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(54) **SYSTEM AND PROCESS FOR ELECTROCHEMICAL CONVERSION OF CARBON DIOXIDE TO CARBON MONOXIDE**

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(57) **ABSTRACT**

The invention provides a system and a process that allow for the selective electrochemical conversion of carbon dioxide to carbon monoxide with high energy efficiency, using a cathode comprised of tin in combination with an anode comprised of platinum. The electrolysis system may be comprised of a single or two compartment cell and may employ an organic electrolyte or an ionic liquid electrolyte. The invention permits the storage of solar, wind or conventional electric energy by converting carbon dioxide to carbon monoxide and liquid fuels.

CO₂ IN   CO₂ OUT   CO₂ IN   CO₂ OUT

Sn-CMEC

PT GAUZE

REFERENCE ELECTRODE

STIR BAR

NAFION MEMBRANE

CO$_2$ OUT

CO$_2$ IN

FIG. 1a

CO$_2$ IN   CO$_2$ OUT   CO$_2$ IN   CO$_2$ OUT
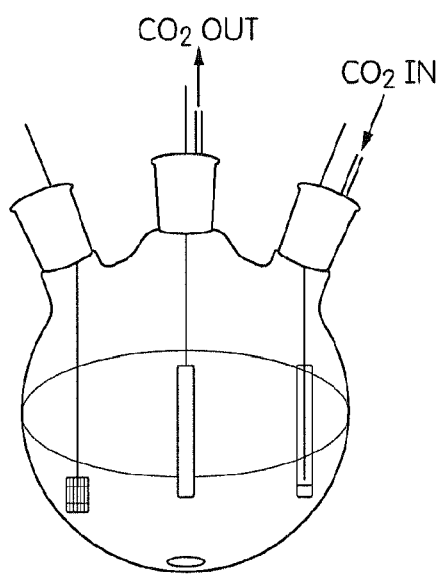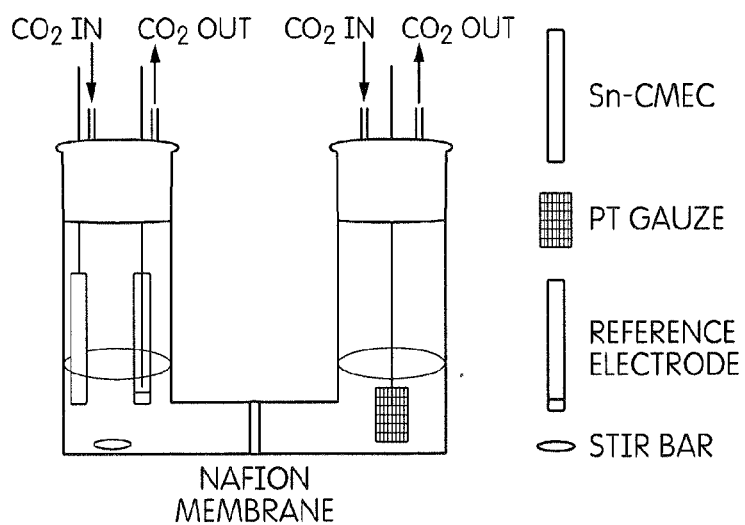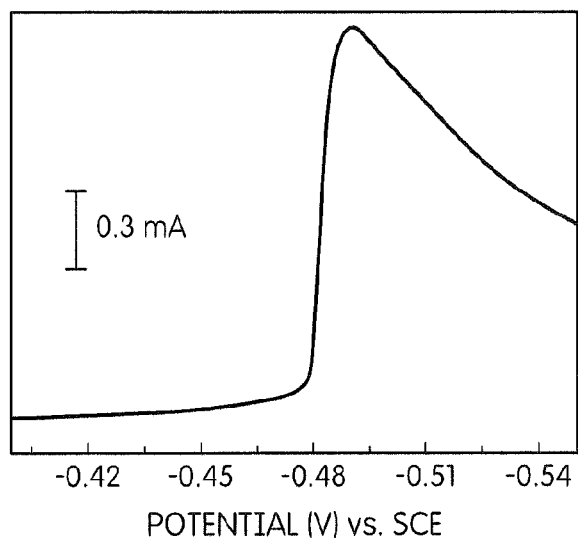
Sn-CMEC

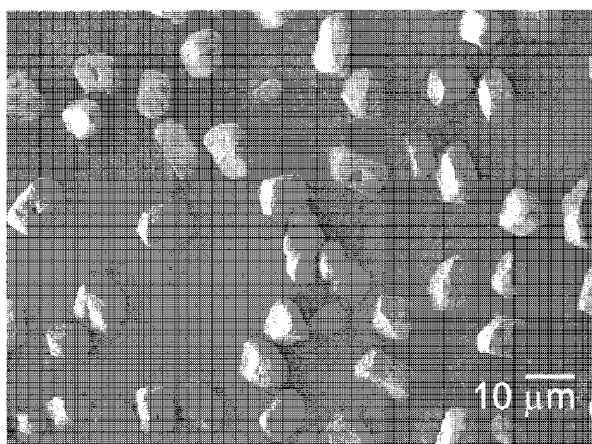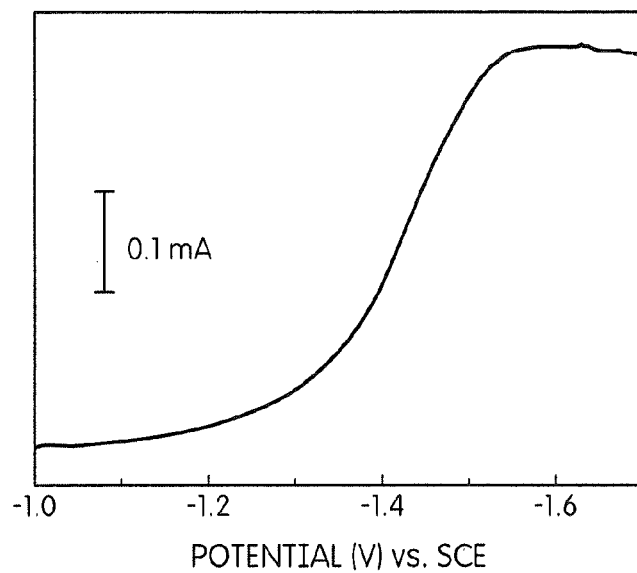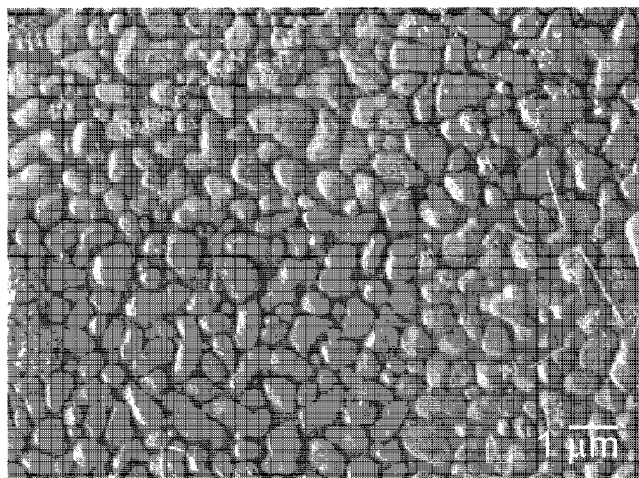PT GAUZE

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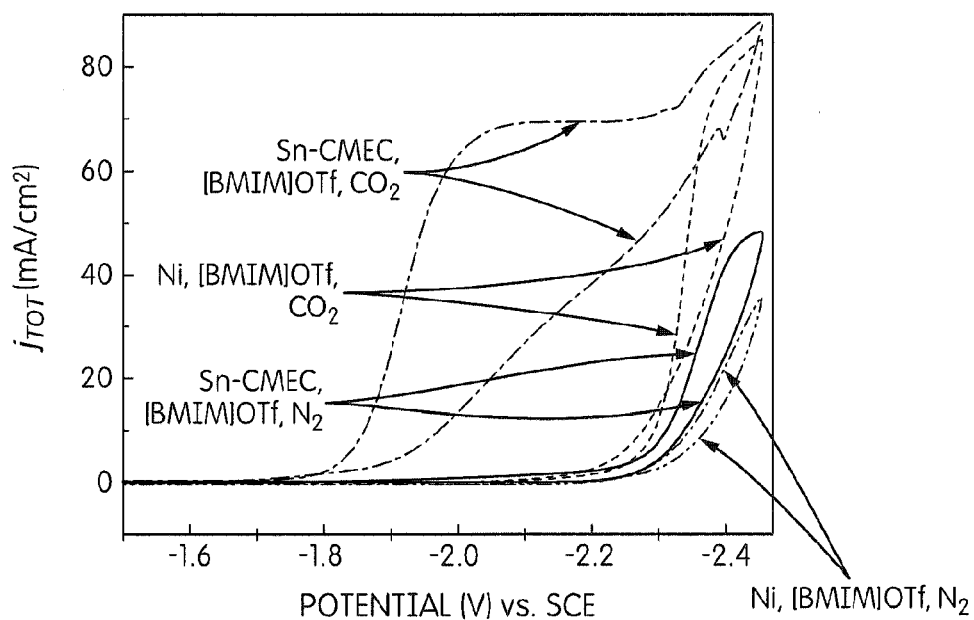STIR BAR

NAFION
MEMBRANE
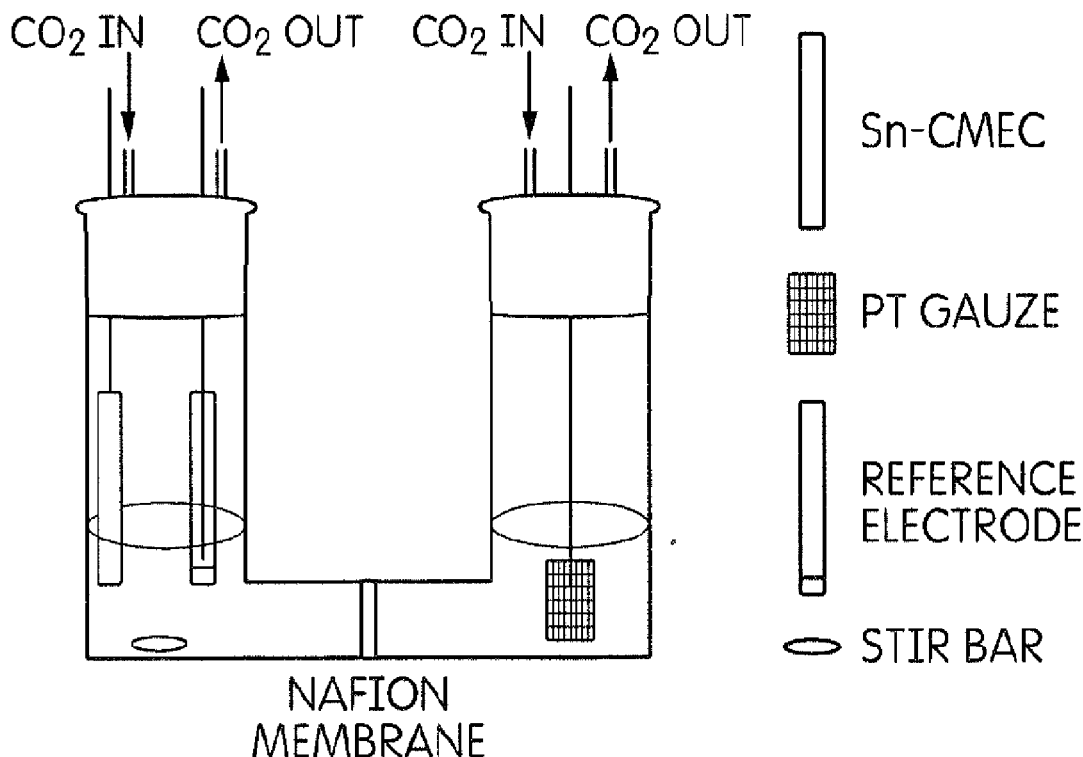
FIG. 1b

FIG. 2a

FIG. 2b

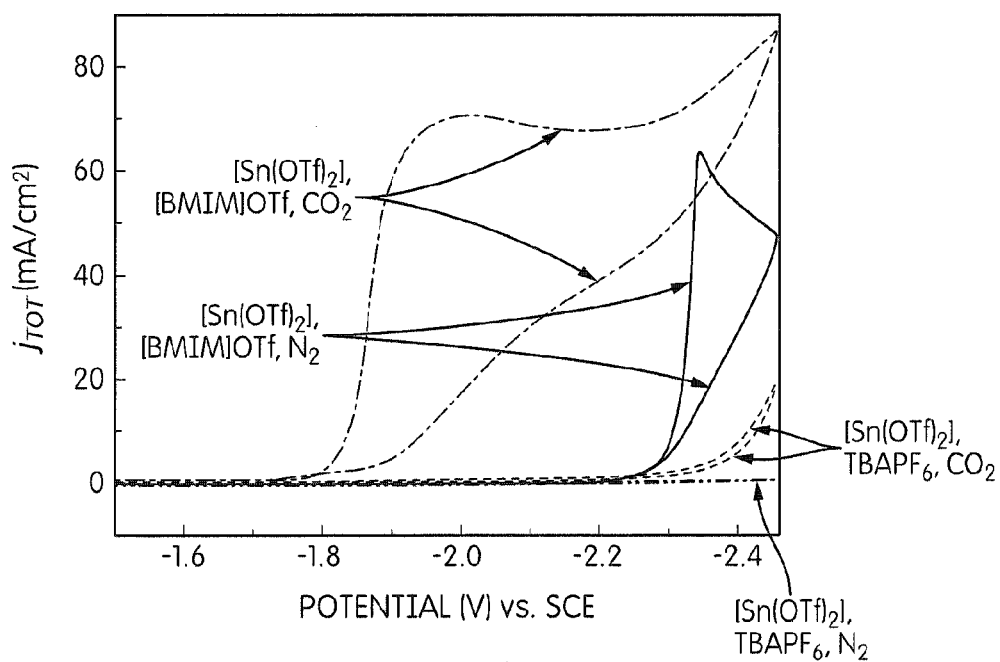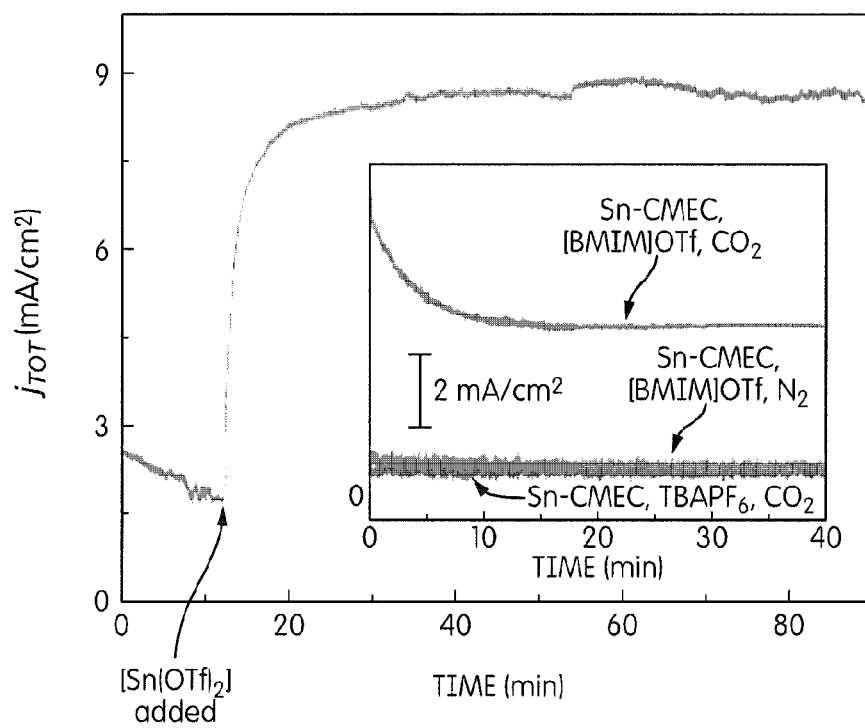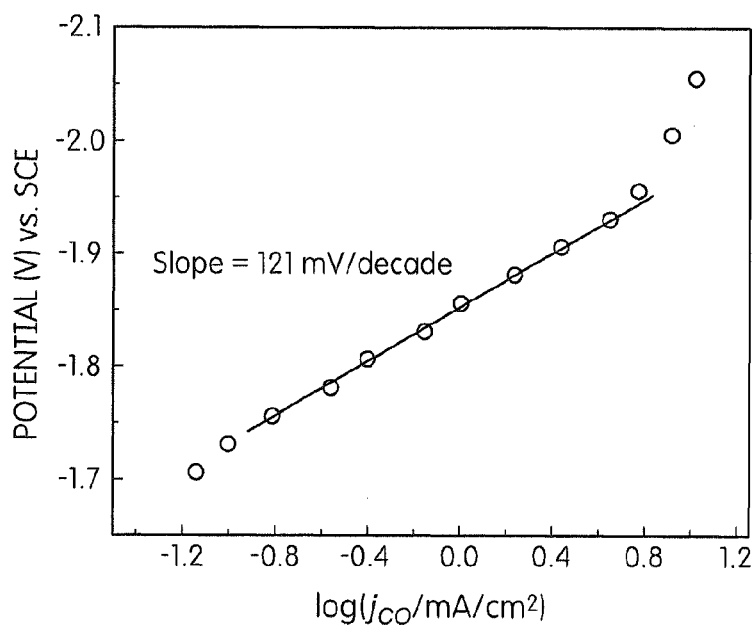FIG. 3a

FIG. 3b

FIG. 4a

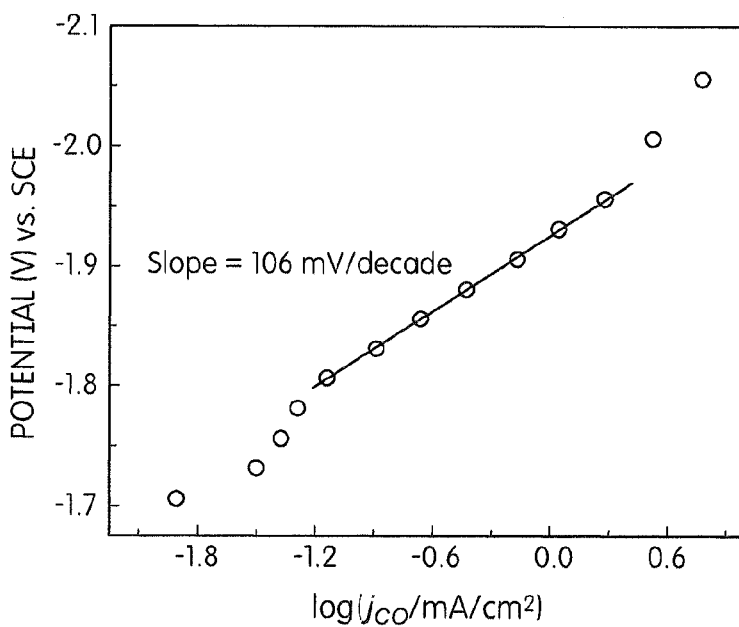
FIG. 4b

FIG. 4c

FIG. 5a

FIG. 5b

SYSTEM AND PROCESS FOR ELECTROCHEMICAL CONVERSION OF CARBON DIOXIDE TO CARBON MONOXIDE

CROSS-REFERENCE TO RELATED APPLICATION

[0001] This application claims priority to U.S. Provisional Application No. 61/971,061, filed Mar. 27, 2014, the entire disclosure of which is incorporated herein by reference in its entirety for all purposes.

FEDERAL FUNDING

[0002] This invention was made with government support under Grant No. P20-RR017716 awarded by the National Institutes of Health (NIH). The government has certain rights in the invention.
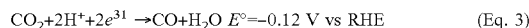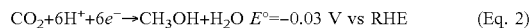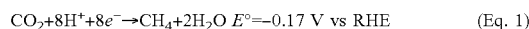
FIELD OF THE INVENTION

[0003] The present invention pertains, to systems and processes useful for the electrochemical conversion of carbon dioxide to carbon monoxide.

BACKGROUND OF THE INVENTION

[0004] Storage of solar and other sources of renewable electricity may be enabled by the endothermic production of chemical fuels such as H_2 or reduced carbon-containing compounds via the electrochemical reduction of H_2O or CO_2, respectively. In particular, the renewable production of liquid fuels provides a clear route to energy supply and distribution and addresses energy needs associated with transportation, which account for more than 20% of US energy demand. Moreover, liquid fuels are compatible with existing infrastructure for energy supply and distribution. The societal importance and economic value of liquid fuel resources clearly highlights the need for new platforms that enable the sustainable generation of liquid fuels from CO_2, and distinguishes CO_2 activation and reduction chemistry as a critical area of focus in the fields of renewable energy storage and molecular energy conversion.

[0005] An attractive strategy for the synthesis of carbon-based fuels using renewable energy is the marriage of a robust electrocatalyst for CO_2 reduction with a photoelectrochemical (PEC) device or a conventional electrolyzer powered by a renewable source of electrical current. Several CO_2 reduction products can be targeted via the half reactions shown in equations 1-3. For instance, the direct electrochemical reduction of CO_2 to methane or methanol (Eq. 1 and 2) are attractive energy storing reactions, however, the kinetic hurdles associated with these multielectron PEC reactions are large, which significantly complicates such processes. By contrast, the $2e^-/2H^+$ reduction of CO_2 to carbon monoxide (Eq. 3) is another energetically uphill half reaction that delivers a versatile and energy rich commodity chemical. In addition to being useful for the industrial production of methanol, acetic acid and some plastics, CO can be reacted with H_2O via the water-gas shift (WGS) reaction to generate H_2. This CO/H_2 mixture (synthesis gas) can be used to generate synthetic petroleum and liquid fuels using existing Fischer-Tropsch (FT) methods for direct integration into existing energy storage and distribution networks.

[0006] Much effort has been devoted to the heterogeneous reduction of CO_2 at metallic electrodes with the goal of driving selective formation of CO via Eq. 3. The majority of such studies have been carried out using aqueous electrolytes with tightly controlled pH requirements (pH~8.5-10.5). Under aqueous conditions, the standard potentials for the two electron reduction of CO_2 to CO is only 0.12 V more negative versus RHE (the reversible hydrogen electrode) than the competing two electron reduction of protons to H_2 (Eq. 3 and 4). As such, for the rate of CO_2 reduction to outcompete hydrogen evolution at the cathode, the proton availability of the aqueous electrolyte must be minimized. This has historically been accomplished by using concentrated aqueous carbonate or bicarbonate electrolytes. Under such conditions, there are a handful of cathode materials that can drive the conversion of CO_2 to CO. However, only noble metals such as Ag and Au have been shown to catalyze this electrochemical reaction with Faradaic Efficiencies (FEs) that are in excess of 80% at ambient pressures. The implementation of Ag and Au cathodes for electrochemical production of CO has been hampered by two distinct factors. Firstly, the exorbitant cost of these noble metals eliminates their practical use on the scale required for alternative fuel synthesis. The second issue concerns the limited current densities associated with CO production at Ag and Au electrodes, which is directly linked to the kinetics of CO_2 electrocatalysis at these platforms.

$$CO_2 + 8H^+ + 8e^- \rightarrow CH_4 + 2H_2O \quad E^\circ = -0.17 \text{ V vs RHE} \qquad \text{(Eq. 1)}$$

$$CO_2 + 6H^+ + 6e^- \rightarrow CH_3OH + H_2O \quad E^\circ = -0.03 \text{ V vs RHE} \qquad \text{(Eq. 2)}$$

$$CO_2 + 2H^+ + 2e^{31} \rightarrow CO + H_2O \quad E^\circ = -0.12 \text{ V vs RHE} \qquad \text{(Eq. 3)}$$

$$2H^+ + 2e^- \rightarrow H_2 \quad E^\circ = 0 \text{ V vs RHE} \qquad \text{(Eq. 4)}$$

[0007] These limited current densities are a direct consequence of the required basic electrolyte solutions for which the solubility of dissolved CO_2 is very low. Several strategies have been employed to combat the inherently low concentration of CO_2 at high pH. These include utilization of 3-dimensional and gas diffusion electrodes, elevation of CO_2 pressure in the electrolysis cell and use of additives such as ionic liquids (ILs) or organic solvents, which can dramatically improve the solubility of CO_2 in the electrolyte solution. Various metal electrodes have been studied for CO_2 reduction activity in non-protic solvents, which display excellent CO_2 solubility at ambient pressure, such as acetonitrile (MeCN) and dimethylformamide (DMF). Although the hydrogen evolution reaction is highly suppressed under these conditions, the electrochemical reduction of CO_2 in organic electrolytes often leads to product mixtures that can include formate, oxalate and glyoxalate in addition to CO. As a result, there are few materials that can catalyze the electrochemical conversion of CO_2 to CO in organic catholyte with even modest FEs. Moreover, the few metals that can drive this electrocatalytic process with reasonable current densities do so only upon application of very large overpotentials. The dearth of cost effective systems that can efficiently and selectively drive Eq. 3 highlights the need for new electrode/electrolyte pairings that can promote the electrocatalytic conversion of CO_2 to CO at appreciable rate (high current density) and with high Faradaic and energy efficiencies.

[0008] Carbon monoxide is a valuable commodity chemical that is required for the production of many other prod-

ucts, including plastics, solvents and acids. It can also be used directly to prepare other valuable reagents such as hydrogen via the industrial Water-Gas-Shift process. Also, carbon monoxide is the principal feedstock for the industrial Fischer-Tropsch process, which allows for the large-scale production of synthetic petroleum.

[0009] Carbon dioxide is also a waste product from conventional power plants. Collection and sequestration of carbon dioxide is commonplace. The ability to convert this waste product to a commodity chemical such as carbon monoxide can offset the cost of sequestration and is of interest to current power producers. Moreover, an attractive strategy for storage of renewable energy resources such as solar or wind is electrochemical fuel synthesis from carbon dioxide. This technology has not yet been realized commercially due to the lack of electrode systems capable of driving the conversion of carbon dioxide to fuels or fuel precursors. Thus, it would be advantageous to develop technology which bridges this gap by allowing electricity from a photovoltaic assembly, wind turbine, etc. to be used to drive fuel production.

[0010] Another desirable development would be technology that provides the ability to generate carbon monoxide directly from carbon dioxide on a small scale. Carbon monoxide is required for commodity chemical synthesis, which includes some pharmaceuticals and other species that require hydroformylation chemistry. Since carbon monoxide is an expensive and toxic feedstock, the ability to generate small quantities of this chemical on demand allows it to be prepared as needed as opposed to relying on large stockpiles of carbon monoxide produced using conventional methods. This strategy would also reduce costs associated with safety and carbon monoxide use.

[0011] The present invention addresses the above-mentioned objectives, among others.

SUMMARY OF THE INVENTION

[0012] The present invention will permit the production of carbon monoxide, which is a valuable commodity chemical and fuel precursor, from atmospheric carbon dioxide or flue gas from a power plant. Since this energy storing process is driven electrochemically, the invention allows carbon monoxide production to be driven using conventional electric and/or renewable energy resources such as wind or solar. Taken together, this invention will permit storage of solar, wind or conventional electric energy by converting carbon dioxide to carbon monoxide and liquid fuels.

[0013] One aspect of the invention provides an electrolytic system for conversion of carbon dioxide to carbon monoxide, the system comprising an electrode comprised of tin and a source of electrical current in electrical communication with the electrode. The electrode comprised of tin may be a cathode and the system may further comprise an anode comprised of platinum (or other suitable anode material such as an iridium oxide, ruthenium oxide, iron oxide, cobalt oxide, nickel oxide and/or mixed metal oxide) and an electrolyte (e.g., an ionic liquid or an organic electrolyte containing one or more salts dissolved therein) in fluid communication with at least one of the cathode comprised of tin or the anode comprised of platinum. The cathode may be in fluid communication with a first electrolyte, the anode is in fluid communication with a second electrolyte, and the first electrolyte and the second electrolyte are the same as or different from each other.

[0014] Another aspect of the invention provides an electrolytic system for conversion of carbon dioxide to carbon monoxide, wherein the system comprises a cathode comprised of tin, an anode comprised of platinum (or other suitable anode material), an electrolyte (e.g., an ionic liquid or an organic electrolyte) in fluid communication with at least one of the cathode and the anode, and a source of electrical current in electrical communication with the cathode and the anode. In one embodiment, the cathode and the anode are present in a single compartment. In another embodiment, the cathode is present in a first compartment, the anode is present in a second compartment, and the first and second compartment are separated by an ion conducting bridge such as a porous glass frit or polymeric membrane. In such an embodiment, the cathode may be in fluid communication with a first electrolyte, the anode may be in fluid communication with a second electrolyte, and the first electrolyte and the second electrolyte may be the same as or different from each other.

[0015] Another aspect of the invention further provides an electrolyte which is an ionic liquid that may comprise one of trifluoromethanesulfonate (triflate) ions, borate ions, phosphate ions, imidazolium ions, pyridinium ions, pyrrolidinium ions, ammonium ions, phosphonium ions, halides and combinations thereof. The electrolyte may also be an organic liquid comprising one of acetonitrile, dimethylformamide, dimethyl sulfoxide, carbonates, bistriflimide, triflate, tosylate and combinations thereof. In one particular embodiment of the invention, the electrolyte is comprised of at least one organic solvent (such as acetonitrile) and at least one imidazolium salt (such as a 1,3-dialkyl imidazolium salt)

[0016] Yet another aspect of the invention provides a method for electrochemically converting carbon dioxide to carbon monoxide, wherein the method comprises electrolyzing carbon dioxide in an electrolytic system comprising an electrode comprised of tin and a source of electrical current in electrical communication with the electrode. The electrolytic system may further comprise an anode comprised of platinum, an electrolyte in fluid communication with at least one of the cathode and the anode, and a source of electrical current in electrical communication with the cathode and the anode, whereby carbon dioxide may be continuously introduced into the electrolytic system.

[0017] Yet another aspect of the invention provides a method of making an electrode comprised of tin, wherein the method comprises electrodepositing a tin-containing material onto a surface of an inert electrode substrate and wherein the method may further comprise reducing a solution comprising a precursor to the tin-containing material (such as a tin(II) salt). The inert electrode substrate may be a nickel electrode or other conducting electrode. In yet another aspect, the invention provides an electrode comprised of tin.

[0018] These and other features of the present invention will be described in more details below in the detailed description of the invention and in conjunction with the following figures.

DESCRIPTION OF THE FIGURES

[0019] The present invention is illustrated by way of example, and not by way of limitation, in the figures of the accompanying drawings and in which:

[0020] FIG. 1a shows a single cell arrangement of an electrolytic system and FIG. 1b shows a dual cell arrangement of an electrolytic system.

[0021] FIG. 2a shows a cyclic voltammogram (CV) for a nickel electrode in a solution of 1.0 M hydrochloric acid (HCl) containing 20 mM Sn^{2+}, and FIG. 2b shows an SEM image of the tin modified nickel electrode.

[0022] FIG. 3a shows a cyclic voltammogram (CV) for a tin modified nickel electrode in a MeCN solution containing 20 mM tin (II) triflate ([$Sn(OTf)_2$])+100 mM tetrabutylammonium hexafluorophosphate ($TBAPF_6$), and FIG. 3b shows an SEM image of the tin modified nickel electrode.

[0023] FIG. 4a and FIG. 4b show CV traces recorded for Sn-modified and bare nickel electrodes in acetonitrile (MeCN) containing 100 mM $TBAPF_6$ or 100 mM 1-butyl-3-methylimidazolium trifluoromethane sulfonate ([BMIM] OTf), under an atmosphere of N_2 or CO_2, for tin-based carbon monoxide evolving catalysts (Sn-CMECs) prepared in organic (MeCN) and aqueous Sn^{2+} solutions, respectively. FIG. 4c shows the representative total current density (j_{tot}) profiles for Sn-CMEC at −1.95 V in MeCN, for the results of FIG. 4a and FIG. 4b.

[0024] FIG. 5 shows Tafel plots for Sn-CMEC on nickel electrodes.

DETAILED DESCRIPTION OF THE INVENTION

[0025] The present invention will now be described in detail with reference to a few preferred embodiments thereof as illustrated in the accompanying drawings. In the following description, numerous specific details are set forth in order to provide a thorough understanding of the present invention. It will be apparent, however, to one skilled in the art, that the present invention may be practiced without some or all of these specific details. In other instances, well known process steps and/or structures have not been described in detail in order to not unnecessarily obscure the present invention.

[0026] Tin (chemical symbol: Sn) represents an attractive material for development of heterogeneous CO_2 reduction catalysts, as this metal is relatively non-toxic and has a small environmental impact. Moreover, the ability of Sn to drive electrochemical conversion of CO_2 to CO would represent an important development in the fields of CO_2 electrocatalysis and renewable energy conversion.

[0027] Cathodes useful in the present invention are electrodes containing metallic tin (Sn^0) or metastable materials such as SnO and SnO_2. The cathode may, for example, be a tin modified electrode wherein a Sn^0 and/or Sn^{2+}/Sn^{4+} containing film(s) has been deposited on a substrate, such as a nickel substrate. The tin film may be deposited electrochemically or via other chemical means including electroless plating, sputtering, CVD (Chemical Vapor Deposition), ALD (Atomic Layer Deposition) and the like. Tin bulk electrodes may also be utilized. Anodes useful in the present invention include electrodes comprised of platinum or metal oxide-based materials, such as iridium oxides, ruthenium oxides, iron oxides, cobalt oxides, nickel oxides and the like (including mixed metal oxides). The platinum may, for example, be in the form of platinum black. Platinum black (Pt black) is a fine powder of platinum with good catalytic properties. Platinized anodes, wherein an electrode substrate (such as a carbon substrate or metallic substrate, such as a platinum or titanium substrate, which could be in the form

of a mesh or screen) is covered with a thin film of platinum black are particularly useful. In common practice, the platinum black is either sprayed or hot pressed onto the substrate. A suspension of platinum black and carbon powder in an aqueous solution may, for example, be applied to the substrate surface. Electrodeposition (electroplating) techniques may also be employed to provide a platinized anode.

[0028] The working electrodes employed for the electrolytic system of the invention may, for example, include either a tin plate, a piece of tin foil or a tin-modified electrode as the cathode and a platinized mesh as the anode. Tin foil electrodes may be preconditioned, for example, by sequential sonication in acetone, deionized water and acetonitrile. Tin plates may be preconditioned, for example, by polishing with a slurry of 0.05 micron alumina powder in water. Residual alumina may be rinsed from the tin surface with Millipore water, and the plate then sonicated in Millipore water for five minutes prior to use. Tin-modified cathodes include cathodes having a surface layer containing tin on top of a conducting support other than metallic tin and may be prepared, for example, by submersing any conducting support such as a glassy carbon support, graphite support, carbon fiber support, carbon paper support, or carbon cloth support or a metallic support such as a nickel plate, nickel foil or a piece of metal in an acidic solution containing any water soluble tin(II) salt such as tin(II) chloride (0.5 to 40 mM) and a protic acid such as hydrochloric acid (0.2 to 2 M). The soluble tin(II) salt functions as a precursor to the tin-containing film deposited on the surface of the conducting support, wherein the tin(II) salt gets reduced during electrolysis. The conducting substrate may then be preconditioned by cycling the applied potential (10 cycles) from 0 to −0.66 V vs. standard calomel electrode (SCE) at a sweep rate of 100 mV/sec. Controlled potential electrolysis at −0.49 V vs SCE may be carried out on the quiescent solution until ~1 C of charge is passed for each square centimeter of submersed substrate. The tin-modified electrode may then be sequentially rinsed with 1 M hydrochloric acid, Millipore water, and acetonitrile prior to being dried under a gentle stream of nitrogen.

[0029] Alternatively, tin-modified cathodes may be prepared, for example, by submersing any conducting support such as a glassy carbon support, nickel plate, nickel foil or a piece of metal in an organic solvent solution (e.g., an acetonitrile, dimethylformamide or other polar organic solvent solution) containing any soluble tin(II) compound such as tin(II) triflate (0.5 to 40 mM) and a supporting electrolyte such as a quaternary ammonium hexafluorophosphate (e.g., tetrabutylammonium hexafluorophosphate) (0.02 to 2 M) or an ionic liquid such as an imidazolium salt-based ionic liquid (1 to 200 mM)(in particular, a 1,3-dialkyl imidazolium triflate). The conducting substrate may then be preconditioned by cycling the applied potential (10 cycles) from −0.26 to −2.26 V vs. SCE at a sweep rate of 100 mV/sec. Controlled potential electrolysis at −1.56 V vs SCE may be carried out on the quiescent solution until ~1 coulomb© of charge is passed for each square centimeter of submersed substrate. A thin tin-containing film derived from soluble tin(II) compound as a precursor may be electrodeposited to a desired total thickness, for example, from 0.2 to 4 C/cm^3. The tin-modified electrode may then be sequentially rinsed with acetonitrile prior to being dried under a gentle stream of nitrogen.

[0030] The plating of tin onto the conducting substrate can be achieved in situ, under a CO_2 atmosphere, at an applied potential around −1.96 V vs. an SCE electrode. Alternatively, the tin-modified cathode may be prepared ex situ in a quiescent polar organic solvent solution (e.g., MeCN solution) containing soluble tin(II) salt and a quaternary ammonium hexafluorophosphate, under a nitrogen atomosphere, by holding the potential around −1.56 V vs. SCE electrode until about 1.0 C of charge is passed for each square centimeter of submersed substrate.

[0031] Thus, in one embodiment of the invention, a tin-modified electrode suitable for use in electrochemically converting carbon dioxide to carbon monoxide may be made by a method comprising contacting an inert electrode substrate with a solution comprised of at least one tin(II) salt and polarizing the inert electrode substrate at a potential effective to electrodeposit a tin-containing material onto a surface of the inert electrode substrate. Such electrodeposition may be performed either ex situ or in situ. The atmosphere above the solution may be an inert atmosphere (e.g., a nitrogen atmosphere) or a CO_2 atmosphere. The solution may comprise one or more polar organic solvents, such as acetonitrile. In another embodiment, the solution may be an aqueous solution. In this embodiment, the solution may further comprise an acid, in particular a strong protic acid such as HCl (e.g., at a concentration of 0.2 to 2 M). The tin(II) salt may be a triflate, nitrate, carboxylate (e.g., acetate), halide or sulfate salt or the like. The concentration of tin (II) salt in solution may be 0.5 to 50 mM, for example. The solution may additionally comprise a quaternary ammonium phosphate, such as tetrabutylammonium phosphate, typically at a concentration of 10 to 500 mM. The solution may alternatively comprise an ionic liquid, in particular an imidazolium-based ionic liquid (e.g., a 1,3-disubstituted imidazolium salt, such as a triflate or tetrafluoroborate salt of a 1,3-dialkyl imidazolium), typically at a concentration of 1 to 300 mM. The potential applied during electrodeposition may, for example, be from −0.1 V to −3.0 V versus SCE. Controlled potential electrolysis (CPE) may be employed.

[0032] The electrolysis device of the invention can be comprised of either a single or dual cell configuration, as shown in FIGS. 1a and 1b, respectively. For the single cell configuration, the cathode, anode and reference electrodes are all immersed in a single housing containing an electrolyte solution. The dual cell configuration incorporates an ion conducting bridge such as a glass or sulfonated tetrafluoroethylene based fluoropolymer (e.g., Nafion®) membrane, which separates the cathode from the anode and is generally more efficient for carbon monoxide electrosynthesis. The ion conducting bridge may be configured to be liquid permeable but to substantially prevent gas flow or transport from the cathode side of the ion conducting bridge to the anode side of the ion conducting bridge and vice versa, including substantially preventing the flow of gas dissolved in the electrolyte or after nucleation of gas bubbles. Generalized schematics for the single and dual cell electrolyzers are shown in FIGS. 1a and 1b. A reference electrode (e.g., a Ag/AgCl or SCE reference electrode) may be present. The electrolytic cell may be configured to be pressurized, to permit the desired electrolysis of carbon dioxide to yield carbon monoxide to proceed at a pressure above atmospheric pressure.

[0033] The electrolyzer may be filled with an electrolyte solution that is comprised as follows. Acetonitrile containing 0-0.10 M tetrabutylammonium hexafluorophosphate or other quaternary ammonium salt(s) and 10-100 mM of one or more imidazolium-based ionic liquid additive such as the triflate (and/or tetrafluoroborate, chloride, bromide, and/or acetate) salts of 1,3-disubstituted imidazolium (such as 1-ethyl-3-methyl imidazolium salts and 1-butyl-3-methyl imidazolium salts, in particular 1-ethyl-3-methyl imidazolium triflate, 1-ethyl-3-methyl imidazolium tetrafluoroborate, 1-butyl-3-methyl imidazolium triflate, and 1-butyl-3-methyl imidazolium tetrafluoroborate). In all cases, dimethylformamide, dimethyl sulfoxide, carbonates (e.g., ethylene carbonate, propylene carbonate, dialkyl carbonate), dimethyl sulfone, sulfolane, gamma butyrolactone, nitriles (propionitrile and buyronitrile, for example), esters (e.g., methyl acetate) and other polar organic solvents and mixtures thereof can be substituted for acetonitrile. Observed current densities and efficiencies are typically optimal in acetonitrile, however. If an ionic liquid additive is employed, the quaternary ammonium hexafluorophosphate can be excluded from the electrolytic cell.

[0034] The 1,3-disubstituted imidazolium may be an imidazolium that is substituted at the 1 and 3 positions with substituents (which may be the same as or different from each other) selected from the group consisting of alkyl groups (e.g., C1-C8 alkyl groups including methyl, ethyl, propyl, butyl, octyl and isomers thereof), aryl groups and halogenated derivatives thereof. The 2 position of the imidazolium may be similarly substituted, as in 1-butyl-2,3-dimethylimidazolium (BMMIM). The heterocyclic ring of the imidazolium may be substituted with one or more halogens. Illustrative suitable imidazolium species include 1-ethyl-3-methylimidazolium (EMIM), 1-butyl-3-methyl-imidazolium (BMIM), 1,3-dimethylimidazolium, 1-methyl-3-propylimidazolium, or any other 1,3-dialkyl or 1,3-diaryl substituted imidazolium.

[0035] The present invention may also be practiced using a pure ionic liquid as the electrolyte. Under these conditions, acetonitrile (or another non-ionic, polar organic solvent) and an ammonium salt are unnecessary. Imidazolium-based ionic liquids containing either triflate, tetrafluoroborate or hexafluorophosphate counter-anions (e.g., imidazolium triflates, imadazolium tetrafluoroborates, imidazolium hexafluorophosphates) are all effective electrolytes in this regard and may be capable of providing faradaic efficiencies for carbon monoxide production of 70-80%. Suitable ionic liquids may, for example, generally consist of bulky and asymmetric organic cations such as imidazolium cations (e.g., 1-alkyl-3-methylimidazolium), pyridinium cations (e.g., 1-alkylpyridinium cations), pyrrolidinium cations (e.g., N-methyl-N-alkylpyrrolidinium cations) and ammonium ions. The cation may also be a phosphonium cation. A wide range of anions may be employed, including simple halides (e.g., chloride, bromide, fluoride), inorganic anions such as tetrafluoroborate and hexafluorophosphate, and large organic anions like triflate, bistriflimide or tosylate.

[0036] Upon sealing the electrolysis device (with septa or stoppers, for example), the solution and head space may be sparged with carbon dioxide at 1 atm for approximately 30 minutes, after which time the electrolysis is initiated. Electrolysis may be carried out by applying a potential suitable to achieve the desired electrochemical conversion of carbon dioxide to carbon monoxide. For example, the potential may be from −1 to −3 V versus SCE. Generation of CO is monitored by either manual injection or direct flow into a

gas chromatograph. On a commercial scale, CO can be separated from the headspace using a standard gas diffusion electrode or other gas sorption technology.

[0037] A source of electrical current is in electrical communication with the cathode and the anode. The power source may implement a variable voltage source. The source of electrical current may be operational to generate an electrical potential between the anode and the cathode. The electrical potential may be a DC voltage.

[0038] The electrolytic system of the present invention may comprise a carbon dioxide source. The carbon dioxide source is generally operational to provide carbon dioxide (as a gas, for example) to a cell comprising the cathode, anode and electrolyte, which may be comprised of one, two or more compartments (chambers). In certain embodiments of the invention, the carbon dioxide is bubbled directly into the compartment containing the cathode.

[0039] The electrolysis can be carried out either under isolation or under a steady flow of carbon dioxide. Under the latter conditions, current densities for CO production are measured to be roughly as high as 10 mA/cm^2, which is comparable to or better than existing technologies. The electrochemical system of the invention has been found to be robust and is capable of demonstrating steady current densities for longer than 8-10 hours. The faradaic efficiency for CO formation using the present invention may be approximately 70-80% and the energy efficiency for carbon dioxide reduction may be approximately 70%. When taken together, the stability as well as the faradic and energy efficiencies are superior or comparable to previously known electrolytic systems that utilize inexpensive cathode materials (e.g. Bi-CMEC).

EXAMPLE 1

[0040] A Sn containing material was electrodeposited onto an inert electrode substrate and the reduction of an aqueous solution of 20 mM $SnCl_2$ containing 1.0 M HCl using a nickel electrode produces the CV trace shown in FIG. **2a**, which is characterized by a broad reduction cathodic wave. Controlled potential electrolysis (CPE) was carried out at −0.49 V versus the standard calomel electrode (SCE; all potentials are referenced to this electrode) for quiescent acidic Sn^{2+} solutions until ~1 C/cm^2 had been passed, leading to electrodeposition of a grey, non-lustrous material on the nickel surface. Nickel was used as the working electrode to ensure that the base conducting substrate supported negligible background activity for CO_2 reduction.

[0041] The morphology of the deposited material was examined by scanning electron microscopy (SEM). As shown in FIG. **2b**, the electrode is coated by an array of micrometer sized crystallites. The surface of the electrodeposited material was also analyzed by x-ray photoelectron spectroscopy (XPS). High-resolution XPS spectra for the tin region reveal Sn 3d5/2 signals at 484.5 eV and 487 eV, which are in the range typical of Sn^0 , Sn^{2+} and Sn^{4+} oxides, respectively. XPS analyses indicate that reduction of acidic solutions of Sn^{2+} leads to deposition of a microcrystalline material containing metallic Sn^0, Sn^{2+} and Sn^{4+} that has incorporated a significant amount of oxygen.

EXAMPLE 2

[0042] A Sn containing material was electrodeposited onto an inert electrode substrate and the reduction of an MeCN

solution of 20 mM $[Sn(OTf)_2]$ containing 0.1 M $TBAPF_6$ using a nickel electrode produces the CV trace shown in FIG. **3a**, which is characterized by a broad cathodic wave centered around −1.6 V vs. SCE. Controlled potential electrolysis (CPE) was carried out at −1.6 V vs. SCE for quiescent Sn^{2+} solution until ~1 C/cm^2 had been passed, leading to electrodeposition of a grey, non-lustrous material on the nickel surface. Nickel was used as the working electrode to ensure that the base conducting substrate supported negligible background activity for CO_2 reduction.

[0043] The morphology of the deposited material was examined by scanning electron microscopy (SEM). As shown in FIG. **3b**, the electrode is coated by a dense array of micrometer sized crystallites. The surface of the electrodeposited material was also analyzed by X-ray photoelectron spectroscopy (XPS). High-resolution XPS spectra for the tin region revealed a Sn $3d_{5/2}$ signal at 488 eV, which is in the range typical of Sn^{2+} and Sn^{4+} oxides. XPS analyses indicate that reduction of an organic solution of Sn^{2+} leads to deposition of a microcrystalline material containing primarily Sn^{2+} and Sn^{4+} ions that has incorporated a significant amount of oxygen.

EXAMPLE 3

[0044] The ability of ex situ Sn-modified electrodes to electrochemically activate CO_2 was assessed in MeCN, which supports a large electrochemical window and is commonly employed for CO_2 electrocatalysis. As shown in FIG. **4a**, scanning to negative potentials in CO_2 saturated solutions of MeCN containing 0.1 M 1-butyl-3-methylimmidazolium triflate ([BMIM]OTf) shows a sharp cathodic wave with onset potential around −1.85 V vs. SCE that is not observed for the corresponding experiment under N_2 (FIG. **4a**, black). 1,3-Dialkyl substituted imidazolum based ionic liquids (ILs) can strongly interact with CO_2 and have found application for carbon sequestration. Moreover, the ability of such ILs to bind reduced CO_2 intermediates at Ag electrodes and mediate electrochemical generation of CO at low overpotentials has also been demonstrated. With these properties in mind, the IL 1-butyl-3-methylimmidazolium triflate ([BMIM]OTf) was added to the CO_2 saturated MeCN solution. The onset of the large, irreversible cathodic wave at −1.85 V is indicative of an electrocatalytic process (FIG. **4a**). This current response cannot simply be attributed to reduction of [BMIM] at the electrode surface, as repeating the same CV experiment in the absence of CO_2 only produces a reduction wave at potentials more negative than −2.2 V (FIG. **4a**, black trace), suggesting that the observed cathodic feature corresponds directly to CO_2 reduction.

[0045] In order to establish that the electrocatalytic response shown in FIG. **4a** corresponded to conversion of CO_2 to a reduced carbon product, controlled potential electrolysis (CPE) experiments were performed for a CO_2 saturated solution of MeCN containing 100 mM [BMIM] OTf using an ex situ plated Sn-CMEC prepared on a nickel disk (disk geometric area=0.07 cm^2). After initiating electrolysis at −1.95 V versus SCE, the reaction headspace was periodically analyzed by gas chromatography (GC). This analysis showed that CO was the sole gaseous product formed during the electrolysis experiment. The measured CO levels corresponded to a FE of nearly 80% for the $2e^-/2H^+$ conversion of CO_2 to CO, with a partial current density of j_{CO}=3.0±0.9 mA/cm^2 (Table 1). Repetition of this experiment in the absence of CO_2 exhibits negligible current

density (FIG. **4***c*, N_2) and very low CO production, indicating that the CO formed under an atmosphere of CO_2 is not simply a product of IL or solvent decomposition.

TABLE 1

Faradaic efficiencies (FE) and current densities for electrocatalytic reduction of CO_2 to CO at an applied potential of −2.0 V vs. SCE in the presence and absence of [BMIM]OTf.

Cathode	[BMIM]OTf concentration	CO % FE	ϕ_{co}	J_{co} (mA/cm²)
Sn-CMEC	100 mM	77 ± 7%	70%	3.0 ± 0.9
Sn-CMEC	None	14 ± 3%	13%	0.10 ± 0.04
Ni, Sn(OTf)₂	100 mM	74 ± 10%	66%	10 ± 2
Ni disk	100 mM	0.64 ± 0.03%	0.6%	0.0040 ± 0.0003
Ni, Sn(OTf)₂	None	25 ± 5	22%	0.7 ± 0.2

[0046] Similarly, repeating this experiment under CO_2 but in the absence of [BMIM] results in a nearly 30-fold decrease in partial current density and a substantial reduction in FE for CO production, as shown in Table 1. Taken together, these control experiments demonstrate that [BMIM] is integral to the observed electrocatalysis, which is distinguished by high current densities for the selective production of CO over other reduced carbon products or H_2.

[0047] Additional experiments demonstrate that the observed electrocatalysis cannot simply be attributed to homogeneous CO_2 reduction mediated by the ionic liquid. If the observed electrocatalysis was homogeneous in nature, the identity of the working electrode should have minimal impact on the observed chemistry. Unlike those obtained using a Sn-modified electrode, CV traces recorded for 100 mM [BMIM]OTf in MeCN under CO_2 with a nickel working electrode, show virtually no current enhancement upon scanning to negative potentials (FIG. **4***a*, green trace). Similarly, CPE of the CO_2 saturated solution of MeCN containing [BMIM] at −1.95 V using a nickel electrode results in negligible charge being passed over the course of a 60 min experiment, and does not produce CO (Table 1). Accordingly, the Sn-modified electrode is intimately involved in the electrocatalytic conversion of CO_2 to CO.

EXAMPLE 4

[0048] The ability of in situ Sn-modified electrodes to electrochemically activate CO_2 was assessed in MeCN, which supports a large electrochemical window and is commonly employed for CO_2 electrocatalysis. As shown in FIG. **4***b*, scanning to negative potentials in CO_2 saturated solutions of MeCN containing 1.0 mM [Sn(OTf)₂] and 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF₆) shows a small current enhancement as compared to the corresponding experiment under N_2. 1,3-Dialkyl substituted imidazolum based ionic liquids (ILs) can strongly interact with CO_2 and have found application for carbon sequestration. Moreover, the ability of such ILs to bind reduced CO_2 intermediates at Ag electrodes and mediate electrochemical generation of CO at low overpotentials has also been demonstrated. With these properties in mind, the IL 1-butyl-3-methylimmidazolium triflate ([BMIM]OTf) was added to the CO_2 saturated MeCN solution. The IL induced a dramatic change in the resultant I/V curves and led to large increases in current at potentials more negative than −1.9 V versus SCE. In particular, the onset of a large, irreversible cathodic wave at −−1.85 V is indicative of an electrocatalytic

process (FIG. **4***b*). This current response cannot simply be attributed to reduction of [BMIM] at the electrode surface, as repeating the same CV experiment in the absence of CO_2 does not produce a reduction wave at potentials more positive than −2.2 V (FIG. **4***b*, black trace), suggesting that the observed cathodic feature corresponds directly to CO_2 reduction.

[0049] In order to establish that the electrocatalytic response shown in FIG. **4***b* corresponded to conversion of CO_2 to a reduced carbon product, controlled potential electrolysis (CPE) experiments were performed for a CO_2 saturated solution of MeCN containing 1.0 mM [Sn(OTf)₂] and 100 mM [BMIM]OTf using a nickel disk (disk geometric area=0.07 cm²). After initiating electrolysis at −1.95 V versus SCE, the reaction headspace was periodically analyzed by gas chromatography (GC). This analysis showed that CO was the sole gaseous product formed during the electrolysis experiment. The measured CO levels corresponded to a FE of nearly 75% for the 2e⁻/2H⁺ conversion of CO_2 to CO, with a partial current density of j_{CO}=10±2 mA/cm² (Table 1).

[0050] Similarly, repeating this experiment under CO_2 but in the absence of [BMIM] results in a nearly 15-fold decrease in partial current density and a substantial reduction in FE for CO production, as shown in Table 1. Taken together, these control experiments demonstrate that [BMIM] is integral to the observed electrocatalysis, which is distinguished by high current densities for the selective production of CO over other reduced carbon products or H_2.

[0051] Additional experiments demonstrate that the observed electrocatalysis cannot simply be attributed to homogeneous CO_2 reduction mediated by the IL. If the observed electrocatalysis was homogeneous in nature, the identity of the working electrode should have minimal impact on the observed chemistry. Unlike those obtained using a Sn-modified electrode, CV traces recorded for 100 mM [BMIM]OTf in MeCN under CO_2 with a bare nickel working electrode, show virtually no current enhancement upon scanning to negative potentials (FIG. **4***a*, green trace). Similarly, CPE of the CO_2 saturated solution of MeCN containing [BMIM] at −1.95 V using a nickel electrode results in negligible charge being passed over the course of a 60 min experiment, and does not produce CO (Table 1). Accordingly, the Sn-modified electrode is intimately involved in the electrocatalytic conversion of CO_2 to CO.

What is claimed is:

1. An electrolytic system for conversion of carbon dioxide to carbon monoxide, the system comprising:
    an electrode comprised of tin and a source of electrical current in electrical communication with the electrode.

2. The electrolytic system of claim **1**, wherein the electrode comprised of tin is a cathode.

3. The electrolytic system of claim **2**, wherein the system further comprises an anode comprised of platinum and an electrolyte in fluid communication with at least one of the cathode comprised of tin or the anode comprised of platinum.

4. The electrolytic system of claim **3**, wherein the cathode is in fluid communication with a first electrolyte, the anode is in fluid communication with a second electrolyte, and the first electrolyte and the second electrolyte are the same as or different from each other.

5. The electrolytic system of claim **3**, wherein the electrolyte is an ionic liquid or an organic electrolyte.

6. The electrolytic system of claim **5**, wherein the ionic liquid comprises at least one component selected from the group consisting of triflate ions, borate ions, phosphate ions, imidazolium ions, pyridinium ions, pyrrolidinium ions, ammonium ions, phosphonium ions, halides and combinations thereof.

7. The electrolytic system of claim **5**, wherein the organic electrolyte comprises at least one component selected from the group consisting of acetonitrile, dimethylformamide, dimethyl sulfoxide, carbonates, bistriflimide, triflate, tosylate and combinations thereof.

8. The electrolytic system of claim **5**, wherein the ionic liquid comprises at least one imidazolium salt.

9. The electrolytic system of claim **2**, wherein the cathode is a conducting tin or tin film cathode and the anode is a platinized anode.

10. A method for electrochemically converting carbon dioxide to carbon monoxide, wherein the method comprises electrolyzing carbon dioxide in an electrolytic system comprising an electrode comprised of tin and a source of electrical current in electrical communication with the electrode.

11. The method of claim **10**, further comprising continuously streaming carbon dioxide into the electrolytic system.

12. The method of claim **10**, wherein the electrode comprised of tin is a cathode and the electrolytic system further comprises an anode comprised of platinum and an electrolyte in fluid communication with at least one of the cathode comprised of tin or the anode comprised of platinum.

13. The method of claim **12**, wherein the electrolyte is an ionic liquid comprising at least one component selected from the group consisting of triflate ions, borate ions, phosphate ions, imidazolium ions, pyridinium ions, pyrrolidinium ions, ammonium ions, phosphonium ions, halides and combinations thereof.

14. The method of claim **12**, wherein the electrolyte is an organic electrolyte comprising at least one component selected from the group consisting of acetonitrile, dimethylformamide, dimethyl sulfoxide, carbonates, bistriflimide, triflate, tosylate and combinations thereof.

15. The method of claim **12**, wherein the ionic liquid comprises one or more imidazolium salts.

16. The method of claim **12**, wherein the cathode is in fluid communication with a first electrolyte, the anode is in fluid communication with a second electrolyte, and the first electrolyte and the second electrolyte are the same as or different from each other.

17. The method of claim **12**, wherein the cathode is a conducting tin or tin film cathode and the anode is a platinized anode.

18. A method of making an electrode comprising electrodepositing a tin-containing material onto a surface of an inert electrode substrate.

19. The method of claim **18**, further comprising reducing a solution comprising a precursor to the tin-containing material and wherein the inert electrode substrate is a nickel electrode.

20. An electrode comprising tin made by the method of claim **18**.

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