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(54) Title: CATALYST SYSTEM FOR CATALYZED ELECTROCHEMICAL REACTIONS AND PREPARATION THEREOF, APPLICATIONS AND USES THEREOF

(57) Abstract: A catalyst system for catalyzed electrochemical reactions, in particular the electrochemical conversion of carbon dioxide into valuable chemical products, such as carboxylates and carboxylic acids, comprises a catalyst, wherein the catalyst comprises bismuth and indium. The catalyst system can be a component of a gas diffusion electrode, that can be used as the cathode electrode in an electrochemical cell.



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**CATALYST SYSTEM FOR CATALYZED ELECTROCHEMICAL REACTIONS AND
PREPARATION THEREOF, APPLICATIONS AND USES THEREOF**

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The present invention generally relates to a catalyst system for catalyzed electrochemical reactions, comprising a conductive support and a catalyst, in particular for reducing carbon dioxide in order to prepare products or intermediates thereof like carboxylates and/or carboxylic acids.

10 The electrochemical conversion of carbon dioxide into economically valuable materials such as fuels and industrial chemicals or intermediate products thereof is gaining interest in view of mitigating the emission of carbon dioxide into the atmosphere, which is responsible for climate alterations, changes in pH of seawater and other potentially damaging effects like melting of polar ice and sea level rise.

15 Catalyzed electrochemical reduction of carbon dioxide for preparing economically valuable products is known in the art.

E.g. WO2013/006711 discloses methods and systems for the electrochemical conversion of carbon dioxide to products like carboxylic acids, glycols and carboxylates in the presence of a homogeneous heterocyclic amine catalyst. In an embodiment the cathode of the electrochemical
20 cell wherein the conversion is performed, comprises a material suitable for the reduction of carbon dioxide. Examples of the cathode materials include metal and metal alloys, amongst others indium and indium alloys.

WO2014/032000 discloses a method of reducing carbon dioxide into one or more organic products in an electrochemical cell, wherein the cathode is an oxidized indium electrode, in
25 particular an anodized indium electrode.

WO2014/042781 discloses the electrochemical conversion of carbon dioxide into products using a high surface area cathode, wherein the cathode includes an indium coating and has a void volume of between about 30% to 98%. The cathode may also include indium coatings and/or metal structures further containing Pb, Sn, Hg, Tl, In, Bi, and Cd, their alloys, and combinations
30 thereof. Metals including Ti, Nb, Cr, Mo, Ag, Cd, Hg, Tl, An, and Pb as well as Cr-Ni-Mo steel alloys among many others may be incorporated. The alloys of indium with other metals, including Sn, Pb, Hg, Tl, Bi, Cu, and Cd and their mixed alloys and combinations thereof on the exposed catalytic surfaces of the electrode preferably comprise 5% to 99% indium.

Preliminary research has indicated that not all the potential catalysts as disclosed in the above prior art documents function as desired in terms of selectivity, activity and Faradaic efficiency. Therefore there is an ongoing need to develop catalyst systems, which show an improvement of one or more of these catalyst properties.

5 In particular the present invention aims at providing a catalyst system having a high Faradaic efficiency for the electrochemical reduction of carbon dioxide and a high selectivity towards valuable reduction products, in particular carboxylic acids or intermediates thereof, such as carboxylate salts.

This invention provides a catalyst system for catalyzed electrochemical reactions, comprising a
10 catalyst, wherein the catalyst comprises 5-94 wt.% bismuth and 6-95 wt.% indium, based on the total amount of bismuth and indium. This catalyst will herein below be referred to as an indium bismuth catalyst.

The catalyst system according to the invention for catalyzed electrochemical reactions, in particular reduction of carbon dioxide, preferably comprises an electrically conductive support
15 and a catalyst, wherein the catalyst comprises 5-94 wt.% bismuth and 6-95 wt.% indium, based on the total amount of bismuth and indium.

Surprisingly it has been found that the binary metal combination of bismuth and indium as catalyst for the electrochemical conversion of carbon dioxide shows a good selectivity for the reduction of carbon dioxide into carboxylic acids and carboxylates, as well as a good Faradaic
20 yield, in particular for the aqueous conversion of carbon dioxide to formate salt.

Compared to other indium based binary metal catalysts the indium bismuth catalyst shows an improved Faradaic yield. The amount of bismuth is in the range of 5-94 wt.% based on the total amount of bismuth and indium, preferably in the range of 10-90 wt.%, more preferably 30-90 wt.%, such as 35-90 wt.%. Experimental results have indicated that an amount of bismuth in the
25 range of 40-60 wt.%, such as 45-55 wt.%, e.g. about 1:1 weight ratio of bismuth to indium, offers improved catalytic properties regarding carbon dioxide to formate conversion.

The catalyst can comprise a combination of bismuth and indium in different thermodynamic phases. Preferably an amorphous combination of bismuth and indium is used. That is, preferably the catalyst system according to the invention comprises a catalyst, wherein the catalyst
30 comprises an amorphous combination of 5-94 wt.% bismuth and 6-95 wt.% indium, based on the total amount of bismuth and indium.

The indium bismuth catalyst according to the invention can be applied without or in combination with an electrically conductive support. It can, for example, be applied without or in combination with a carbon containing support. Preferably the indium bismuth catalyst is applied in

combination with an electrically conductive support. Therefore, the catalyst system is preferably a catalyst system for catalyzed electrochemical reactions, comprising an electrically conductive support and a catalyst, wherein the catalyst comprises 5-94 wt.% bismuth and 6-95 wt.% indium, based on the total amount of bismuth and indium.

5 As a conductive support a particulate material, in particular carbon particles, is used. Preferably the conductive support comprises a porous structure of carbon particles bonded together. A preferred binding material is a hydrophobic binder, such as a fluorinated binder. The catalyst is deposited onto or adhered to the conductive material. The weight ratio of indium and bismuth to carbon can advantageously be in the range of 0.10-1.50, e.g. about 30 wt.%.

10 Typically, the electrochemical reduction of carbon dioxide into chemical reduction products is performed in an electrochemical cell or photochemical cell having at least two cell compartments containing the respective electrodes. Carbon dioxide is supplied to the cathode. The cathode is preferably a gas-diffusion electrode providing a high surface area or interface for solid-liquid-gas contact. Such a gas-diffusion electrode comprises an electrically conductive substrate, which
15 may serve as a supporting structure for a gas-diffusion layer. The gas-diffusion layer provides a thin porous structure or network e.g. made from carbon, for passing a gas like carbon dioxide from one side to the other. Typically the structure is hydrophobic to distract water. The gas-diffusion layer may comprise a catalytically active material.

Therefor a further aspect of the invention relates to a gas-diffusion electrode, comprising a gas-
20 diffusion layer on an electrically conductive substrate, wherein the gas-diffusion layer comprises the catalyst system according to the invention as outlined above. The binary metal catalyst system of bismuth and indium according to the invention may be embedded in the gas-diffusion layer structure or provided as one or more additional separate layers thereof. As explained above, a particulate carbon is a preferred example of the conductive support for the catalyst.

25 The catalyst system is preferably bonded to the electrically conductive substrate using a hydrophobic binder such as PTFE. Examples of suitable substrates include metal structures like expanded or woven metals, metal foams, and carbon structures including wovens, cloth and paper.

30 Yet another aspect of the invention is an electrochemical cell comprising at least one gas chamber and at least one liquid chamber, which chambers are separated by a gas-diffusion electrode according to the invention.

Generally the reduction of carbon dioxide is performed in an electrochemical cell, typically a divided cell having two cell compartments. One cell compartment contains the anode, and the other cell compartment contains a gas-diffusion cathode electrode according to the invention,

comprising the binary metal electrocatalyst of bismuth and indium. The two cell compartments may be separated by a suitable membrane, e.g. made from porous glass frit, microporous material, ion exchanging membrane or ion conducting bridge, allowing ionic species to travel from one compartment to the other, such as protons generated at the anode to the cathode compartment.

A further aspect of the invention concerns a method of preparing a gas-diffusion electrode as defined above, comprising the binary metal electrocatalyst system according to the invention. This manufacturing method comprises a step of providing an electrically conductive substrate and a step of applying the catalyst system according to the invention, comprising indium and bismuth and an electrically conductive support, in particular particulate support material, and a binder to the gas-diffusion layer of the gas-diffusion electrode.

The electrocatalyst loaded gas-diffusion electrode can be manufactured in various ways including spraying, casting and sintering, often using one or more suitable binders.

The invention also relates to a method of electrocatalytically converting carbon dioxide into valuable products or product intermediates. This method comprises:

introducing an anolyte to a first cell compartment of an electrochemical cell, the first cell compartment comprising an anode;

introducing a catholyte and carbon dioxide to a second cell compartment of the electrochemical cell, the second cell compartment comprising a cathode, and

applying an electrical potential between the anode and the cathode sufficient to reduce carbon dioxide to a reduced reaction product,

wherein the cathode comprises a catalyst system according to the invention, in particular the cathode is a gas-diffusion electrode according to the invention.

The method according to the invention allows to reduce carbon dioxide to carboxylic acid and intermediates, including salts such as formate, glycolate, glyoxylate, oxalate and lactate, carboxylic acids, and glycols. The production of a carboxylic acid or carboxylic acid intermediate may be dependent on the pH of the electrolyte solution in the cell, with lower pH ranges favoring carboxylic acid production. The pH of the cathode compartment may be adjusted to favor production of one of a carboxylic acid or carboxylic acid intermediate over production of the other, such as by introducing an acid (e.g., HCl or H₂SO₄) to the cathode compartment. The pH of the catholyte is preferably between about 1 and 8. A pH range of 1-4 is preferable for production of carboxylic acids from carbon dioxide. A pH range of 4-8 is preferable for production of carboxylic acid intermediates from carbon dioxide.

The electrical potential may be a DC voltage. In preferred embodiments, the applied electrical potential is generally between about -1.5V vs. SCE and about -6V vs. SCE, preferably from about -1.5V vs. SCE to about -5V vs. SCE, such as in the range of -3V vs. SCE to -5V vs SCE and more preferably from about -1.5V vs. SCE to about -4V vs. SCE.

- 5 High Faradaic yield and selectivity of the catalyst system according to the invention for conversion of carbon dioxide into formate/formic acid have been shown at the cathode according to the reaction $\text{CO}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{HCOOH}$, while at the anode water may be oxidized into oxygen and hydrogen ions according to $2\text{H}_2\text{O} \rightarrow 4\text{H}^+ + \text{O}_2 + 4\text{e}^-$.

10 The hydrogen ions pass through the ion exchange membrane from the anolyte compartment to the catholyte compartment in the electrochemical cell.

The carbon dioxide conversion to formate/formic acid is typically performed in an aqueous medium, wherein the CO_2 is bubbled through the aqueous medium or distributed to the gas-diffusion electrode, e.g. using perculator systems.

15 Non-aqueous media may also be used, e.g. in the direct conversion of carbon dioxide to oxalic acid or oxalate.

A homogeneous heterocyclic catalyst may be added to the cathode compartment of the cell containing the cathode. The homogeneous heterocyclic catalyst may include, for example, one or more of 4-hydroxy pyridine, adenine, a heterocyclic amine containing sulfur, a heterocyclic amine containing oxygen, an azole, a benzimidazole, a bipyridine, furan, an imidazole, an
20 imidazole related species with at least one five-member ring, an indole, a lutidine, methylimidazole, an oxazole, phenanthroline, pterin, pteridine, a pyridine, a pyridine related species with at least one six-member ring, pyrrole, quinoline, or a thiazole, and mixtures thereof. If present, the homogeneous heterocyclic catalyst is preferably present at a concentration of between about 0.001M and about 1M, and more preferably between about 0.01M and 0.5M.

25 The chemicals derived as reaction products from the direct electrochemical conversion according to the invention can be processed further into industrial products. E.g. oxalic acid can be used as a starting material for the production of ethylene glycol and/or glycine. See e.g. US2016/0017503. Hydrogen may be introduced to the carboxylic acid or carboxylic acid intermediate to produce a glycol or a carboxylic acid, respectively. Hydrogen may be derived
30 from natural gas or water.

The invention is further illustrated by the attached drawings and examples.

In the drawings

Fig. 1 shows an embodiment of an electrochemical cell according to the invention; and

Fig. 2 is an embodiment of a gas-diffusion electrode according to the invention.

In FIG. 1 a block diagram of a system 100 is shown in accordance with an embodiment of the present invention. System 100 may be utilized for electrochemical production of carboxylic acid intermediates, carboxylic acids, and glycols from carbon dioxide and water (and hydrogen for glycol production). The system 100 generally comprises an electrochemical cell 102, a liquid source 104, an energy source 106, a carbon dioxide source 108, a product extractor 110 and an extractor 112, the latter in this embodiment for the recovery of oxygen produced at the anode. In an embodiment the liquid source 104 is a water source. In another embodiment the liquid source is an organic solvent source. A product or product mixture may be obtained from the product extractor 110 after extraction. An output gas containing oxygen may be output from the oxygen extractor 112 after extraction.

In the embodiment shown the cell 102 is a divided electrochemical cell. The cell 102 reduces carbon dioxide into products or product intermediates. The reduction may take place by introducing such as bubbling carbon dioxide into an electrolyte solution in the cell 102. At the cathode 120 comprising the catalyst system according to the invention carbon dioxide is reduced into a carboxylic acid or a carboxylic acid intermediate.

The cell 102 generally comprises two or more cell compartments 114a, 114b, a separator 116 e.g. an ion exchange membrane, an anode 118 in anode cell compartment 114a, and a cathode 120 in cathode cell compartment 114b on an opposite side of the separator 116. The cathode 120 includes a catalyst system according to the invention suitable for the reduction of carbon dioxide. An electrolyte solution e.g., anolyte 122a and catholyte 122b may fill the respective cell compartments 114a and 114b.

The liquid source 104 preferably includes a water source, such that the liquid source 104 may provide pure water to the cell 102. The liquid source 104 may provide other fluids to the cell 102, including an organic solvent, such as methanol, acetonitrile, and dimethylfuran. The liquid source 104 may also provide a mixture of an organic solvent and water to the cell 102.

The catholyte 122 may include an aromatic heterocyclic catalyst, e.g. in a concentration of about 10 mM to 1 M. The electrolyte may also include one or more suitable salts, such as KCl, NaNO₃, Na₂SO₄, NaCl, NaF, NaClO₄, KClO₄, K₂SiO₃ or CaCl₂, e.g. at a concentration of about 0.5 M. Other additives may include Group I cations (H, Li, Na, K, Rb and Cs except Fr), divalent cations (e.g., Ca²⁺, Mg²⁺, Zn²⁺) ammonium, alkylammonium cations and alkyl amines. Examples of anions comprise halides, carbonates, bicarbonates, nitrates, nitrites, perchlorates, phosphates, polyphosphates, silicates and sulfates. Bicarbonate is a preferred anion.

The pH of the cathode compartment 114b is preferably between about 1 and 8.

The energy source 106 may include a variable voltage source. The energy source 106 may be operational to generate an electrical potential between the anode 118 and the cathode 120.

The gas source 108 preferably includes a carbon dioxide source, such that the gas source 108 may provide carbon dioxide to the cell 102. E.g. the carbon dioxide is bubbled directly into the compartment 114b containing the cathode 120. For instance, the compartment 114b may include a carbon dioxide input, such as a port 126a configured to be coupled between the carbon dioxide source and the cathode 120.

The carbon dioxide may be obtained from any source, preferably a renewable source. The product extractor 110 may include an organic product and/or inorganic product extractor. The product extractor 110 generally facilitates extraction of one or more products e.g., carboxylic acid, and /or carboxylic acid intermediate from the electrolyte 122. The extraction may occur via one or more of a solid sorbent, carbon dioxide- assisted solid sorbent, liquid-liquid extraction, nanofiltration, crystallization and electrodialysis. The extracted products may be presented through a port 126b of the system 100 for subsequent storage, consumption, and/or processing by other devices and /or processes at A. In an embodiment the carboxylic acid or carboxylic acid intermediate is continuously removed from the cell 102, where cell 102 operates on a continuous basis, such as through a continuous flow-single pass reactor where fresh catholyte and carbon dioxide is fed continuously as the input, and where the output from the reactor is continuously removed. In other embodiments, the carboxylic acid or carboxylic acid intermediate is continuously removed from the catholyte 122 via one or more of adsorbing with a solid sorbent, liquid-liquid extraction, and electrodialysis.

The separated carboxylic acid or carboxylic acid intermediate may be placed in contact with a hydrogen stream at A, e.g. in an additional reactor, to produce a glycol or carboxylic acid, respectively.

Oxygen may be discharged from extractor 112 through port 128.

An embodiment of a gas-diffusion electrode according to the invention is shown in Fig. 2.

Fig. 2 represents a schematic illustration of an electrochemical cell 200 utilizing an anode electrode 202 for the anode reaction, in this specific embodiment a hydrogen gas-diffusion electrode, and a carbon dioxide gas-diffusion electrode 204 for the cathode reaction of reducing carbon dioxide e.g. to formate. The cathode 204 may have a carbon dioxide internal gas plenum 206 in the current collector 208 of the electrode 204 to distribute carbon dioxide evenly into the gas-diffusion electrode. A cathode trickle bed solution distributor or percolator 210 is present in the catholyte cell compartment 212. The catholyte solution may be introduced at the top entry 214 of the catholyte compartment 212 and the catholyte solution is distributed evenly down the

cell and is discharged via exit 216 at the bottom of the catholyte compartment 212. Alternatively, the flow may be reversed, so that the flow is in the upward vertical direction. The solution may be fed at specific rates, such as in the range of 0.001 to 10 liters per minute or more depending on the electrochemical cell dimensions, so that the cathode gas diffusion electrode 204 may not be flooded with the catholyte solution due to excessive pressure, and so as to maintain good ionic contact with the cathode gas diffusion electrode 204 for the transfer of electrons into the solution in the reduction of carbon dioxide. The flow and pressure of the catholyte flow are such that minimal amounts of catholyte solution pass through the gas diffusion electrode 204 into the carbon dioxide gas plenum 206 inside the cathode current collector 208, and that the carbon dioxide gas reduction within the gas diffusion electrode is sufficient, so as to obtain a reasonable cathode current density, e.g. in the range of 10 mA/cm² to 1000 mA/cm², or more preferably in a range of about 50 to 500 mA/cm². An energy source (not shown) is operably coupled with the electrodes 202 and 204 to reduce carbon dioxide at the cathode 204. Carbon dioxide is fed to the gas-diffusion electrode 204 via entry 218 into the gas plenum 206. Micro-channels 220 may be provided to pass carbon dioxide from the plenum 206 to the gas-diffusion electrode 204 that comprises the bismuth indium catalyst system. Carbon dioxide leaves the cell through exit 222.

The anode side of the cell is similarly constructed. In this embodiment hydrogen gas is fed via entry 224 to gas plenum 226 provided with microchannels 228 and leaves the cell via exit 230. Anolyte is introduced at entry 232, flows through a distributor 234 down to the exit 236. A ion exchange membrane 238 is arranged between the anolyte and catholyte distributors 234 and 210.

The cathode trickle bed 210 may include a thin construction, e.g. made from non-conductive corrosion resistant polymer plastics, such as PTFE, polypropylene and the like, in the form of screen-like or convoluted forms so to distribute the catholyte solution evenly as it passes down the gas-diffusion electrode 204. Alternatively, the trickle bed material may include conductive carbon and graphite, or potentially be manufactured from metal. The entry and exit ports of the catholyte compartment are designed such that the flow distribution of liquid is uniform along the cross section of the trickle bed at the top and bottom. In another embodiment the GDE cathode may be able to be operated in a partially flooded or possibly fully flooded condition, and the flow conditions and electrolyte may be adjusted to operate the cathode in this mode.

Example 1 Screening catalyst

Various binary metal catalysts were screened for their formate Faradaic yield in a test set up. The test set up comprised a 3 chambered glass cell wherein the electrodes were positioned. 0.75M KHCO₃ was used as electrolyte. Potentiostatic (xV vs SCE) electrolysis for the electrochemical reduction of CO₂ to formate was performed during 3.5-5 hrs. Tables 1 and 2 show the results. It has appeared that a 50 wt.% Bi sample showed the best results in this screening test, while a 10 wt.% Bi sample outperformed a 90 wt.% Bi sample.

Table 1. Screening test results

Catalyst	E1/2 (V) vs SCE)	Formate Faradaic Yield (%)
In/Bi 50/50	-1.90	79.88
In/Bi 90/10	-1.90	76.81
Anodized In	-1.75	75.73
In/Bi 10/90	-1.90	71.97
Bi/Pb 55.5/44.5	-1.90	70.87
Sn/Zn 60/40	-1.90	57.81
In/Sn 70/30	-1.90	53.64
In/Zn 90/10	-1.90	51.81
Sn/Pb 50/50	-1.90	48.42
In/Sn 30/70	-1.90	45.00
In/Sn 50/50	-1.90	41.46
In/Sn 30/70	-1.60	30.24
In/Sn 96/4	-1.75	28.79
Au/Ni (82/18)	-1.90	3.35
In	-1.9	63.47

Table 2. Screening Test Results

Alloy	E1/2 (V) vs SCE	Formate Faradaic Yield (%)
In/Sn 50:50 rod	-1.46	7.69
	-1.60	16.91
	-1.90	54.21
Sn/Zn 60/40	-1.90	57.81
Bi:Pb	-1.60	18.25
	-1.75	68.78
	-1.90	70.87
Sn:Pb	-1.75	41.97
	-1.90	48.42
In/Sn 70/30	-1.60	19.39
	-1.75	46.87
	-1.90	53.64
In/Sn 30/70	-1.60	30.24
	-1.75	51.88
	-1.90	45.00
In/Sn 96/4	-1.60	27.28
	-1.75	28.79
In/Sn 50/50	-1.90	41.46
In/Bi 90/10	-1.75	82.26
	-1.80	68.83
	-1.90	76.82
In/Bi 10/90	-1.75	57.53
	-1.80	65.57
	-1.90	71.97
In/Bi 50/50	-1.75	73.70
	-1.80	82.13
	-1.90	79.88
In/Zn 90/10	-1.70	52.30
	-1.80	59.64
	-1.90	51.81

Example 2. Preparation of binary metal catalyst system In/Bi on C

InCl₃, Bi(NO₃)₃·5H₂O and tri-sodium citrate dehydrate were weighted as shown in Table 3 and put inside a two-neck round bottom flask containing 100 mL of tri-ethylene glycol and Vulcan carbon (available from Cabot). The round bottom flask was placed in an oil bath and fitted with a condenser. The system was continuously purged with N₂ gas. The oil bath temperature was set to 100 °C. The content of the flask was stirred. After the system reached the desired value of the temperature, it was allowed to stabilize for about 10 minutes, before rapidly injecting a water solution of NaBH₄ using a syringe and needle. The NaBH₄ was freshly prepared and sonicated in order to speed up the solubilization process. As soon as the NaBH₄ was injected, a vigorous bubbling was observed in the mixture. The color of the suspension was black and no change in it was observed throughout the course of the reaction. After injecting NaBH₄, the system was maintained at 100 °C under stirring for 15 minutes. Then the heater was turned off and the suspension was allowed to cool slowly. At room temperature the suspension was transferred into 4 centrifuge tubes and centrifuged at 8000 rpm for 30 min. The supernatant was poured out and ethanol was added into the tubes, followed by a thorough washing. The washing was performed by sonicating the suspension for 10 min. Then centrifugation at 8000 rpm for 30 minutes was performed. This process was repeated 3 times. At the end ethanol (90 mL) was added into the tubes and the overall content was transferred in a 100 mL glass jar. The resulting mixture was sonicated for 40 minutes at room temperature and then magnetically stirred for 15 minutes. The thus obtained emulsion (catalyst ink) was ready for spray application. The In:Bi weight ratio in the thus prepared catalyst is 52.3:47.6.

Table 3

Material	Mass (mg)
InCl ₃	310
BiNO ₃ x H ₂ O	340
Na ₃ Citrate	441
Carbon	716
NaBH ₄	946

Example 3. Preparation of Gas Diffusion Electrode (GDE)

- 5 A gas-diffusion electrode with a geometric surface area of about 172 cm² was cut using a metallic blade. The GDE thus prepared was fixed on an aluminum panel using magnets and positioned at an angle of about 60° from the horizontal planed inside a ventilated fume hood. The catalyst ink was sprayed on the GDE using a manual air brusher at room temperature under atmospheric conditions.

CLAIMS

1. Catalyst system for catalyzed electrochemical reactions, comprising a catalyst, wherein the catalyst comprises 5-94 wt.% bismuth and 6-95 wt.% indium, based on the total amount of bismuth and indium.
5
2. Catalyst system according to claim 1, comprising an electrically conductive support and a catalyst, wherein the catalyst comprises 5-94 wt.% bismuth and 6-95 wt.% indium, based on the total amount of bismuth and indium.
10
3. Catalyst system according to claim 1 or 2, wherein the amount of bismuth is in the range of 10-90 wt.%, based on the total amount of bismuth and indium.
4. Catalyst system according to any one of claims 1 to 3, wherein the amount of bismuth is in the range of 40-60 wt.%, based on the total amount of bismuth and indium
15
5. Catalyst system according to claim 2, wherein the conductive support comprises a porous structure of carbon particles.
- 20 6. Gas-diffusion electrode comprising a gas-diffusion layer on a conductive substrate, the gas-diffusion layer comprising the catalyst system according to any one of the preceding claims.
7. Gas-diffusion electrode according to claim 6, wherein the catalyst system is bonded to the conductive substrate by a hydrophobic binder.
25
8. Electrochemical cell comprising at least one gas chamber and at least one liquid chamber, which chambers are separated by a gas-diffusion electrode according to any one of claims 6 to 7.
- 30 9. Method of preparing a gas-diffusion electrode according to any one of claims 6 to 7, comprising a catalyst system according to any one of claims 1 to 5, the method comprising the steps of
providing a conductive substrate;
applying bismuth, indium, conductive support and a binder to the conductive substrate.

10. Method according to claim 9, wherein the binder is a hydrophobic binder.
11. Method of electrocatalytically reducing carbon dioxide, comprising
5 introducing an anolyte to a first cell compartment of an electrochemical cell, the first cell compartment comprising an anode;
introducing a catholyte and carbon dioxide to a second cell compartment of the electrochemical cell, the second cell compartment comprising a cathode, and
applying an electrical potential between the anode and the cathode sufficient to reduce the
10 carbon dioxide to a reduced reaction product,
wherein the cathode comprises a catalyst system according to any one of claims 1 to 5.
12. Method according to claim 11, wherein the cathode is a gas-diffusion electrode according to any one of claims 6 to 7.
- 15 13. Method according to claim 11 or 12, wherein carbon dioxide is reduced to a reaction product selected from carboxylates and carboxylic acids.
14. Method according to any one of claims 11 to 13, wherein carbon dioxide is reduced to
20 formate or formic acid in an aqueous medium.
15. Method according to any one of claims 11 to 13, wherein carbon dioxide is reduced to oxalate or oxalic acid in a non-aqueous medium.

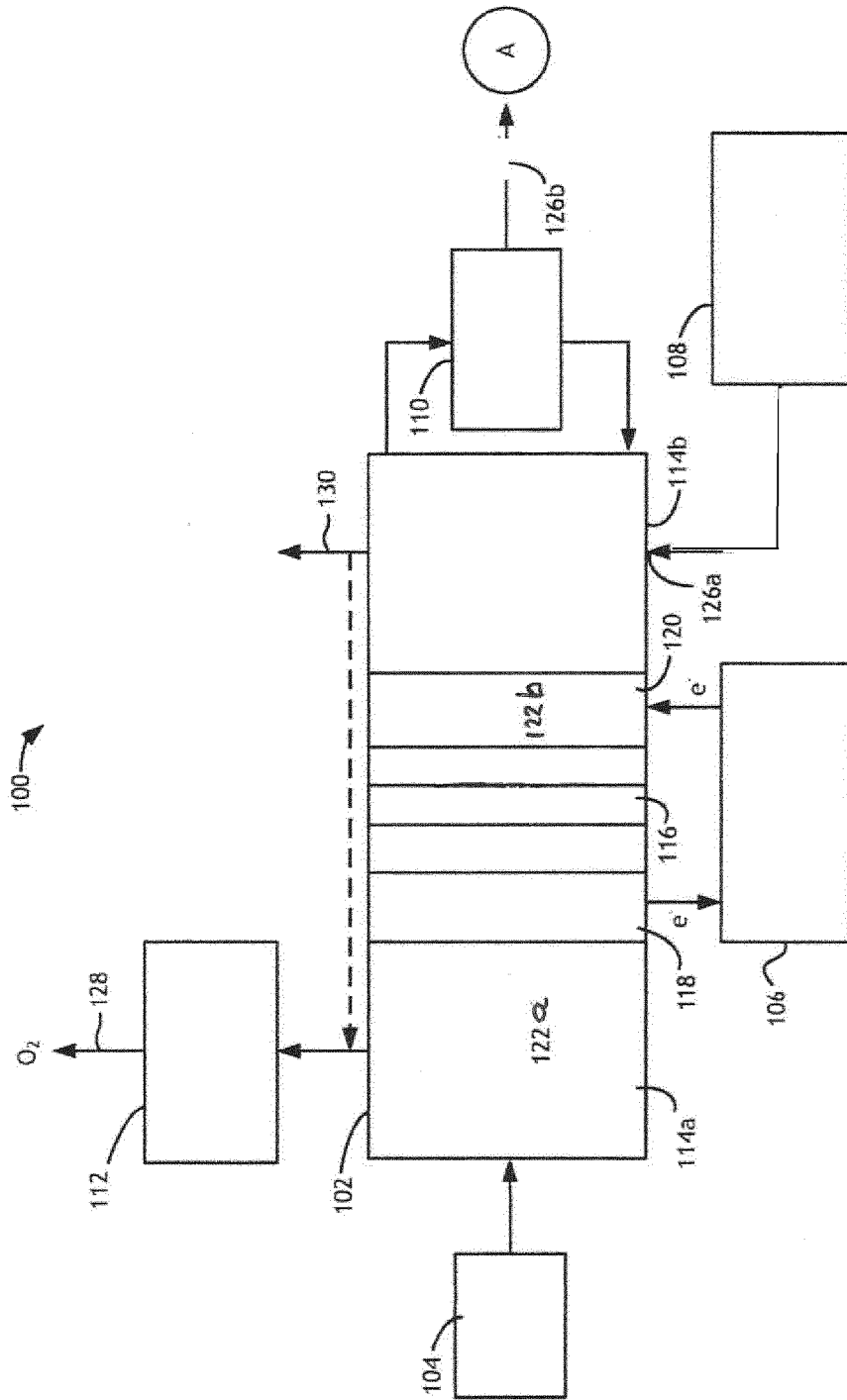


FIG. 1

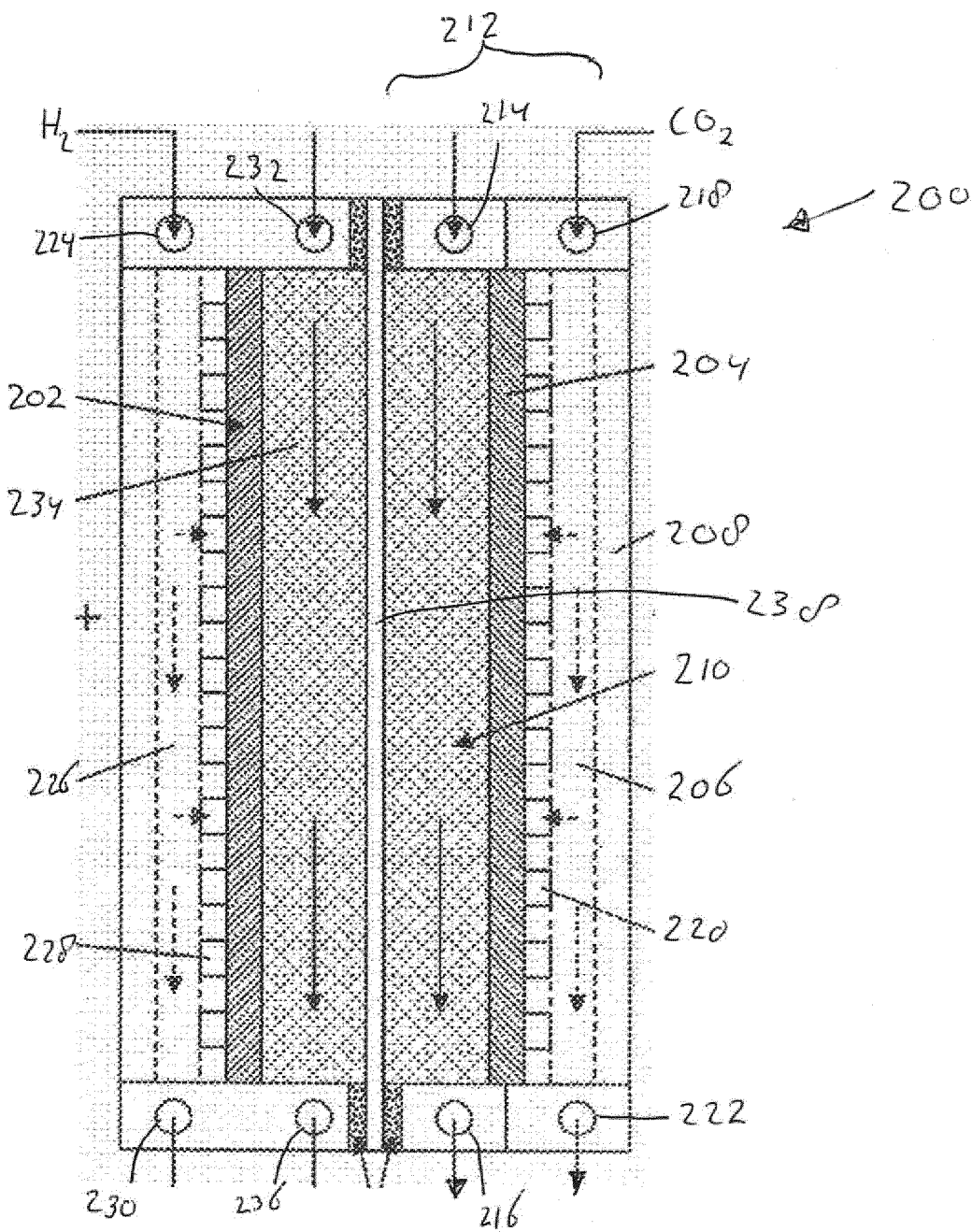


Fig. 2

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2019/051296

A. CLASSIFICATION OF SUBJECT MATTER
INV. C25B11/04 C25B11/03 C25B3/04 C25B1/00
ADD.
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED
Minimum documentation searched (classification system followed by classification symbols)
C25B
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	CANEGALLO ET AL: "Mechanism of indium electrodeposition on bismuth cathodes and time evolution of the deposits", JOURNAL OF ALLOYS AND COMPOUNDS, ELSEVIER SEQUOIA, LAUSANNE, CH, vol. 228, no. 1, 15 September 1995 (1995-09-15), pages 23-30, XP022269200, ISSN: 0925-8388, DOI: 10.1016/0925-8388(95)01668-6 the whole document ----- -/--	1-4

Further documents are listed in the continuation of Box C.

See patent family annex.

* Special categories of cited documents :

<p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier application or patent but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p>	<p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</p> <p>"&" document member of the same patent family</p>
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Date of the actual completion of the international search 16 April 2019	Date of mailing of the international search report 03/05/2019
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Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Hammerstein, G
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International application No
PCT/EP2019/051296

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	VIJAY BHOOSHAN KUMAR ET AL: "Formation of particles of bismuth-based binary alloys and intermetallic compounds by ultrasonic cavitation", NEW JOURNAL OF CHEMISTRY, vol. 39, no. 7, 1 January 2015 (2015-01-01), pages 5374-5381, XP055581269, GB ISSN: 1144-0546, DOI: 10.1039/C5NJ00781J page 5376, right-hand column - page 5378, left-hand column -----	1-4
X	US 2013/105304 A1 (KACZUR JERRY J [US] ET AL) 2 May 2013 (2013-05-02) paragraph [0058] - paragraph [0059]; claims 1-4,18,19,23,24 -----	1-14
X	FR 3 007 427 A1 (IFP ENERGIES NOUVELLES [FR]) 26 December 2014 (2014-12-26) claims 1,2,10-14 -----	1-14
X	WO 2017/118712 A1 (AVANTIUM HOLDING B V [NL]) 13 July 2017 (2017-07-13) paragraphs [0001], [0015], [0053] -----	1-3,5, 11,15

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2019/051296

Patent document cited in search report	Publication date	Patent family member(s)	Publication date	
US 2013105304	A1	02-05-2013	US 2013105304 A1	02-05-2013
			US 2013180863 A1	18-07-2013
			US 2014367273 A1	18-12-2014

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			WO 2014202856 A1	24-12-2014

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