

LEWIS/BRONSTED ACID/BASE AND NICKEL PHOSPHIDE BINARY CATALYST-SYSTEM (CO-CATALYSTS) FOR DIRECT ELECTROCHEMICAL CO₂ REDUCTION TO HYDROCARBONS

CROSS REFERENCE TO RELATED APPLICATIONS

[0001] This application claims priority to U.S. Nonprovisional Patent Application Serial No. 16/878,165, filed on May 19, 2020, which is a Continuation-in-Part (CIP) of U.S. Patent Application No. 15/765,896, filed on April 4, 2018, which is the U.S. National Stage entry of International Application No. PCT/US16/56026, filed on October 7, 2016, which claims the benefit of priority pursuant to 35 U.S.C. §119(e) of U.S. Provisional Patent Application No. 62/239,389, filed on October 9, 2015. The disclosures of all of the above are incorporated herein by reference in their entirety.

FIELD OF INVENTION

[0002] The present invention relates to a novel binary catalyst system combining an acid/base co-catalyst and a nickel phosphide electrocatalyst for the direct electrochemical reduction of carbon dioxide and/or carbon monoxide and/or alpha-hydrogen reactive aldehydes and ketones to hydrocarbons, carbohydrates and other useful products, collectively referred to below as oxygenated hydrocarbons (or oxyhydrocarbons).

BACKGROUND

[0003] Conventional fossil resources are being depleted through human activities which contributes carbon dioxide to the atmosphere in ever increasing amounts. This is the greatest challenge of the current generation - to stop creating an uninhabitable planet. A critical part of this challenge is to provide commercially viable examples of sustainable chemical manufacturing in which waste products are fully recycled and fossil energy is replaced with renewable energy. The present application centers on these objectives. The inherently intermittent nature of most renewable energy sources (*e.g.* solar and wind) necessitates the need for energy storage. A safe way to store massive amounts of energy is in chemical bonds. Chemical bonds are also essential for making bulk chemicals (feedstocks) that are used as for manufacturing more complex materials. The chemical industry relies on chemical transformations to produce these materials presently from petroleum, natural gas and coal (fossil resources). Fossil resources complex and variable mixtures of chemical compounds. The future renewable economy has yet to learn how to replicate these products. Manufacturing of complex chemicals made directly from CO₂ and

water is one such possible solution to both energy storage and a sustainable chemical industry that can close the carbon loop. With the recent availability of large natural gas resources in the US a large investment in industries, relying on cheap natural gas is growing. The relatively clean stream of waste CO₂ produced from the combustion of natural gas by these industries is available as a resource for recycling both for energy storage and chemical feedstock production. The present application provides a direct method for achieving this recycling.

[0004] Electrochemical reduction of CO₂ (Direct CO₂ Reduction Reaction, DCRR) uses water as the hydrogen source (H⁺/e⁻) to perform hydrogenation, producing alkanes on Cu and alcohols on noble metals and copper oxides. These technologies are unable to make a significant impact owing to these limitations and more: in water the competition with H₂ production (by-product) is significant, the high cost of noble metal electrocatalysts, and the poor product selectivity incapable of producing single alkane or alkene product when using abundant Cu as electrocatalyst.

[0005] Thus, selective, cheaper, and more energy efficient DCRR catalysts are eagerly sought to produce a variety of useful carbon-based products such as fuels, chemicals, and plastics from carbon dioxide.

SUMMARY OF THE INVENTION

[0006] A more efficient and improved two-component catalyst system and methods for implementation for DCRR are provided by the present invention.

[0007] In the present disclosure, all surface-bound intermediates are designated by an asterisk (*). Based on the above identified problem of competition between hydrogen evolution and DCRR, it might seem intuitive to propose to use the least active H₂ evolution electro-catalysts (*e.g.*, SnO₂) for DCRR. However, the reduction of CO₂ and CO to hydrogenated products requires an electrocatalyst that forms surface-bound hydrogen species (*H). Such hydrogen species may differ in partial charge and include hydrides (*H^{δ-}), atomic hydrogen (*H), and/or partially reduced protons (*H^{δ+}), where δ is between 0-1. These are collectively referred to as hydrides herein. These are the same precursors needed to produce H₂ in water. Therefore, understanding and controlling the types of surface hydrides and their relative reactivity with water vs CO₂/CO and DCRR reaction intermediates are important factors in achieving selective DCRR electrocatalysts. The previously disclosed electrocatalysts based on transition metal

phosphides for the electroreduction of CO₂ to hydrocarbons (US Patent Application Serial No. 15/765,896), shows how the selectivity between H₂ and CO₂/CO can be controlled using such binary compounds as the sole electrocatalyst.

[0008] It has now been discovered that adding a different class of catalysts (herein denoted co-catalysts) to the previously disclosed electrocatalysts (based on transition metal phosphides for the electroreduction of CO₂ to hydrocarbons; US Patent Application Serial No. 15/765,896) will provide enhanced product selectivity specifically to form carbon products containing one or more carbon atoms. The joint electrocatalyst plus co-catalyst when used together is called the catalyst system. These act on in addition to carbon dioxide and/or carbon monoxide, the following additives and intermediates: hydrocarbons, aldehydes or ketones type. The presently claimed co-catalysts encompass all possible additives to the binary compounds of nickel and phosphorous that modify the performance of the catalytic process without being consumed themselves. Additives can include any element or compound which is not a binary compound of nickel and phosphorus (i.e., a nickel phosphide), under 50% by weight of the composition.

[0009] This co-catalyst binds to a reaction intermediate either in solution or on the surface: 1) influencing the intermediate's binding orientation and binding strength, thereby 2) activating the intermediate for subsequent reaction with surface-bound hydrides or with other CO₂/CO or other C_n reaction intermediates, thereby 3) facilitating the formation of new reaction intermediates on the surface or, thereby 4) leading to desorption of the reaction intermediates, by this means increasing selectivity towards this product.

[0010] The combination of the co-catalyst with the transition metal phosphide catalyst changes the carbon product selectivity while having only a small effect on the H₂ vs DCRR selectivity. For example, the catalyst system alters the partitioning among the following chemical classes of carbon products: hydrocarbons, carboxylic acids, aldehydes, ketones, ethers, and alcohols (either aromatic or aliphatic). The co-catalyst may act on the reaction intermediate as above or on the electrocatalyst (the catalyst system) to achieve this overall outcome without requiring a separate stage or reactor. The co-catalyst may act either directly by binding to the electrocatalyst (so-called "push effect") or to any of the surface-bound reaction intermediates (so-called "pull effect"). Alternatively, the co-catalyst may act indirectly in solution to modify the reactant or product concentrations in such a way that influences the availability of each for activation by the

electrocatalyst (transition metal phosphide). In the latter case, these intermediates may or may not form on the electrocatalyst alone. The co-catalyst can be immobilized on the electrocatalyst in a subsequent synthesis step, incorporated directly during electrocatalyst synthesis, incorporated in the support, or dissolved in the electrolyte solution together with the reactants.

[0011] The improved product selectivity provided by such a catalyst system enables an electrochemical method for producing purer compounds that require less processing. For example, ethylene glycol can be produced from CO₂, water, and renewable electricity, which would allow green and sustainable polymers to be produced for various markets. Ethylene glycol and related diols are commercially used as monomers in polymer production. Similarly, a variety of other feedstocks and monomers can be made from CO₂, such as the C₃ compound, methylglyoxal (1,2-propanedione; MEG), and the C₅ compound mixture of 3-hydroxy-2-furancarboxaldehyde and 2-hydroxy-3-furancarboxaldehyde, which mixture has possible utility as an octane booster in fuels among others.

[0012] One aspect of the invention is directed to a combination of 1) a cathode for direct electrochemical reduction of carbon dioxide and/or carbon monoxide with/without carbohydrates containing aldehyde or ketone functional groups with active alpha-hydrogens (together called feedstock) to form oxyhydrocarbon products, the cathode comprising a conductive support substrate, a co-catalyst other than a nickel phosphide, and an electrocatalyst coating, the electrocatalyst coating comprising nanoparticles of Ni_xP_y, (also referred to herein as “Ni-P”) where x and y represent integers such that the compounds are selected from the group consisting of Ni₃P, Ni₅P₂, Ni₁₂P₅, Ni₂P, Ni₅P₄, NiP₂, and NiP₃; or the electrocatalyst coating comprising nanoparticles of Ni_xP_y is selected from the group consisting of Ni₃P, Ni₅P₂, Ni₁₂P₅, Ni₂P, Ni₅P₄, NiP₂, and NiP₃, and further alloyed with Fe₂P, where the alloy has a Ni-P:Fe₂P ratio between about 99:1 and 1:99 wt%; where the conductive support substrate comprises hydrophobic regions and hydrophilic regions to aid in adsorption of the feedstock from gas or aqueous phase to achieve separation from water molecules, where at least some of the electrocatalyst nanoparticles are located in the hydrophobic regions of the conductive support substrate and catalytically interact with the feedstock by electrical reduction to produce oxyhydrocarbon products; and 2) where the co-catalyst is positioned to act together with the electrocatalyst by incorporation into the hydrophilic or hydrophobic regions or the by dissolution in the electrolyte or by direct anchoring/incorporation into the catalyst surface.

[0013] The co-catalyst can comprise any acid; the acid can be selected from a Lewis acid or a Bronsted-Lowry acid. For example, the acid can be selected from d-block or p-block ions such as: Zn^{+2} , Fe^{+2} , Fe^{+3} , Ca^{+2} , Mg^{+2} , Al^{+3} , AlO^{+} , Si^{+4} , SiO^{+2} , H_3BO_3 , $\text{H}_x\text{BO}_y\text{R}_z$ (where x, y, and z are each independently 0 or an integer selected from 1 to 3, wherein $-(x + (-2y) + (z \cdot n)) = -5$ or -1 or 0 or 1 or 2 or 3 , where n is -1 , -2 , or -3 for various substitutions on R), so that boric acid esters include, for example, $\text{B}(\text{OH})_2(\text{OR})$ and $\text{B}(\text{OH})(\text{OR})_2$, where R = alkyl, aryl, arylalkyl, heteroaryl, heteroarylalkyl, where the heteroatoms of heteroaryl and heterarylalkyl are selected from nitrogen, oxygen and sulfur), and mixtures of two or more thereof.

[0014] The co-catalyst can comprise any base; the base can be selected from a Lewis base or a Bronsted-Lowry base. The base can be selected from the group consisting of the conjugate base of each of the Lewis acids above or each of the Bronsted-Lowry acids above. For example, borates, carboxylates, NH_3 , carbamide, urea, hydrazine, primary amines, secondary amines, tertiary amines, pyridines, and mixtures of two or more thereof.

[0015] The cathode can be in contact with an electrolyte solution comprising the co-catalyst or the co-catalyst can be an ionic liquid electrolyte that possesses HCO_3^- or CO_3^{2-} or H^+ transport functionality and is in contact with the cathode. Alternatively, the co-catalyst can comprise an ionomer or a conducting polymer or a modification or doping of the electrode support.

[0016] Further, the co-catalyst can comprise a salt of Cu, Ag, Au, Zn, mixtures of two or more thereof, or salts or oxides thereof. The salt or oxides may also become soluble at an appropriate pH. Alternatively, the co-catalyst can comprise a simple metal or alloy selected from the group consisting of Cu, Ag, Au, Zn, and intermetallic compounds thereof. The co-catalytic metal or intermetallic compounds can be in the form of molecular ions, nanoparticles or larger particles.

[0017] Without wishing to be bound by any particular theory, it is believed that the co-catalyst of the above combination binds to a reaction intermediate, such as but not limited to formate, formyl/formaldehyde, glycoaldehyde, methylglyoxal or furan derivatives, on the electrocatalyst surface, and 1) influences the intermediate's binding orientation, and/or 2) activates the intermediate for subsequent reaction with surface-bound hydrides or other CO_2/CO reaction intermediates, and/or 3) influences the intermediate's binding strength to become stronger or weaker, and/or 4) facilitates the formation of new reaction intermediates on the surface. Through

the above action, the co-catalyst increases the carbon product selectivity towards a particular hydrocarbon or oxyhydrocarbon product.

[0018] The cathode can be in contact with the electrolyte solution comprising the co-catalyst with the conductive support further comprising the same co-catalyst. The conductive support substrate can further incorporate a material to be reduced, whereby the electrocatalyst coating catalytically interacts with the material to be reduced, which is incorporated into the conductive support substrate. Preferably the material to be reduced comprises carbon dioxide, carbon monoxide, a mixture thereof, or any other oxyhydrocarbon molecules containing either aldehyde or ketone functional groups and reactive alpha-hydrogens. Alternatively, the conductive support substrate can be an ionomer or a conducting polymer.

[0019] Another aspect of the invention is directed to a method for generating oxyhydrocarbon products from water, carbon dioxide and/or carbon monoxide via an electrolysis reaction, performed by: (a) placing the cathode of the above combination in an electrolyte together with an anode; (b) placing the anode and cathode in conductive contact with an external source of electric current; (c) providing a carbon source of carbon dioxide and/or carbon monoxide to the cathode; and (d) applying the electric current to drive an electrolysis reaction at the cathode, whereby oxyhydrocarbon products are generated selectively from the carbon dioxide and/or carbon monoxide. In the method, the electrocatalyst and co-catalyst are selected to generate a product selected from 2,3-furandiol, 2-formylfuran-3-ol, ethylene glycol, 1,3-propanediol, 1,2-propanediol, stereo-isomers thereof, and combinations thereof.

[0020] Preferably the source of carbon dioxide, carbon monoxide or any other oxyhydrocarbon molecules containing either aldehyde or ketone functional groups and reactive alpha-hydrogens. is a flowing source. The flowing source can be a flow reactor.

[0021] A further aspect of the invention is directed to a method for reduction of carbon dioxide to oxyhydrocarbon products, performed by: (a) placing a cathode in an aqueous electrolyte together with an anode and a co-catalyst (as described above), where the cathode includes a conductive support substrate, co-catalyst (as described above), and an electrocatalyst coating including nanoparticles of Ni_xP_y where x and y represent integers such that the compounds are selected from Ni_3P , Ni_5P_2 , Ni_{12}P_5 , Ni_2P , Ni_5P_4 , NiP_2 , and NiP_3 , where the co-catalyst can be on the conductive support, in the electrolyte, or both; (b) placing the anode and cathode in

conductive contact with an external source of electric current; (c) providing a flowing source of carbon dioxide to the cathode; and (d) applying the electric current to drive an electrolysis reaction that generates electrons at the anode that are delivered to the cathode, whereby oxyhydrocarbon product is generated from the carbon dioxide, electrons and water, and the electrocatalyst and co-catalyst are selected so that the oxyhydrocarbon product that is generated is selected from carbohydrates, carboxylic acids, aldehydes, ketones and mixtures of two or more thereof.

[0022] Another aspect of the invention is directed to a method for reducing carbon dioxide to oxyhydrocarbon products, performed by: (a) placing a cathode in an electrolyte together with an anode and a co-catalyst, where the cathode includes a conductive support substrate and an electrocatalyst coating, the electrocatalyst coating includes nanoparticles of Ni_xP_y where x and y are integers such that the compounds are selected from Ni_3P , Ni_5P_2 , Ni_{12}P_5 , Ni_2P , Ni_5P_4 , NiP_2 , and NiP_3 , where the co-catalyst can be on the conductive support, in the electrolyte, or both; where the co-catalyst binds to an aldehyde, ketone, carboxylic acid, diol, or alcoholic functional group of a reaction intermediate, thereby activating it for further reaction with the electrocatalyst; (b) placing the anode and cathode in conductive contact with an external source of electric current; (c) providing a flowing source of carbon dioxide to the cathode; and (d) applying the electric current to drive an electrolysis reaction to generate electrons at the anode that are delivered to the cathode, where oxyhydrocarbon product is generated from the carbon dioxide, and the electrocatalyst and co-catalyst are selected so that the oxyhydrocarbon product that is generated is selected from carbohydrates, carboxylic acids, aldehydes, ketones and mixtures of two or more thereof. The co-catalyst can include a metal selected from Cu, Ag, Au, Zn and intermetallic compounds thereof. The co-catalytic metal or intermetallic compounds can be nanoparticles.

BRIEF DESCRIPTION OF THE FIGURES

[0023] FIG. 1 shows the faradaic efficiency (electron efficiency) for the Ni_3P , Ni_{12}P_5 , Ni_2P , Ni_5P_4 , NiP_2 electrocatalysts in the absence of co-catalysts in CO_2 purged potassium bicarbonate (electrolyte). The potential was corrected for the pH dependence of the standard H_2 electrode (i.e. reversible H_2 electrode, RHE).

[0024] FIG. 2 shows the faradaic efficiency (electron efficiency) for the Ni₂P electrocatalysts with two different co-catalysts in CO₂ purged potassium bicarbonate (electrolyte). Electrical current difference between the two catalyst systems and the electrocatalyst without co-catalyst shows the effect of the combined catalyst system. The potential was corrected for the pH dependence of the standard H₂ electrode (i.e. reversible H₂ electrode, RHE).

[0025] FIGS. 3A, 3B, 3C and 3D show proposed changes in mechanism caused by the addition of the aforementioned various co-catalysts.

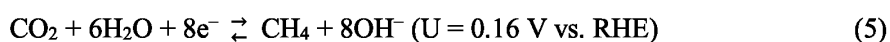
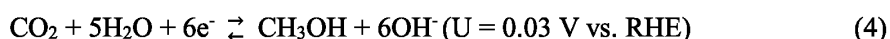
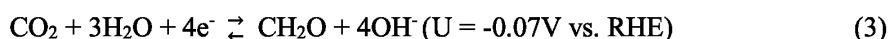
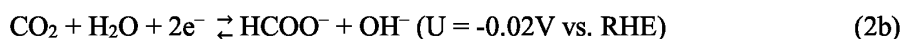
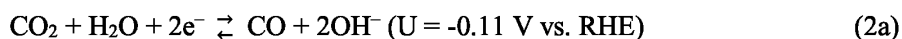
[0026] FIG. 4A shows ¹H NMR of products demonstrating change in selectivity upon addition of 25 mM boric acid. The electrocatalyst is a solid pellet of Ni₂P at 0V vs RHE at pH 7.5. FIG. 4B shows the corresponding HPLC (refractive index detector trace) demonstrating change in selectivity upon addition of 25 mM boric acid. The electrocatalyst is a solid pellet of Ni₂P at 0V vs RHE at pH 7.5. Comparison is shown to the electrolyte blank and pure ethylene glycol standard.

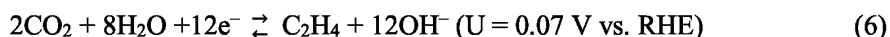
[0027] FIG. 5 shows a ¹H NMR spectrum demonstrating change in product selectivity upon deposition of Cu metal onto the electrocatalyst (solid pellet of Ni₂P at 0V vs RHE at pH 1).

DETAILED DESCRIPTION OF THE INVENTION

[0028] The presently disclosed technology is directed to the preparation of oxyhydrocarbons that are common chemical feedstocks which can readily be handled by existing transport and export facilities.

[0029] CO₂ reduction may be carried out by direct electrolysis at room temperature, but at least 4 electrons (e⁻) are needed to form valuable fuels (eqs. 3-7). From the listed potentials it becomes evident that CO₂ reduction occurs in thermodynamic competition with the simpler 2 e⁻ hydrogen evolution reaction (HER) (U = 0 V vs. RHE at 1 atm. H₂) as well as most of oxyhydrocarbon products (all formed at nearly the same potential).





[0030] Therefore, the challenge is to produce an electrocatalyst which preferentially provides hydrogen equivalents (H^* or hydrides) to reduce CO_2 to a specific carbon product rather than forming a mixture of products or H_2 . Common CO_2 reduction electrocatalysts based on Cu electrodes form a mixture of products where optimized results show selectivity towards hydrocarbons of 72.3% (CH_4 was the major product) achieved at -1.04V vs. the reversible hydrogen electrode (“RHE”), which is about 1.2 V more negative than the thermodynamic limit of +0.16V vs. RHE. However, such an immense over-potential greatly lower energy efficiency and eliminates the applicability of this approach to the production of synthetic fuels. Nonetheless, copper remains the best performing single component transition metal DCRR electrocatalyst to date.

[0031] A viable technology to produce fuels from CO_2 must quantitatively compare to industrial procedures. Currently, industrial methanol production from CO is estimated at 51% energy efficiency. The theoretical maximum energy efficiency for DCRR—assuming 0V over-potential and complete recovery of products—is 73%, indicating that DCRR is a technology theoretically capable of significantly outperforming the current industrial standard. Efficiency for the electrochemical reduction (also referred to herein as “electroreduction”) of CO_2 to CH_4 is currently 13% on Cu surfaces assuming oxygen evolution is the anode reaction.

[0032] The replacement of electrocatalysts (electrodes) is an expensive down-time investment for any commercial process, hence it is critical to maintain extended life-times of excellent electrocatalyst performance. There are currently very few examples of tests exceeding even 2 hours of DCRR on transition metal electrodes. The electrocatalysts of the invention target at least 16 hours of continuous activity. Industrial application requires significantly longer stabilities than hours. For example, industrial anodes for the chlor-alkali process (based on RuO_x and IrO_x) have lifetimes of about 7 years.

[0033] Ni_3P , Ni_{12}P_5 , Ni_2P , Ni_5P_4 , and NiP_2 have now been synthesized as highly compacted powders forming approximately flat surfaces for the inventive family of direct CO_2 reduction electrocatalysts. This allows direct observation of catalytic activity on the most stable crystal

phase termination, and is directly comparable to optimized Cu-foils of the prior art. Their activity as DCRR electrocatalysts in the absence of co-catalyst are shown in the data below (FIG. 1). The selectivity of these electrocatalysts for DCRR was found to be tunable based on composition and structure. The high natural abundance of both Ni and P elements ensures the scalable production of these electrocatalysts for industrial applications.

[0034] Further, it has been discovered that the nickel phosphide electrocatalysts above together with the co-catalyst changes the carbon product selectivity by interacting with selected reaction intermediates. These co-catalysts are selected from all Lewis or Bronsted-Lowry acids Al^{+3} , AlO^+ , Si^{4+} , SiO^{2+} , H_3BO_3 , $H_xBO_yR_z$ (where x, y, and z are each independently 0 or an integer selected from 1 to 3, wherein $-(x + (-2y) + (z \cdot n)) = -5$ or -1 or 0 or 1 or 2 or 3 , where n is -1 , -2 , or -3 for various substitutions on R), so that boric acid esters include, for example, $B(OH)_2(OR)$ and $B(OH)(OR)_2$, and boronic acid esters include, for example, $RB(OH)_2$ and $RB(OR')_2$ where R and R' = alkyl, aryl, arylalkyl, heteroaryl, heteroarylalkyl, where the heteroatoms of heteroaryl and heteroarylalkyl are selected from nitrogen, oxygen and sulfur), and mixtures of two or more thereof, or oligomer/polymer chains.

[0035] Further, anion exchange membranes allow for the transport of CO_3^{2-} and neutral $CO_2(aq)$ and H_2O to the electrocatalyst surface, while restricting H^+ accessibility due to charge repulsion. DCRR activity is known to be sensitive to pH in that higher pH improves selectivity but limits CO_2 availability. Hence, locally controlling proton availability by using an anion exchange membrane, rather than increasing the pH of bulk solution, strongly favors DCRR over HER. Therefore, one aspect of the present invention is directed to a composite electrode of an inventive binary electrocatalyst and co-catalyst and various polymers with anion conduction properties near the electrocatalyst surface.

[0036] Further, hydrophobic polymer materials incorporated into the electrode substrate allow for the transport of neutral $CO_2(g)$ to the electrocatalyst and co-catalyst. DCRR is critically dependent on mass-transport when producing liquid products or operating in liquid electrolytes. Hence, locally decreasing the transport resistance to gas molecules by the exclusion of water caused by hydrophobic domains strongly favors high DCRR reaction rates. Therefore, one aspect of the present invention is directed to a composite electrode of the above electrocatalyst and co-

catalyst in various polymers with varying hydrophobicity or of varying composition as to tune the electrodes ensemble hydrophobicity.

[0037] In another aspect the use of an anionic ionomer may be replaced with an ionic liquid that possesses HCO_3^- or CO_3^{2-} or H^+ transport functionality. In other aspects of the invention the bicarbonate, carbonate, or H^+ functional groups are bound to either a polymer or a soluble molecule, where the soluble molecule can be of variable size: small, medium, or large.

RESULTS FROM USING ONLY THE ELECTROCATALYST

[0038] Some data for nickel phosphides with different structures (Ni_3P , Ni_{12}P_5 , Ni_2P , Ni_5P_4 , and NiP_2) are shown in FIG. 1. FIG. 1 also illustrates how going from Ni_3P (high nickel content) to NiP_2 (high phosphorous content), an increased DCRR selectivity at low applied voltages can be observed. At higher applied voltages, H_2 evolution is favored over DCRR. Ni_2P and NiP_2 show the highest selectivity for DCRR but the former favors a C_4 product whereas the latter favors a C_3 product. This indicates that, for this family of binary compounds, where only the crystalline phase changes (the same binary elements), there is a clear difference in how the surfaces bind CO_2 and therefore in the carbon product.

[0039] None of the electrocatalysts Ni_3P , Ni_{12}P_5 , Ni_2P , Ni_5P_4 , or NiP_2 show the production or release of CO as a gaseous product, possibly due to its absence of formation or irreversible bonding on these surfaces.

ACHIEVING HIGH SELECTIVITY CONTROL OF CO_2 ELECTROREDUCTION BY USING A CO-CATALYST

[0040] As defined herein co-catalysts encompass all possible additives to the binary compounds of nickel and phosphorous that modify the performance of the catalytic process without being consumed themselves. Additives include any element or compound that is not a binary compound of nickel and phosphorus, under 50% by weight of the composition.

[0041] This co-catalyst binds to a reaction intermediate on the surface or in solution: 1) influencing the intermediate's binding orientation, and/or 2) activating the intermediate for subsequent reaction with surface-bound hydrides or other CO_2/CO reaction intermediates, and/or 3) influencing the intermediate's binding strength to become stronger or weaker, and/or 4) facilitating the formation of new reaction intermediates on the surface.

[0042] As such, the co-catalysts of the invention that are ionic are conjugate acid/base pairs and charged ions that are used together with the transition metal phosphide electrocatalysts as dopants incorporated during electrocatalyzed synthesis, co-deposited on the transition metal phosphide electrocatalyst, or added to the electrolyte bathing the electrodes. Other chemical terms used to denote these co-catalysts are Lewis acid/base pairs, Bronsted-Lowry acid/base pairs (also known as Bronsted acids/bases) and cations/anions, respectively. Particularly for those co-catalysts in the electrolyte solution, adjustment of pH can provide a mixture of acidic and conjugate base species. Thus, boric acid can be added to the electrolyte solution, and adjustment of pH provides a mixture of boric acid and borate species. Similarly, sodium borate can be added to the electrolyte solution, and adjustment of pH provides a mixture of boric acid and borate. In another aspect the co-catalyst is non-ionic and affects reaction on the transition metal phosphide electrocatalyst as a deposit on the surface (or as a dopant in the catalyst surface) binding reaction intermediates such that they can react with the transition metal phosphide surface, or DCRR intermediates bound to the transition metal phosphide electrocatalyst surface.

[0043] It has now been shown that the product selectivity for CO₂ reduction on nickel phosphides can be greatly altered by addition of co-catalysts (i.e., species or materials that are not consumed and can exist either as soluble molecules in the electrolyte, adsorbed molecules on the electrocatalyst surface, incorporated into the electrocatalyst support or ionomer or conductive polymer, or as dopant ions throughout the electrocatalyst bulk). These two classes of co-catalysts are illustrated in FIG. 2 and its associated Table 1, showing the range of products and their yields that are formed independently on Ni₂P using three different soluble co-catalysts at fixed pH (7.5) in electrolyte solution. A major shift in product selectivity occurs on addition of the Lewis acid-base pair boric acid/borate (H₃BO₃/B(OH)₄⁻) or the cationic Bronsted acid/base pair hexamethylenetetramine (C₆H₁₂N₄H⁺/C₆H₁₂N₄), predominantly to the C₂ product ethylene glycol (93% and 72%, resp.) relative to the baseline products (mainly C₃+C₄). The change in carbon selectivity vs the benchmark Ni₂P electrocatalyst is preserved across a range of applied potentials, as shown in FIG. 2. By contrast, Mg²⁺ (classified as a cation or Lewis acid) forms minimal C₂ product and a increased level of formic acid compared to the electrocatalyst only; however, this is still below 15% max likely due to the solubility limit of MgCO₃ co-catalyst. A method of improvement could be the use of other co-catalysts with higher solubility or the incorporation of the co-catalyst in the conductive catalyst support positioned primarily in the

hydrophilic regions. As the applied negative bias is increased, the yield of oxyhydrocarbon products decreases in competition with increasing H₂ yield on all electrocatalysts with or without co-catalysts. This offers direct insight into the mechanism (see FIGS. 3A-3D).

Table 1. Products and yields with or without soluble co-catalysts of the invention

Catalyst	Potential [V vs RHE]	Formate Faradaic Efficiency (%)	Furandiol Faradaic Efficiency (%)	Methylglyoxal (MEG) Faradaic Efficiency (%)	Ethylene Glycol Faradaic Efficiency (%)
Ni ₂ P	0.00	1.6	72	27	0.0
	-0.10	0.6	10	3.2	0.0
	-0.20	0.0	11	4.6	0.0
Ni ₂ P + Mg ²⁺	0.00	13	0.6	0.2	0.0
	-0.10	12	0.9	1.4	0.0
	-0.20	3.0	0.2	0.0	0.0
Ni ₂ P + H ₃ BO ₃	0.00	0.0	15	6.0	79
	-0.10	2.8	7.6	0.0	7.7
	-0.20	1.4	2.5	0.1	2.2
Ni ₂ P + Hexamethylenetetramine (HMA)	0.00	0.0	16.6	11	73
	-0.10	0.0	3.6	2.7	54
	-0.20	0.0	1.6	1.5	10

Reaction Mechanism (FIGS. 3A-3D)

[0052] Without wishing to be bound by any particular theory, we believe that the competition between surface-bound *C₂ intermediate and regeneration of the initial H* covered surface indicates that the reaction forming the C₂ precursor to the final MEG product can dissociate from the electrocatalyst. This information guides as to which type of co-catalyst is needed to enhance the specific oxyhydrocarbon over other DCRR products.

[0053] FIGS. 3A and 3B. Glycoaldehyde reduction: Lewis (or Bronsted) acid activation of the aldehyde group of surface-bound glycoaldehyde*. This activates the aldehyde for reduction into the corresponding alcohol. This mechanism is supported by the activation at low pH.

[0054] FIG. 3C. Glycoaldehyde-formaldehyde disproportionation reaction: The Lewis or Bronsted base-catalyzed hydrolysis of surface-bound formaldehyde* sets up its disproportionation reaction with surface-bound glycoaldehyde* (by intermolecular hydride transfer) to form formic acid and ethylene glycol, respectively. The base-catalyzed disproportionation reaction of two carbonyls to produce a carboxylic acid and alcohol is an example of a class of reactions called the Cannizzaro reaction. The formic acid* product is further electro-reduced to form-aldehyde* at the electrode surface and ultimately consumes all CO₂ to make ethylene glycol.

[0055] FIG. 3D. Oxalic acid pathway: A third possible pathway that fits the available data is CO₂ insertion into the C-H bond of surface-bound formic acid*. This step forms oxalate which can react further with surface hydride to generate ethylene glycol and water.

[0056] Boric acid or boronic acid or corresponding esters are known to reversibly bind to diols, such as the ethylene glycol. However, the present invention incorporates the discovery that by binding the intermediate the co-catalyst works to lower the desorption energy of the intermediate from the surface thereby making it the primary product.

[0057] Ni₂P was prepared by solid state synthesis and pressed into a pellet. The tests were performed under the specified applied potentials in CO₂-saturated electrolyte (a solution containing 0.5 M KHCO₃ and one of the three co-catalysts selected from 25 mM hexamethylene tetraamine, 25 mM boric acid, or 1.5 mM Mg²⁺). The tests were conducted at ambient pressure and temperature, at pH 7.5, for 16 h per experiment. Ambient temperature typically fell between 70 and 80°F. The composition of the headspace was monitored by gas chromatography, and the liquid products were analyzed by HPLC and NMR.

[0058] FIG. 4A shows the ¹H NMR of the electrolyte, where the major peak is ethylene glycol (as confirmed by the HPLC trace FIG. 4B), confirming the shift in selectivity caused by the addition of the co-catalyst.

[0059] The co-catalysts are effective when applied to all members of the nickel phosphide family of electrocatalysts disclosed above, including Ni₃P, Ni₅P₂, Ni₁₂P₅, Ni₂P, Ni₅P₄, NiP₂, and NiP₃ as well as the electrocatalyst nanoparticles of an alloy of one or more of the above Ni_xP_y compounds and Fe₂P, where the alloy has a Ni-P:Fe₂P ratio of between 100:0 to 0:100 wt%, and preferably between about 99:1 and 1:99 wt%. Particularly preferred nickel phosphides for co-catalysis include Ni₃P, Ni₁₂P₅, Ni₂P, Ni₅P₄, and NiP₂.

[0060] The co-catalyst concentration in the electrolyte can range from very low up to its limit of solubility, and is typically about 0.1 mM to about 10 M. Preferably the concentration range of the co-catalyst is about 0.5 mM to about 5 M. Alternatively, the concentration range of the co-catalyst can be about 1 mM to about 1 M, or about 1 mM to about 100 mM, or about 1.5 mM to about 50 mM, or about 1.5 mM to about 25 mM. The concentration of soluble co-catalyst can range from about 0.1 mM to about 100 mM. The co-catalyst can be present in the electrolyte in about 1.5 mM or about 25 mM.

[0061] As disclosed herein, a number of ranges of values are provided. It is understood that each intervening value, to the tenth of the unit of the lower limit, unless the context clearly dictates otherwise, between the upper and lower limits of that range is also specifically disclosed. Each smaller range between any stated value or intervening value in a stated range and any other stated or intervening value in that stated range is encompassed within the invention. The upper and lower limits of these smaller ranges may independently be included or excluded in the range, and each range where either, neither, or both limits are included in the smaller ranges is also encompassed within the invention, subject to any specifically excluded limit in the stated range. Where the stated range includes one or both of the limits, ranges excluding either or both of those included limits are also included in the invention. The term “about” generally includes up to plus or minus 10% of the indicated number. For example, “about 10%” may indicate a range of 9% to 11%, and “about 20” may mean from 18 to 22. Preferably “about” includes up to plus or minus 6% of the indicated value. Alternatively, “about” includes up to plus or minus 5% of the indicated value. Other meanings of “about” may be apparent from the context, such as rounding off, so, for example “about 1” may also mean from 0.5 to 1.4.

[0062] Alternatively, addition of a co-catalyst in the form of a second catalytic metal on the surface, or doping of another metal (or metal ion) into/on the surface, or within the bulk of the electrocatalyst is possible. The co-catalysts of the present invention encompass all possible additives to the binary compounds of nickel and phosphorous that modify the performance of the catalytic process without being consumed themselves.

[0063] This second co-catalytic metal or metal ion must be selected from a group that is known to facilitate the reduction of CO₂ or CO or other reaction intermediates from the DCRR. This includes, without limitation, metals such as Cu, Ag, Au, Zn, and intermetallic or oxide compounds thereof. The co-catalytic metal, intermetallic or oxide are preferably nanoparticles ranging in size from about 0.1 to about 1000 nm. The co-catalyst particle size can be about 0.5 nm to about 1000 nm, or about 0.5 nm to about 500 nm, or about 0.5 nm to about 50 nm, or about 0.5 nm to about 20 nm. The co-catalyst particle size can be about 0.1 nm to about 500 nm, or about 0.1 nm to about 50 nm, or about 0.1 nm to about 5 nm, or about 0.1 nm to about 2 nm.

[0064] Deposition of such a co-catalyst on nickel phosphide alters the selectivity of the reaction by changing the populations and binding affinities of reaction intermediates on the surface. The ¹H NMR spectrum in FIG. 5 shows the CO₂ reduction products formed upon electrodeposition of

copper metal on Ni₂P nanoparticles, or soluble Cu salts on Ni₂P nanoparticles at 0V vs RHE and acidic pH. The data demonstrate the formation of two C₅ compounds (3-hydroxy-2-furancarboxaldehyde and 2-hydroxy-3-furancarboxaldehyde).

FLOW SYSTEMS

[0065] Herein, binary transition metal phosphide electrocatalyst compounds in combination with the co-catalyst have been demonstrated to have surprising DCRR carbon product selectivity for hydrocarbons or oxyhydrocarbons. Upon switching to a flow reactor in which CO₂ is continuously passed over the working electrode, the carbon-containing products are formed at higher rates and in higher concentrations. This constitutes another aspect of the invention.

[0066] An aspect of the invention is directed to a combination of 1) a cathode for direct electrochemical reduction of carbon dioxide and/or carbon monoxide, together with any other added hydrocarbon molecules containing either aldehyde or ketone functional groups and reactive alpha-hydrogens to oxyhydrocarbon products, the cathode including a conductive support substrate and an electrocatalyst coating, the electro-catalyst coating including nanoparticles of Ni_xP_y, where x and y represent integers such that the compounds are selected from Ni₃P, Ni₅P₂, Ni₁₂P₅, Ni₂P, Ni₅P₄, NiP₂, and NiP₃; or the electro-catalyst coating including nanoparticles of Ni_xP_y is selected from Ni₃P, Ni₅P₂, Ni₁₂P₅, Ni₂P, Ni₅P₄, NiP₂, and NiP₃, and further alloyed with Fe₂P, where the alloy has a Ni-P:Fe₂P ratio between about 99:1 and 1:99 wt%; where the conductive support substrate includes hydrophobic regions and hydrophilic regions to aid in adsorption of carbon dioxide and/or carbon monoxide from gas or aqueous phase to achieve separation from water molecules, where at least some of the electrocatalyst nanoparticles are located in the hydrophobic regions of the conductive support substrate and catalytically interact with the carbon dioxide and/or carbon monoxide by electrical reduction to produce oxyhydrocarbon products; and 2) a co-catalyst for the reduction of carbon dioxide and/or carbon monoxide, other than a nickel phosphide, positioned to act together with the electro-catalyst. The Ni-P:Fe₂P ratio can be between about 99:1 to about 1:99 wt%. The NiP:Fe₂P ratio can be between about 95:5 to about 5:95 wt%. The Ni-P:Fe₂P ratio can be between about 90:10 to about 10:90 wt%. The Ni-P:Fe₂P ratio can be between about 25:75 to about 75:25 wt%.

[0067] The co-catalyst can comprise an acid; the acid can be selected from a Lewis acid or a Bronsted-Lowry acid. The acid can be selected from the group consisting of Zn⁺², Fe⁺², Fe³⁺,

Ca^{2+} , Mg^{2+} , Al^{+3} , AlO^{+} , Si^{+4} , SiO^{2+} , H_3BO_3 , $\text{H}_x\text{BO}_y\text{R}_z$ (where x, y, and z are each independently 0 or an integer selected from 1 to 3, wherein $-(x + (-2y) + (z \cdot n)) = -5$ or -1 or 0 or 1 or 2 or 3, where n is -1, -2, or -3 for various substitutions on R). so that boric acid esters include, for example, $\text{B}(\text{OH})_2(\text{OR})$ and $\text{B}(\text{OH})(\text{OR})_2$, where R = alkyl, aryl, arylalkyl, heteroaryl, heteroarylalkyl, where the heteroatoms of heteroaryl and heterarylalkyl are selected from nitrogen, oxygen and sulfur), and mixtures of two or more thereof. Suitable R = alkyl groups include, without limitation, methyl, ethyl, n-propyl, iso-propyl, n-butyl, sec-butyl, iso-butyl, tert-butyl, n-pentyl, iso-pentyl, sec-pentyl, tert-pentyl, neopentyl. Suitable R = aryl groups include, without limitation, phenyl, biphenyl and naphthyl, optionally substituted with one or more of halogen, alkoxy, alkylthio, alkyl, cyano, nitro, alkylsulfoxide, alkylsulfone, arylsulfone.

[0068] The co-catalyst can comprise a boron compound of the formula $\text{H}_x\text{BO}_y\text{R}_z$ having an oxidation state of -5, -1, 0, +1, +2, or +3, so that the integers x, y and z are defined by the equation $-(x + (-2y) + (z \cdot n)) = -5$ or -1 or 0 or 1 or 2 or 3; where n is -1, -2, or -3 for various substitutions on R, with R defined as above. In addition to the boric acid esters $\text{B}(\text{OH})_2(\text{OR})$ and $\text{B}(\text{OH})(\text{OR})_2$, where R = CH_3 , alkyl, C_6H_5 , aryl, etc., this also includes $(\text{C}_6\text{H}_5)_3\text{B}$ (triphenyl borane) and H_3NBH_3 when x or y is 0, and H_3BO_3 (boric acid) and BH_3 when z is 0.

[0069] The co-catalyst can comprise a base; the base can be selected from a Lewis base or a Bronsted-Lowry base. The base can be selected from NH_3 , carbamide, urea, hydrazine, primary amines, secondary amines, tertiary amines, pyridines, and mixtures of two or more thereof.

[0070] The cathode can be in contact with an electrolyte solution containing the co-catalyst or the co-catalyst can be an ionic liquid electrolyte that possesses HCO_3^- or CO_3^{2-} or H^+ transport functionality and is in contact with the cathode. Alternatively, the co-catalyst can be an ionomer or a conducting polymer.

[0071] Further, the co-catalyst can include a soluble salt of Cu, Ag, Au, Zn, mixtures of two or more thereof, or salts or oxides thereof. The salts or oxides become soluble at an appropriate pH. Alternatively, the co-catalyst can include a simple metal or alloy selected from Cu, Ag, Au, Zn, and intermetallic compounds thereof. The co-catalytic metal or intermetallic compounds can be in the form of nanoparticles. The co-catalytic metal, inter-metallic or oxide nanoparticles range in size from about 0.1 to about 1000 nm. The co-catalyst particle size can be about 0.5 nm to about 1000 nm, or about 0.5 nm to about 500 nm, or about 0.5 nm to about 50 nm, or about 0.5

nm to about 20 nm. The co-catalyst particle size can be about 0.1 nm to about 500 nm, or about 0.1 nm to about 50 nm, or about 0.1 nm to about 5 nm, or about 0.1 nm to about 2 nm.

[0072] Without wishing to be bound by any particular theory, it is believed that the co-catalyst of the above combination binds to a reaction intermediate on the electrocatalyst surface or in solution and 1) influences the intermediate's binding orientation, and/or 2) activates the intermediate for subsequent reaction with surface-bound hydrides or other CO₂/CO reaction intermediates, and/or 3) influences the intermediate's binding strength to become stronger or weaker, and/or 4) facilitates the formation of new reaction intermediates on the surface.

[0073] The cathode can be in contact with the electrolyte solution comprising the co-catalyst with the conductive support further comprising the same co-catalyst. The conductive support substrate can further incorporate a material to be reduced, whereby the electrocatalyst coating catalytically interacts with the material to be reduced which is incorporated into the conductive support substrate. Preferably the material to be reduced comprises carbon dioxide, carbon monoxide, or a mixture thereof. Alternatively, the conductive support substrate can be an ionomer or a conducting polymer.

[0074] Another aspect of the invention is directed to a method for generating oxyhydrocarbon products from water, carbon dioxide and/or carbon monoxide via an electrolysis reaction, performed by: (a) placing the combination of the electrocatalyst-coated cathode and a co-catalyst in an electrolyte together with an anode; (b) placing the anode and cathode in conductive contact with an external source of electric current; (c) providing a carbon source of carbon dioxide and/or carbon monoxide to the cathode; and (d) applying the electric current to drive an electrolysis reaction at the cathode, whereby oxyhydrocarbon products are generated selectively from the carbon dioxide and/or carbon monoxide. In the method, the electrocatalyst and co-catalyst are selected to generate a product selected from 2,3-furandiol, 2-formylfuran-3-ol, ethylene glycol, 1,3-propanediol, 1,2-propanediol, stereo-isomers thereof, and combinations thereof.

[0075] Preferably the source of carbon dioxide and/or carbon monoxide is a flowing source. The flowing source can be a flow reactor.

[0076] A further aspect of the invention is directed to a method for reduction of carbon dioxide to oxyhydrocarbon products performed by (a) placing a cathode in an aqueous electrolyte together with an anode and a co-catalyst of an acid or a base or a charged ionic species, where

the cathode includes a conductive support substrate, a co-catalyst including an acid or a base or a charged ionic species, and an electrocatalyst coating of nanoparticles of Ni_xP_y where x and y represent integers such that the compounds are selected from Ni_3P , Ni_5P_2 , Ni_{12}P_5 , Ni_2P , Ni_5P_4 , NiP_2 , and NiP_3 , where the co-catalyst can be on the conductive support, in the electrolyte, or both; (b) placing the anode and cathode in conductive contact with an external source of electric current; (c) providing a flowing source of carbon dioxide to the cathode; and (d) applying the electric current to drive an electrolysis reaction that generates electrons at the anode that are delivered to the cathode, whereby oxyhydrocarbon product is generated from the carbon dioxide, electrons and water, and the electrocatalyst and co-catalyst are selected so that the oxyhydrocarbon product that is generated is selected from carbohydrates, carboxylic acids, aldehydes, ketones and mixtures of two or more thereof.

[0077] Yet another aspect of the invention is directed to a method for reducing carbon dioxide to oxyhydrocarbon products, performed by: (a) placing a cathode in an electrolyte together with an anode and a co-catalyst, where the cathode includes a conductive support substrate and an electrocatalyst coating, the electrocatalyst coating includes nanoparticles of Ni_xP_y where x and y are integers such that the compounds are selected from Ni_3P , Ni_5P_2 , Ni_{12}P_5 , Ni_2P , Ni_5P_4 , NiP_2 , and NiP_3 , where the co-catalyst can be on the conductive support, in the electrolyte, or both; where the co-catalyst binds to an aldehyde, ketone or alcoholic functional group of a reaction intermediate, thereby activating it for further reaction with the electrocatalyst; (b) placing the anode and cathode in conductive contact with an external source of electric current; (c) providing a flowing source of carbon dioxide to the cathode; and (d) applying the electric current to drive an electrolysis reaction to generates electrons at the anode that are delivered to the cathode, where oxyhydrocarbon product is generated from the carbon dioxide, and the electro-catalyst and co-catalyst are selected so that the oxyhydrocarbon product that is generated is selected from carbohydrates, carboxylic acids, aldehydes, ketones and mixtures of two or more thereof. The co-catalyst can be a metal selected from Cu, Ag, Au, Zn, and inter-metallic compounds thereof. The co-catalytic metal or intermetallic compounds can be nanoparticles.

[0078] The electrocatalysts in the examples below were synthesized and characterized by physical characterization methods to ascertain their atomic structure and their HER activity is tested electrochemically and by gas chromatography. The inventive electrocatalysts can be supported on a titanium film electrode, for example, by being pressed into a pellet and bonded to

a titanium film electrode via silver paint and sealed in a non-conducting epoxy. Alternatively, the electrocatalysts can be supported on carbon or ceramic powder.

[0079] The as-synthesized electrocatalysts of this disclosure have grain sizes in the range from about 5 nm to about 5000 nm, preferably from about 5 nm to about 1000 nm, more preferably from about 5 nm to about 500 nm, and even more preferably from about 5 nm to about 20 nm. The grain sizes can range from about 10 to about 4000 nm, or from about 25 to about 3000 nm, or from about 50 to about 2500 nm. The particle size can be at least 100 nm. These grains are part of larger 0.3-1.8 μm spherical particle agglomerates. The durability of the electrocatalyst under electrolysis conditions in both 1M H_2SO_4 acid and 1M NaOH, was found to be very good. Evidence comes from both electrochemical stability and X-ray fluorescence confirming atomic composition of the surface, and from physical appearance at the macroscale.

SUPPORT SUBSTRATES

[0080] According to another aspect of the invention the electrocatalyst comprises a catalytic group and a conductive support substrate supporting a plurality of the catalytic groups. The support substrate can be capable of incorporating hydrogen cations, and at least some of the catalytic groups supported by the support substrate are able to catalytically interact with the hydrogen cations incorporated into the support substrate. The support substrate can be capable of incorporating water molecules, and at least some of the catalytic groups supported by the support substrate are able to catalytically interact with water molecules incorporated into the support substrate. The support substrate can be capable of incorporating carbon dioxide, and at least some of the catalytic groups supported by the support substrate are able to catalytically interact with CO_2 molecules incorporated into the support substrate. The support substrate can be capable of incorporating the co-catalyst and at least some of the catalytic groups comprising the support substrate are able to catalytically interact with the co-catalyst incorporated into the support substrate.

[0081] The support substrate has a plurality of porous regions that are microporous, mesoporous, and/or macroporous. The support substrate can be a microporous substrate having an average pore size of less than about 2 nm. The support substrate can be a mesoporous substrate having an average pore size of from about 2 to about 50. The support substrate can be a macro-porous substrate having an average particle size of greater than about 50 nm.

[0082] The support substrate is conductive to electrons so that when an electric potential difference is present across separate points on the support substrate, the mobile charges within the support substrate are forced to move, and an electric current is generated between those points. The support substrate can be rendered conductive by applying a thin layer of the support substrate on a conductive material. Suitable conductive materials include glassy carbon, carbon nanotubes and nanospheres, titanium foils/wires/meshes/foams/knitted wire meshes, aluminum foils/wires/meshes/foams/knitted wires meshes, fluoride doped tin oxide (FTO or $(\text{F})\text{SnO}_2$) coated glass and indium tin oxide (ITO) (or any of the transparent conductive oxides) coated glass, and multilayer structures having nano-structured semiconductor films coated onto the conductive substrates. Other means of causing the support substrate to be conductive are within the scope of the invention. For example, the support substrate can contact a sensitized semiconductor.

[0083] Preferably, the support substrate has hydrophobic regions and hydrophilic regions, and contributes co-catalyst function. With regard to the reduction of water or CO_2 , while not wishing to be limited by theory, it is thought that at least some of the catalytic groups can be supported in the hydrophobic regions of the support substrate and once supported are able to catalytically interact with water or CO_2 molecules in the hydrophilic regions. Effectively, the support substrate is thought to act as an interface between hydrogen cations, water molecules or CO_2 molecules and the catalytic groups that are otherwise insoluble in aqueous solution.

[0084] The hydrophobic regions can be formed by a hydrophobic polymeric backbone and the hydrophilic regions are regions of ionizable functional groups, preferably on the polymer backbone that can serve as sites for proton conductance. Preferably the ionizable functional groups are sulfonate groups ($-\text{SO}_3\text{H}$) that lose a proton to form negatively charged sulfonate groups. Alternatively, the ionizable functional groups can form positively charged functional groups that can serve as sites for hydroxide or carbonate ion conductance, if preferred.

[0085] The support substrate can be, for example, polysulfones, polysulfonates, and polyphosphonates. The support substrate can comprise a sulfonated fluoro-polymer (sold under the trade mark of NAFION®). The hydrophobic $\text{CF}_2\text{CF}(\text{CF}_3)\text{O}-$ polymer backbone of NAFION® forms a hydrophobic solid that is penetrated by aqueous channels lined with the hydrophilic ionizable sulfonic acid groups. Investigations into the sub-structure of NAFION® coatings on solid surfaces have revealed that the polymer layers contain these hydrophilic channels

throughout the otherwise hydrophobic regions of the membrane. These channels allow the diffusion of small molecules such as water.

[0086] Other support substrates that can be used include, for example, perfluorinated sulfonic acid polymer cation-exchange membranes such as F-14100, F-930 and F-950, the GEFC perfluorinated proton exchange membranes, polysulfone ionomers, nanostructured films formed by metal oxide nanoparticles suitably decorated with organic acids including perfluorinated sulfonic acids, nanostructured films formed by the hydrolysis of alkoxysilanes suitably decorated with organic acids including perfluorinated sulfonic acids.

[0087] Other supporting substrates can be, for example, polyfluorinated alkaline exchange membranes (AEM) that rely upon fixed cationic functional groups within the polymer to prevent the conduction of protons and allow conduction of mobile anions for conductivity. Examples of commercial AEMs include TOKUYAMA® AEM. Also within the scope are heterogeneous-homogeneous colloidal systems, two-phase (bi-phasic) mixtures (stabilized and unstabilized with surfactant), conducting polymers (e.g., poly(3,4-ethylenedioxythiophene) (PEDOT)), surface-modified silica and titania.

[0088] Other support substrates that can be used to contribute co-catalyst functionality include borate/boronic acid- or amine/ammonium-functionalized polymers with an alkyl or aryl or polyfluorinated polymer backbone.

[0089] Other support substrates that can be used to contribute hydrophobic functional domains include alkyl or aryl or polyfluorinated polymer backbone polymers.

[0090] Any means of contacting the electrocatalyst with water, CO₂ or carbonate mineral is within the scope of the invention. The electrocatalyst can be immersed in a solution containing water molecules. The solution can be an aqueous solution containing electrolyte. The aqueous solution can be a solution from which water is preferentially removed (i.e. solid liquid separation). For example when the aqueous solution is salt water or sea water the water could be removed leaving the salt behind (i.e., desalination). In one example, about 0.5M electrolyte is sufficient.

[0091] The following examples are provided to further illustrate the methods and compositions of the present invention. These examples are illustrative only and are not intended to limit the scope of the invention in any way.

EXAMPLES

Example 1. Electrode Fabrication

[0092] 1 g of electrocatalyst powder was mixed with 250 μ L of 5% NAFION® suspension previously neutralized with NaOH. The electrocatalyst powder was continuously mixed with the NAFION® suspension by mortar and pestle until dried. To fully dry these they were further dried under vacuum for several hours.

[0093] The resulting electrocatalyst/polymer composite was pressed under 5-29 tons of pressure in a 30 mm diameter die. The resulting pellet was mounted on a conductive aluminum support using Kapton tape. The geometric surface area was determined applying a silicone polymer gasket with a predefined opening on the exposed surface.

Example 2. Electrochemical Measurement

[0094] All solutions were prepared using MILLIPORE® water. A three electrode setup with a NAFION® membrane or anion-exchange membrane separator of working and counter compartment was used for all the electro-chemical measurements. A Pt or Ir/C electrode was used as a counter electrode during measurements. A Hg/HgSO₄ (Sat'd KCl) reference electrode was used and calibrated against a commercial Saturated Calomel electrode (Hack) at open circuit potential prior to each measurement. Chronoamperometric data was manually compensated for IR-drop, by measuring the IR-drop before and after experiments and manually applying a correct bias.

[0095] Electrolytes were prepared from MILLIPORE® water using high purity grade reagents. Furthermore, as a further precaution to remove potential metal impurities solutions were filtered through K⁺-CHELEX® 100 matrix. Electrolytes were stored in Piranha-cleaned flasks until used. Just prior to measurements the electrolytes were saturated with CO₂ (Airgas CD1200) cleaned using a Supelco hydrocarbon trap (Sigma) to < 6ppm CH₄ (the major hydrocarbon impurity).

[0096] Product analyses were conducted on a HP5890 Series II GC with a 5A MSieve (Restek) 0.53 mm capillary column using Ar carrier gas (cleaned for hydrocarbons and moisture on a Supelco Hydrocarbon, moisture trap). Calibrations were performed using certified mixed gasses *i.e.* 1.04% CH₄/Ar from Airgas, 1.02% H₂/Ar, and pure C₂H₄ likewise from Airgas.

Catalyst Fabrication: Solid State Synthesis

[0097] 1.5 mol% stoichiometric excess of red phosphorous (Alfa-Aesar 99%) and stoichiometric amounts of nickel (Sigma-Aldrich <150 μ m) were thoroughly mixed in a mortar. Transferred to a quartz tube evacuated and sealed after cleaning with Ar by back filling 2-3 times. The evacuated tubes were placed in a furnace and ramped to 700°C and kept there for 24 hours. Ramp rates were modest to avoid excessive heating upon reaction. Temperatures were ramped from 80°C to 250°C over 580 min with a 360 min dwell time, then to 350°C over 300 min with a 200 min dwell time, then to 450°C over 300 min with a 200 min dwell time, and finally to 700°C over 350 min with a 24 hour dwell time. Samples were then cooled to room temperature under ambient conditions. Sample purity was checked by powder X-ray diffraction (PXRD) and additional Ni or P was added if necessary, mixed and sealed as above, and reheated using an accelerated sequence (580 min from 80°C to 750°C with a 24 hour dwell time).

[0098] Nanoparticulate nickel phosphides were prepared starting from 20 nm Ni nanoparticles (99.9% USNano Ltd.) which were lightly mixed with 101.5 mol% red P in a glovebox under Ar. The sample was sealed in an evacuated quartz tube and heated slowly to 450°C with a dwell time of 48 hours. The ramp was 80°C to 175°C in 580 min, followed by dwell for 360 min, ramp to 250°C in 580 min, followed by dwell time of 360 min, then ramped to 350°C in 360 min, followed by dwell time 300 min, and then finally to 450°C in 360 min, followed by 48 hours dwell time. The sample cooled to room temperature under ambient conditions, and phase purity was checked by PXRD. Additional P could then be added in air analogous to the solid-state reaction in 1). Ramp rates for additional P addition were 580 min from 80°C to 450°C and dwell time of 48 hours. Occasionally, small impurities of Ni(PO₃)₂ were formed during air exposure and this phase was removed by acid washing in diluted HCl (approximately 1:10 concentrated HCl to water by volume).

[0099] Crystal phase characterization was done on a Bruker AXS D8 Advance x-ray diffractometer with Cu K α 1 radiation (1.54056 Å), a scan time of 1 hr or 12 hr, and a 2 θ range of 15–70° or 10–120°. Samples were analyzed prior to electrochemical testing by dispersing the powder between two glass microscope slides.

Example 3. Ni₂P Electrocatalyst Synthesis

[0100] The electrocatalysts were synthesized using the hydrothermal method. In a typical experiment 3.685g NiCl₂·6H₂O (Sigma-Aldrich), 1.09g hexamethylenetetramine (Sigma-Aldrich) was dissolved in 340ml Millipore water. The solution was mixed thoroughly with 75 g red phosphorous (Alfa-Aesar, 98.9%, 325 mesh) by stirring. The mixture was loaded into a PTFE lined autoclave and heated to 180 °C for 10 hr. After recovery the sample was washed in water, 3% hydrochloric acid, water and acetone before drying under vacuum at 30-60°C overnight. The final product was checked by PXRD.

Example 4. Characterization of Ni₂P Nanoparticles

[0101] PXRD analysis was performed on a Bruker AXS D8 Advance using a Cu K α X-ray tube (1.546Å), a scan time of 1 hour or 12 hours and a 2 θ range of 15–70° or 10-120°. Samples were analyzed prior to electrochemical testing by dispersing the powder on a glass microscope slide and flattening the powder surface using another glass slide.

Catalyst Fabrication: Hydrothermal or Solvothermal Methods

[0102] Nanoparticles were also successfully prepared by hydrothermal or solvothermal methods as described in literature:

[0103] Henkes, A. E., and Schaak, R. E. (2007). Trioctylphosphine: A general phosphorus source for the low-temperature conversion of metals into metal phosphides. *Chemistry of Materials*, 19(17), 4234–4242. doi:10.1021/cm071021w

[0104] Laursen, A. B., Patraju, K. R., Whitaker, M. J., Retuerto, M., Sarkar, T., Yao, N., ... Dismukes, G. C. (2015). Nanocrystalline Ni₅P₄: a hydrogen evolution electrocatalyst of exceptional efficiency in both alkaline and acidic media. *Energy Environ. Sci.*, 8(3), 1027–1034. doi:10.1039/C4EE02940B

[0105] Muthuswamy, E., Savithra, G. H. L., and Brock, S. L. (2011). Synthetic Levers Enabling Independent Control of Phase, Size, and Morphology in Nickel Phosphide Nanoparticles. *ACS Nano*, 5(3), 2402–2411. doi:10.1021/nn1033357

[0106] Prins, R., and Bussell, M. E. (2012). Metal Phosphides: Preparation, Characterization and Catalytic Reactivity. *Catalysis Letters*, 142(12), 1413–1436. doi:10.1007/s10562-012-0929-7

[0107] The current efficiency measurements were conducted after purging the electrochemical cell and electrolyte for 20-60 min with 4.0 grade CO₂ further purified with a hydrocarbon trap

(Supelpure HC). The flow of CO₂ during electrolysis was 5 sccm, measured with a gas mass-flow controllers. A constant potential was applied for 16-20 hours. The GC auto-sampler injected a 500 µL sample from the effluent gas every 30 minutes. The current efficiency (CE) was then calculated using the equation:

$$CE = \frac{nFe\dot{V}}{I}$$

where n is the number of moles of a given product, F is Faraday's constant, e is the number of electrons necessary to generate one molecule of product (2 for H₂, 8 for CH₄, 12 for C₂H₄), $\dot{V}$ is the gas flow rate in ml/s divided by the sample volume (0.50 mL) and I is the current.

Example 8. Gas Chromatography

[0108] An HP 5890 Series II gas chromatograph equipped with a TCD and a FID detectors arranged in series and a 30 m megabore molecular sieve 5A column (Restek) was employed for quantifying gaseous products. The GC was calibrated with gas standards and the number of moles of the products in the headspace of the cell determined by the ideal gas law.

Example 9. Reaction in the Presence of Co-catalyst

[0109] Ni₂P was prepared by solid state synthesis and pressed into a pellet as described in Calvinho, K. U. D., Laursen, A. B., Yap, K. M. K., Goetjen, T. A., Hwang, S., Mejia-Sosa, B., Lubarski, A., Teeluck, K. M., Murali, N., Hall, E. S., Garfunkel, E., Greenblatt, M., and Dismukes, G. C. "Selective CO₂ Reduction to C₃ and C₄ Oxyhydrocarbons on Nickel Phosphides at Overpotentials as Low as 10 mV" *Energy & Environmental Science*, 2018, 11, 2550-2559.

[0110] The Ni₂P pellet was tested under constant applied potential in CO₂-saturated electrolyte (a solution containing 0.5 M KHCO₃ and co-catalyst (25 mM hexamethylene tetraamine, 25 mM boric acid, or 1.5 mM Mg²⁺). The tests were conducted at ambient pressure and temperature, at pH 7.5, for 16 h per experiment. The composition of the headspace was monitored by gas chromatography, and the liquid product was analyzed by HPLC and NMR according to methods described in Calvinho et al, *Energy & Environmental Science*, 2018, 11, 2550-2559. FIG. 4A shows NMR of the electrolyte, where the major peak is ethylene glycol, confirming the shift in selectivity caused by the addition of co-catalyst. This result is corroborated by HPLC using a refractive index detector showing boric acid and ethylene glycol as the major peaks (FIG. 4B).

[0111] Deposition of a metal or metal cation co-catalyst on nickel phosphide also alters the selectivity of the reaction by changing the populations and binding affinities of reaction intermediates on the surface. The ^1H NMR spectrum in FIG. 5 shows the CO_2 reduction products formed upon electrodeposition of copper metal or soluble Cu salts on Ni_2P nanoparticles at 0V vs RHE and acidic pH. The data demonstrate the formation of two C_5 compounds (3-hydroxy-2-furancarboxaldehyde and 2-hydroxy-3-furancarboxaldehyde).

NASA's Carbon Dioxide Conversion Challenge

[0112] The CO_2 Conversion Challenge is a \$1 million competition funded by NASA to convert carbon dioxide into sugars such as glucose, as a step toward creating mission-critical resources, particularly for future Mars missions. Such technologies will allow the manufacture of products using local, indigenous resources on Mars, as well as being applicable to Earth, by using waste and atmospheric carbon dioxide as a resource.

[0113] On Earth, plants convert CO_2 into carbohydrates and oxygen, supplying food and breathable air. There are no plants on Mars, but there is abundant CO_2 . When astronauts begin exploring Mars, they will need to use local resources, freeing up launch cargo space for other mission-critical supplies. Thus, NASA is seeking novel ways to convert CO_2 into useful compounds, such as sugars, which will be key to providing supplies for human explorers on long-term missions on Mars.

[0114] Phase 2 of NASA's CO_2 Conversion Challenge has just been initiated, with the goal of building a system that demonstrates the conversion of CO_2 in combination with hydrogen, and without the use of plants, to produce simple sugars such as glucose. The selective, efficient co-catalyst technology described herein provides one solution that fulfills the requirements of the CO_2 Conversion Challenge.

Industrial Application

[0115] Electrocatalysts for the direct CO_2 reduction to hydrocarbons may be realized through flow electrolyzers of similar types to the chlor-alkali producing cells currently used on an industrial scale. CO_2 sources could be point sources such as power stations, cement plants, or similar large CO_2 emitting industries or from extraction directly from the atmosphere. The Ni_xP_y phase would be applied as nanoparticles or microparticles (5-5000 nm) on a conductive substrate

electrode. The particles may be affixed using one or more polymers with or without chemical binding groups for coordination of protons or CO₂. This polymer may be of the same type as the supporting membrane conducting ions from the anode to cathode. Electrolysis may be performed around neutral pH using carbonate, phosphate, KCl, or sulfate electrolytes.

[0116] The inventive Ni_xP_y together with a co-catalyst system have the potential to be a direct alternative to fossil raw materials (crude oil, coal, and natural gas) as a source for chemical feedstocks and energy storage. Carbon neutral synthetic fuels resulting from this technology will not need the expensive and environmentally impactful fossil fuel supply chain (mining/drilling, pipelines/tankers, refineries). Fuel could be made on demand and at strategic locations near hubs. Carbon chemical feedstocks could be tailor-made and would not be the result of the inefficient processing of raw fossil materials.

[0117] Without further elaboration, it is believed that one skilled in the art, using the preceding description, can utilize the present invention to its fullest extent. Furthermore, while the present invention has been described with respect to aforementioned specific embodiments and examples, it should be appreciated that other embodiments utilizing the concept of the present invention are possible, and within the skill of one in the art, without departing from the scope of the invention. The preceding preferred specific embodiments are, therefore, to be construed as merely illustrative, and not limitative of the disclosure in any way whatsoever.