 and CE1 in 0.5 mol L^{-1} CsHCO_3 are summarized in Table 1, below:

Table 1: Summary of the electrocatalytic selectivity (Faradic Efficiency: FE) for CuAg alloy electrodes EM1 ($x = 0.9$, electrolyte under CO_2 supersaturated) and CE1 ($x = 0.9$, electrolyte under Ar saturated) and the 0.5 mol L^{-1} CsHCO_3 without and with CO_2 supersaturated.

CO ₂ supersaturation		-1.2V			-1.0V		
E-dep.	CO ₂ RR	C ₂₊	CO ₂ RR	H ₂	C ₂₊	CO ₂ RR	H ₂
NO	NO	2.65	8.02	86.5	0.3	5.84	83.42
YES	NO	0	7.08	84.32	0.6	6.28	84.05
NO	YES	1.3	11.19	80.2	2.7	12.37	80.4
YES	YES	3.1	14.31	76.4	24.17	40.02	49.6
CO ₂ supersaturation		-0.7V			-0.6V		
E-dep.	CO ₂ RR	C ₂₊	CO ₂ RR	H ₂	C ₂₊	CO ₂ RR	H ₂
NO	NO	0.7	8.91	79.63	0.9	10.43	78.1
YES	NO	0.6	9.2	77.28	0.6	11.24	74.13
NO	YES	11.3	19.53	76.13	10.7	17.23	76.32
YES	YES	50.37	58.9	32.12	48.54	57.36	38.6
CO ₂ supersaturation		-0.9V			-0.8V		
E-dep.	CO ₂ RR	C ₂₊	CO ₂ RR	H ₂	C ₂₊	CO ₂ RR	H ₂
NO	NO	3.7	11.15	81.25	2.4	12.02	79.6
YES	NO	4.3	12.97	77.25	2.9	12.81	75.4
NO	YES	17.28	25.04	62.45	14.05	21.49	65.8
YES	YES	40.99	51.37	40.18	43.68	56.21	39.6
CO ₂ supersaturation		-0.4V					
E-dep.	CO ₂ RR	C ₂₊	CO ₂ RR	H ₂			
NO	NO	0.3	11.47	76.82			
YES	NO	0.2	9.7	84.32			
NO	YES	6.2	13.91	80.2			
YES	YES	9.76	16.82	76.4			

[0041] The performance in terms of selectivity (Faradaic efficiency) of the reaction (FE) and current density were compared in table 1. The results show that the CO_2 oversaturation during the electrodeposition (EM1) process translates into lower selectivity for the hydrogen evolution reaction while the CO_2 oversaturation with CsHCO_3 electrolyte induces more C_{2+} product during CO_2 RR. Remarkably, when both the E-deposition process and the electrolyte for CO_2 RR is CO_2 supersaturated, we observe the uncommon C_{3+} liquid product: isopropanol (i-Pr-OH) at the potential window from -0.4 to -1.0 V vs. reversible hydrogen electrode (RHE) (Figure 2-3).

Example 4: Effect of the concentration of the electrolyte in a CO₂ conversion process

[0042] Experiments of example 3 were repeated with an increase in the concentration of the electrolyte. As shown in Figure 4, when one increases the concentration of the electrolyte from 0.5 mol L⁻¹ CsHCO₃ to 1.0 mol L⁻¹ CsHCO₃, the FE of isopropanol further increases from 36.45% to 38.62%, the total FE C₂₊ increased from 50.37% to 54.67%.

[0043] Results of the selectivity of EM1 in 1.0 mol L⁻¹ CsHCO₃ are summarized in Table 2, below:

Table 2: Summary of the electrocatalytic selectivity (Faradic Efficiency: FE) for CuAg alloy electrodes EM1 (x = 0.9, electrolyte under CO₂ supersaturated) and CE1 (x = 0.9, electrolyte under Ar saturated) and the 1.0 mol L⁻¹ CsHCO₃ without and with CO₂ supersaturated.

CO ₂ supersaturation		-1.2V			-1.0V		
E-dep.	CO ₂ RR	C ₂₊	CO ₂ RR	H ₂	C ₂₊	CO ₂ RR	H ₂
NO	NO	15.2	19.22	69.62	13.49	21.91	68.52
YES	NO	15.8	19.1	68.35	14.55	24.85	65.46
NO	YES	12.7	16.3	61.42	20.28	31.52	59.12
YES	YES	33.4	38.56	44.56	47.03	59.83	33.8
CO ₂ supersaturation		-0.73V			-0.7V		
E-dep.	CO ₂ RR	C ₂₊	CO ₂ RR	H ₂	C ₂₊	CO ₂ RR	H ₂
NO	NO	11.45	20.67	66.78	8.6	16.58	79.63
YES	NO	12.52	22.32	64.32	9.3	14.92	78.65
NO	YES	21.18	27.01	56.28	20.2	28.63	65.12
YES	YES	55.28	62.71	32.42	54.67	60.53	32.11
CO ₂ supersaturation		-1.2V			-1.0V		
E-dep.	CO ₂ RR	C ₂₊	CO ₂ RR	H ₂	C ₂₊	CO ₂ RR	H ₂
NO	NO	2.65	8.02	86.5	0.3	5.84	83.42
YES	NO	0	7.08	84.32	0.6	6.28	84.05
NO	YES	1.3	11.19	80.2	2.7	12.37	80.4
YES	YES	3.1	14.31	76.4	24.17	40.02	49.6
CO ₂ supersaturation		-0.7V			-0.6V		
E-dep.	CO ₂ RR	C ₂₊	CO ₂ RR	H ₂	C ₂₊	CO ₂ RR	H ₂
NO	NO	0.7	8.91	79.63	0.9	10.43	78.1
YES	NO	0.6	9.2	77.28	0.6	11.24	74.13
NO	YES	11.3	19.53	76.13	10.7	17.23	76.32
YES	YES	50.37	58.9	32.12	48.54	57.36	38.6

[0044] These further results reveal that increasing the concentration of the electrolyte is also another strategy to enhance the C₂₊ efficiency with CO₂ supersaturated electrolyte.

[0045] More importantly, at a low potential of -0.73 V vs. RHE, a 39.26 % Faradaic efficiency was obtained for isopropanol which is the highest recorded value. A FE of 55.28 % for C₂₊ products (i.e.: C₂+C₃ molecules) is also 2.61 times higher compared with the same material without CO₂ supersaturated in the electrolyte (Table 2). Importantly, no isopropanol was detected when using the non-supersaturated electrolyte.

[0046] To the best of knowledge of the applicants, this performance is the highest ever reported for the production of isopropanol and among the highest for C₃₊ at such a low potential.

[0047] The concentration of the electrolyte was further increased. As shown in Figure 5, when increased the concentration of the electrolyte from 1.0 mol L⁻¹ CsHCO₃ to 5.0 mol L⁻¹ CsHCO₃, the FE of isopropanol is not increasing along

with the increase of the concentration of Cs^+ . These results reveal that the $1.0 \text{ mol L}^{-1} \text{ Cs}^+$ is the best parameter for adjusting the Cs^+ concentration with CO_2 supersaturated electrolyte.

Example 5: Preparation of EM1 at higher CO_2 concentrations and study of their activity

[0048] A customized-designed high-pressure CO_2 electrolyzer was then used to prepare the EM1 electrodes at higher CO_2 concentrations. Using a high-pressure CO_2 electrolyzer can make the overall process to produce the multi-carbon product more efficiently at a higher current density. The experiments were carried out at room temperature (20°) with a CO_2 pressure from 1 up to 25 bar corresponding to CO_2 concentration in the liquid electrolyte from 0.3 M up to 7.5 M. Such a process is indeed compatible with compressed CO_2 from the atmosphere.

[0049] Using 1.0 M CsHCO_3 as electrolyte our results demonstrate a 57.61% Faradaic efficiency for isopropanol at -0.7 V vs. RHE together under 10 bar of CO_2 with a doubled current density of $102.98 \text{ mA cm}^{-2}$ and specific current density for isopropanol of 59.33 mA cm^{-2} which is ≈ 3.4 times higher compared with the measured performed at atmospheric pressure. (Figure 6) Importantly the long-term stability of the CuAg alloy electrodes in a high-pressure electrolyzer under continuous operation at a CO_2 flow rate of 100 sccm and a cell voltage of -0.70 V vs. RHE was measured. The performance of the electrode was found to be stable over 200 hours with an average $\text{FE}_{\text{isopropanol}}$ of 56.08% and an average current density of around $104.71 \text{ mA cm}^{-2}$ (Figure 7). After 200 hours, the retention of the $\text{FE}_{\text{isopropanol}}$ and the current density were estimated to be 94.26% and 89.53%, respectively. The stability of the CO_2RR properties is further accompanied by high stability of the catalyst morphology and surface

List of references

[0050]

- [1] Whipple D T, Kenis P J A. Prospects of CO_2 utilization via direct heterogeneous electrochemical reduction[J]. The Journal of Physical Chemistry Letters, 2010, 1(24): 3451-3458.
- [2] Xia C, Zhu P, Jiang Q, et al. Continuous production of pure liquid fuel solutions via electrocatalytic CO_2 reduction using solid-electrolyte devices[J]. Nature Energy, 2019, 4(9): 776-785.
- [3] Hernández S, Farkhondeh M A, Sastre F, et al. Syngas production from electrochemical reduction of CO_2 : current status and prospective implementation[J]. Green Chemistry, 2017, 19(10): 2326-2346.
- [4] Hori Y, Wakebe H, Tsukamoto T, et al. Electrocatalytic process of CO selectivity in electrochemical reduction of CO_2 at metal electrodes in aqueous media[J]. Electrochimica Acta, 1994, 39(11-12): 1833-1839.
- [5] Bagger A, Ju W, Varela A S, et al. Electrochemical CO_2 reduction: a classification problem[J]. ChemPhysChem, 2017, 18(22): 3266-3273.

Claims

1. A method of preparing a copper based electrocatalyst material, comprising a step of in-situ electrodeposition or co-electrodeposition, in an electrolyte solution, of at least one catalytic metal in the presence of a gas comprising CO_2 , under electrochemical deposition conditions onto a conductive support, wherein
 - the at least one catalytic metal comprises copper and is electrodeposited or co-electrodeposited onto the conductive support, and
 - the gas comprising CO_2 is supersaturated in the electrolyte solution.
2. The method according to claim 1, wherein the at least one catalytic metal further comprises silver.
3. The method according to claim 1 or 2, wherein the at least one catalytic metal consists of copper and silver, preferably the atomic ratio Cu:Ag is from 1:9 to 9.9:0.1, preferably 7:3 to 9.8:0.2, more preferably from 8.5:1.5 to 9.5:0.5 or even preferably 9:1.
4. The method according to any of preceding claims, wherein the gas comprises from 0.04 wt.% to 100 wt.% of CO_2 , preferably the gas is CO_2 .
5. The method according to any of preceding claims, wherein the concentration of the gas, in the electrolyte solution, is from 0.05 to 7.5 mol L^{-1} , preferably from 0.5 to 1.5 mol L^{-1} , more preferably 1 mol L^{-1} .

6. The method according to preceding claim, wherein the concentration of the gas, in the electrolyte solution, is maintained constant by continuous gas injection in the electrolyte during the step of in-situ electrodeposition or co-electrodeposition.
- 5 7. The method according to any of preceding claims, wherein the conductive support is a carbon-based conductive support, preferably a gas diffusion layer or a graphite foil electrode.
8. The method according to any of preceding claims, comprising a step of hydrophilic pre-treatment of the conductive support.
- 10 9. The method according to any of preceding claims, wherein the electrodeposition or co-electrodeposition is provided under a voltage of -0.80 to -2.20 V vs. Ag / AgCl (KCl saturated).
- 15 10. The method according to any of preceding claims, wherein the controlling electrodeposition or co-electrodeposition is provided under a current density of 1.0 to 20.0 mA cm⁻².
11. The method according to any of the preceding claims, wherein the electrolyte solution is a carbonated water-based electrolyte solution, and wherein the carbonated water-based electrolyte is preferably chosen from CsHCO₃, KHCO₃ and K₂SO₄, preferably CsHCO₃, preferably at a concentration from 0.5 mol L⁻¹ to 5.0 mol L⁻¹, preferably 0.5 to 1.5 mol L⁻¹, more preferably 1 mol L⁻¹.
- 20 12. A copper based electrocatalyst material obtained according to the method of any of the preceding claims, comprising at least one catalytic material and a conductive support.
- 25 13. The copper based electrocatalyst material according to the preceding claim, wherein the at least one catalytic metal is in the form of a monometallic crystal or dendric alloy.
14. The copper based electrocatalyst material according to the preceding claim, wherein the layer of monometallic crystal or dendric alloy on the conductive support has a thickness from 5.0 to 15.0 μm.
- 30 15. A process of conversion of CO₂ into small molecules, such as ethylene, ethanol and isopropanol, comprising a step of contacting CO₂ with a copper based electrocatalyst material according to any of claims 12 to 14.
16. The process according to the preceding claim, wherein the conversion reaction of CO₂ is done under a pressure from 1.0 bar to 25.0 bar and at a temperature from 15 to 25°C, in an solution comprising an electrolyte and CO₂ (gas) at a concentration from 0.05 to 7.5 mol L⁻¹.
- 35 17. The process according to the preceding claim, wherein the electrolyte is a carbonated water-based electrolyte, and wherein the carbonated water-based electrolyte is preferably chosen from CsHCO₃, KHCO₃ and K₂SO₄, preferably at a concentration from 0.5 mol L⁻¹ to 5.0 mol L⁻¹, more preferably from 0.5 mol L⁻¹ to 1.5 mol L⁻¹, more preferably 1 mol L⁻¹.
- 40 18. Use of the copper based electrocatalyst material according to any of claims 12 to 15 to convert CO₂ into small molecules, such as ethylene, ethanol and isopropanol.
- 45
- 50
- 55

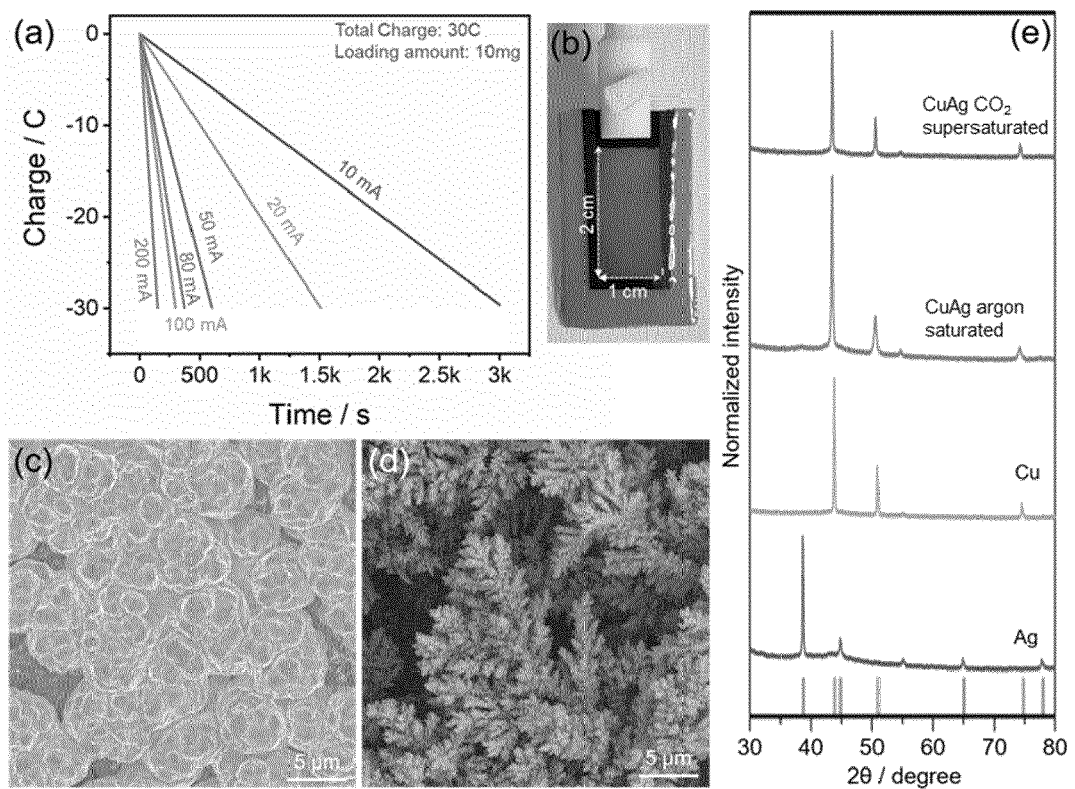


Figure 1

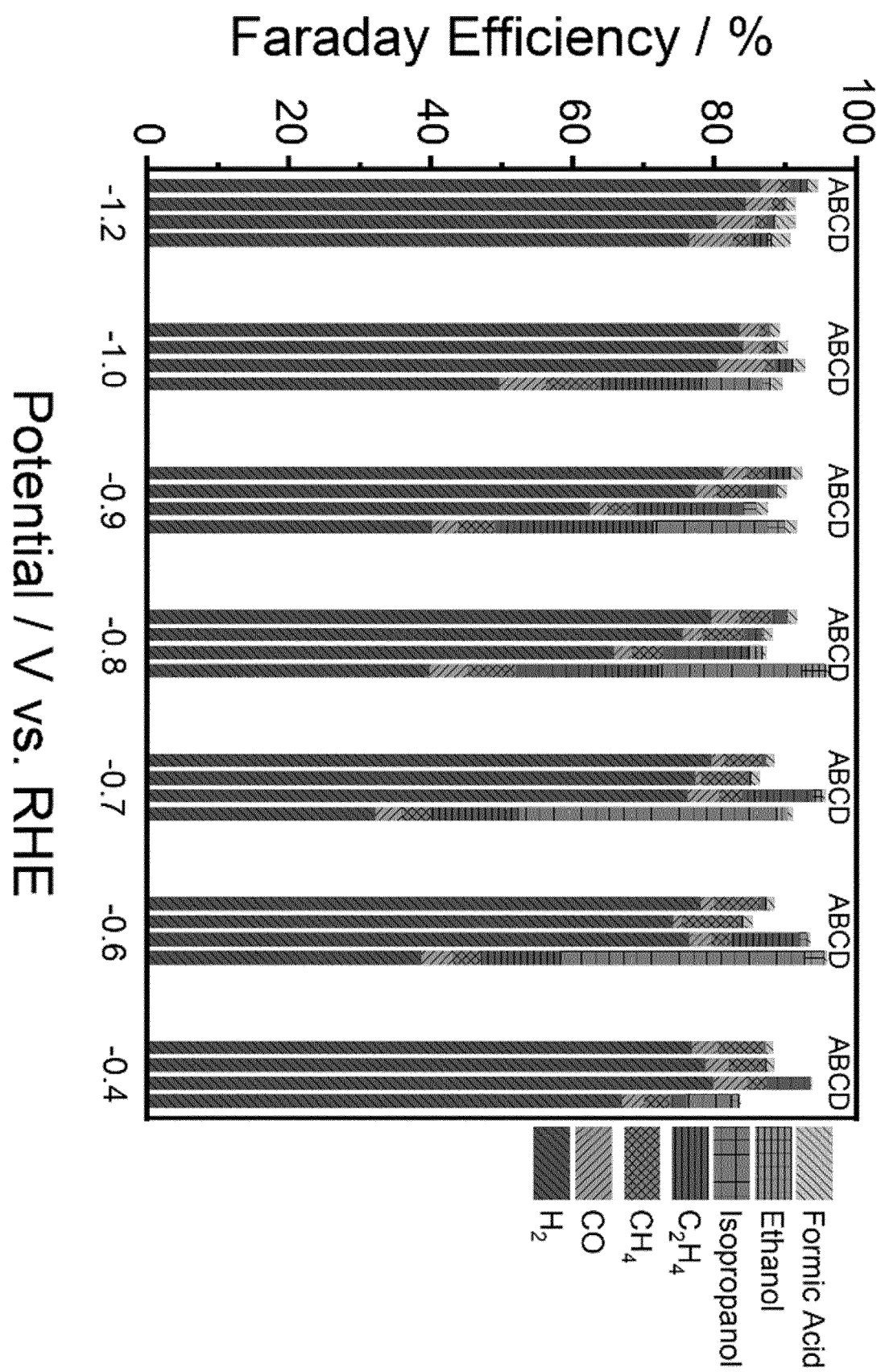


Figure 2

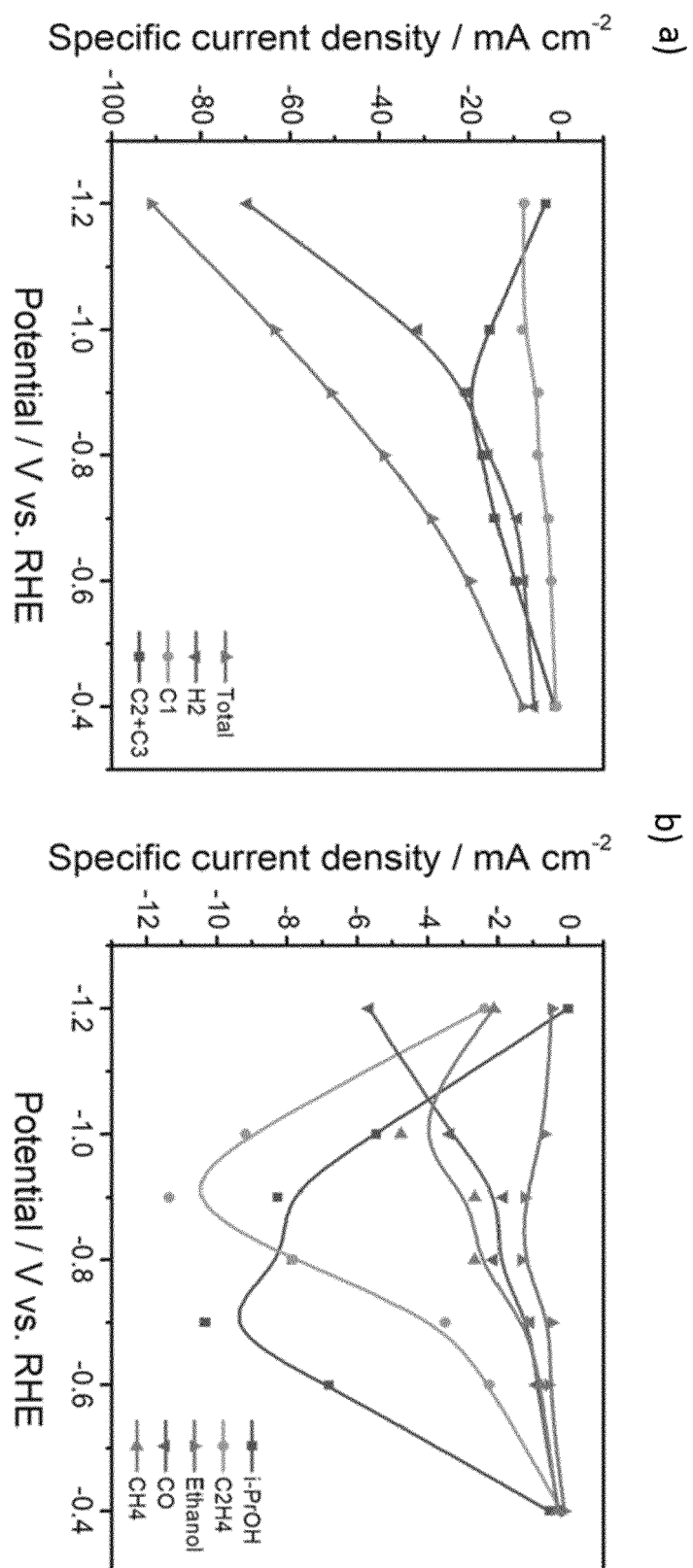


Figure 3

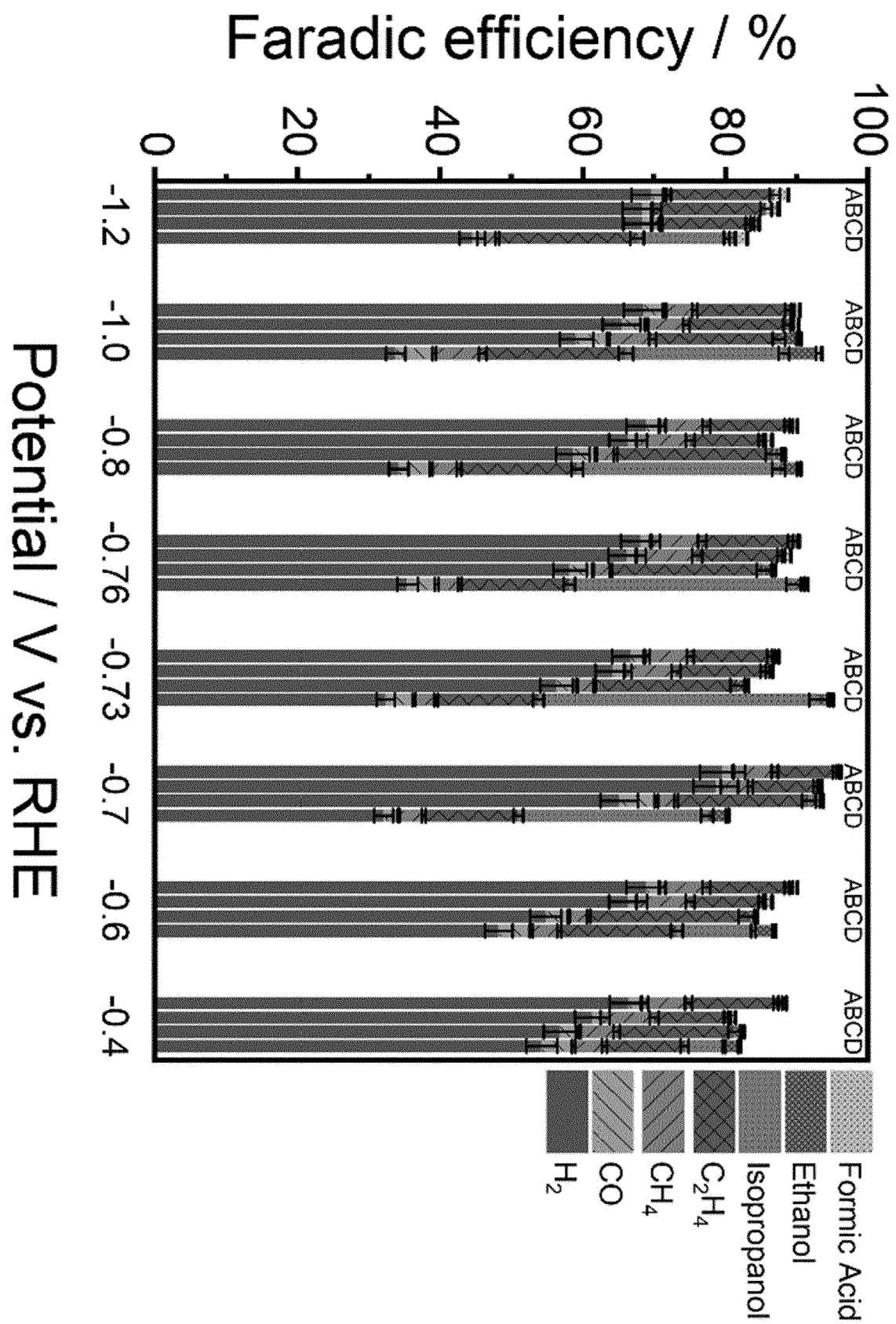


Figure 4

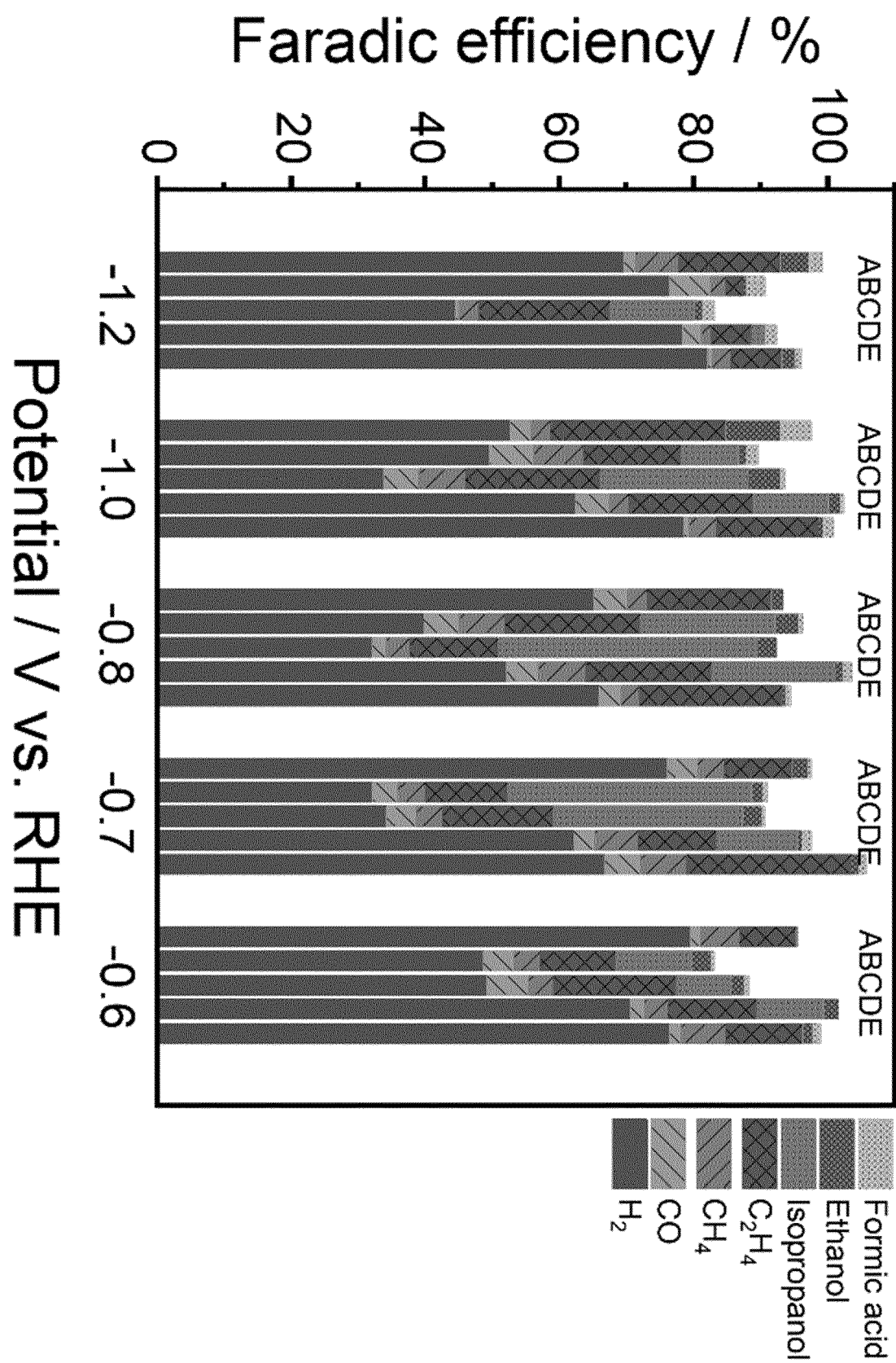


Figure 5

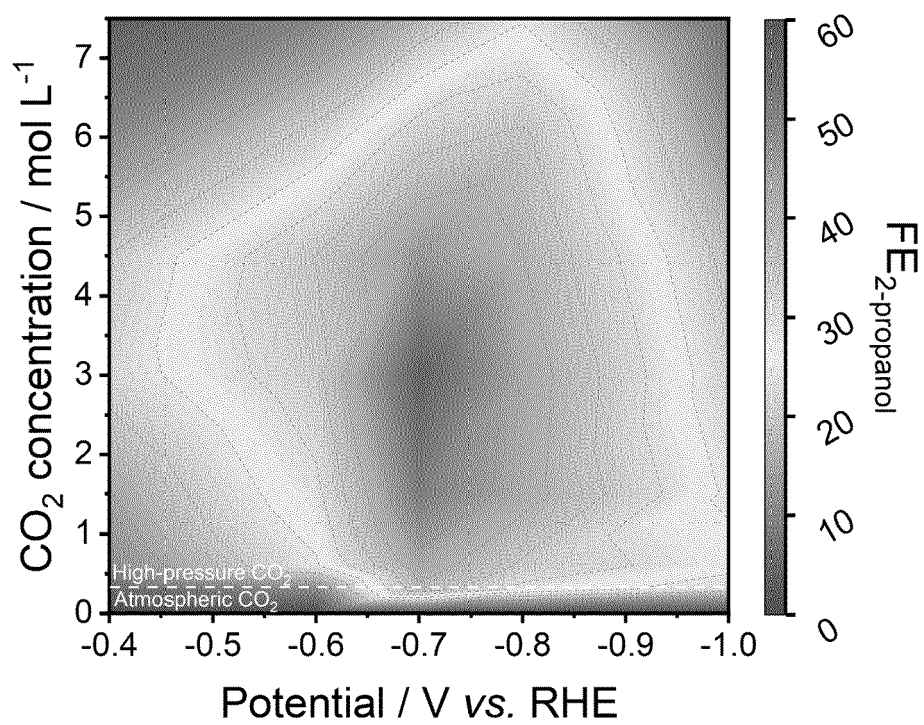


Figure 6

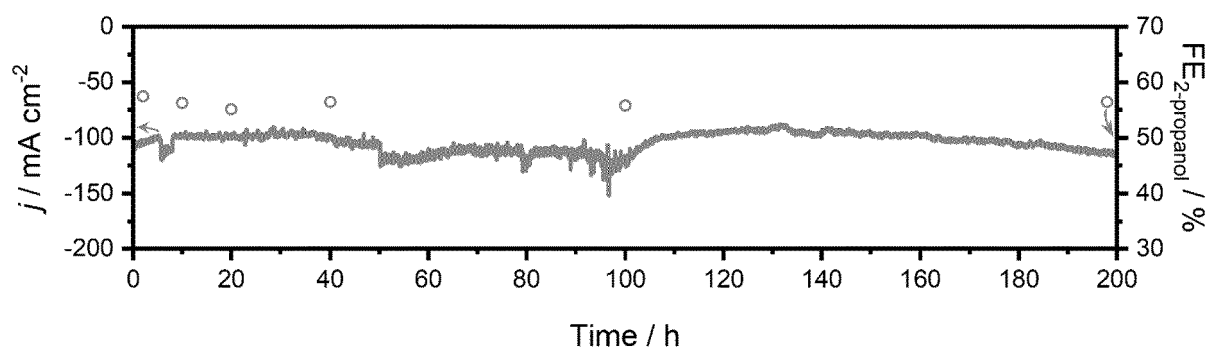


Figure 7



EUROPEAN SEARCH REPORT

Application Number

EP 22 30 5020

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	GANESAN MUTHUSANKAR ET AL: "Post-supercritical CO ₂ electrodeposition approach for Ni-Cu alloy fabrication: An innovative eco-friendly strategy for high-performance corrosion resistance with durability", APPLIED SURFACE SCIENCE , vol. 577, 18 November 2021 (2021-11-18), page 151955, XP055929387, AMSTERDAM, NL ISSN: 0169-4332, DOI: 10.1016/j.apsusc.2021.151955	1-5, 7-14	INV. C25B3/07 C25B3/26 C25B11/032 C25B11/052 C25B11/065 C25B11/089 C25D3/58 C25D3/64 C25D5/00
A	* the whole document *	6	
X	CHUANG H C ET AL: "Material characterization in TSV fabricated by supercritical carbon dioxide electroplating", 2018 INTERNATIONAL CONFERENCE ON ELECTRONICS PACKAGING AND IMAPS ALL ASIA CONFERENCE (ICEP-IAAC), JAPAN INSTITUTE OF ELECTRONICS PACKAGING, 17 April 2018 (2018-04-17), pages 506-508, XP033354221, DOI: 10.23919/ICEP.2018.8374357 [retrieved on 2018-06-06]	1-5, 9, 12-14	
A	* the whole document *	6	
X	CN 112 501 662 A (SHENZHEN RESEARCH INSTITUTE OF CENTRAL SOUTH UNIV) 16 March 2021 (2021-03-16)	1, 4-18	
Y	* the whole document *	2, 3	
Y	WO 2021/102561 A1 (GOVERNING COUNCIL UNIV TORONTO [CA]) 3 June 2021 (2021-06-03) * claims 1, 2, 3, 7, 8 *	2, 3	
The present search report has been drawn up for all claims			

1

Place of search	Date of completion of the search	Examiner
Munich	21 June 2022	Ritter, Thomas
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document		

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21-06-2022

10	Patent document cited in search report	Publication date	Patent family member(s)	Publication date
	CN 112501662 A	16-03-2021	NONE	
15	WO 2021102561 A1	03-06-2021	NONE	
20				
25				
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35				
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Non-patent literature cited in the description

- **WHIPPLE D T ; KENIS P J A.** Prospects of CO₂ utilization via direct heterogeneous electrochemical reduction[J. *The Journal of Physical Chemistry Letters*, 2010, vol. 1 (24), 3451-3458 **[0050]**
- **XIA C ; ZHU P ; JIANG Q et al.** Continuous production of pure liquid fuel solutions via electrocatalytic CO₂ reduction using solid-electrolyte devices[J. *Nature Energy*, 2019, vol. 4 (9), 776-785 **[0050]**
- **HERNÁNDEZ S ; FARKHONDEHFAL M A ; SASTRE F et al.** Syngas production from electrochemical reduction of CO₂: current status and prospective implementation[J. *Green Chemistry*, 2017, vol. 19 (10), 2326-2346 **[0050]**
- **HORI Y ; WAKEBE H ; TSUKAMOTO T et al.** Electrocatalytic process of CO selectivity in electrochemical reduction of CO₂ at metal electrodes in aqueous media[J. *Electrochimica Acta*, 1994, vol. 39 (11-12), 1833-1839 **[0050]**
- **BAGGER A ; JU W ; VARELA A S et al.** Electrochemical CO₂ reduction: a classification problem[J. *ChemPhysChem*, 2017, vol. 18 (22), 3266-3273 **[0050]**