Abstract: A method for electrochemically reducing CO or CO₂, is provided. A cathode is provided, wherein the cathode comprises a conductive substrate with a catalyst of a metal and a metal oxide-based coating on a side of the cathode. An anode is spaced apart from the cathode. An ionic transport is provided between the anode and cathode. The cathode is exposed to CO or CO₂ and H₂O. The anode is exposed to H₂O. A voltage is provided between the cathode and anode.
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CATALYSTS FOR LOW TEMPERATURE ELECTROLYTIC CO2 OR CO REDUCTION

CROSS REFERENCE TO RELATED APPLICATIONS


BACKGROUND OF THE INVENTION

[0002] This invention relates generally to the reduction of CO2. Sustainable production of C-based fuel requires using renewable energy to power the reductive fixation of CO2. Coupling renewable electricity to an electrolytic device is an attractive strategy for this goal because it enables the use of multiple renewable energy sources and independent optimization of catalysis. Solid oxide electrolytic cells reduce CO2 to CO efficiently at high current densities, but require operating temperatures of 750-900 °C and cannot access other products.

[0003] Materials that catalyze electrochemical CO2 reduction under mild conditions would enable the development of electrolyzers that operate at more convenient temperatures and provide access to alternative reduction products such as formic acid, alcohols and hydrocarbons. Researchers over the past three decades have identified several materials that are capable of reducing CO2 electrochemically in aqueous solutions, but none that is efficient and stable enough for practical use. In general, available electrodes suffer from one or more of three major problems: 1) a requirement for excessive reducing potentials ("overpotentials") to reduce CO2 in preference to reducing H2O, resulting in low energetic efficiency; 2) rapid loss of CO2 reduction activity resulting from electrode poisoning; 3) production of multiple CO2 reduction products with little selectivity. There is a pressing need to discover and develop new electrochemical CO2 reduction catalysts in order for sustainable fuels to be a significant contributor to a renewable energy economy.
SUMMARY OF THE INVENTION

[0004] In accordance with the invention, a method for electrochemically reducing CO or CO₂ is provided. A cathode is provided, wherein the cathode comprises a conductive substrate with a catalyst of a metal and a metal oxide based coating on a side of the cathode. An anode is spaced apart from the cathode. An ionic transport is provided between the anode and cathode. The cathode is exposed to CO or CO₂ and 340. The anode is exposed to H₂O. A voltage is provided between the cathode and anode.

[0005] In another manifestation of the invention, a method for electrochemically reducing CO or CO₂ is provided. A coating is formed on a cathode by heating a metal layer of the cathode in air, electrochemically oxidizing the metal layer of the cathode, or by a metal oxide deposition to form a metal and metal oxide interface. An anode is spaced apart from the cathode. An ionic transport is provided between the anode and cathode. The coating is exposed to CO or CO₂ and H₂O. The anode is exposed to H₂O. A voltage is provided between the cathode and anode.

[0006] In another manifestation of the invention an apparatus, for electrochemically reducing CO or CO₂ is provided. An anode is provided. An oxidized cathode is spaced apart from the anode. A chamber for exposing the anode and oxidized cathode to at least one electrolyte is adjacent to the anode and oxidized cathode. A gas chamber for exposing the oxidized cathode to CO or CO₂ is adjacent to the oxidized cathode. A CO or CO₂ source for providing CO or CO₂ to the gas chamber is connected to the gas chamber.

[0007] The invention and objects and features thereof will be more readily apparent from the following detailed description and appended claims when taken with the drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

[0008] FIG. 1A shows the XPS spectra of untreated Sn foil before and after electrolysis and Sn foil after etching in HBr.

[0009] FIG. 1B is a plot of total current density vs time, CO faradaic efficiency vs time, and overall HCO₂H faradaic efficiency at -0.7 V vs RHE in CO₂-saturated 0.5 M NaHCO₃ for untreated Sn.

[0010] FIG. 1C is a plot of total current density vs time, CO faradaic efficiency vs time, and overall HCO₂H faradaic efficiency for untreated Sn at -0.7 V vs RHE in CO₂-saturated 0.5 M NaHCO₃ for etched Sn.
FIG. 2A depicts the bulk electrolysis trace at -0.7 V in NaHC03/C02 electrolyte for a Ti cathode before and after the addition of 1 mM SnCl2 to the electrolyte.

FIG. 2B shows SEM images of a Ti electrode before and after deposition showing the formation of a porous, particulate film with -100 nm-diameter pieces atop a more uniform layer.

FIG. 2C is a high resolution Sn 3d5/2 XPS of a Sn/SnOx catalyst removed 30 min or 12 h after the addition of Sn2+

FIG. 2D provides graphs of XRD patterns showing Sn°, SnCl2, and Ti peaks after 30 min or 12 h.

FIGS. 3A-C shows the comparison of CO2 reduction catalysis for unexcited Sn foil and in situ deposited Sn/SnOx thin film electrodes.

FIGS. 4A-E shows the total geometric current density \( \theta_{\text{tot}} \) vs time, the faradaic efficiency (FE) for CO vs time and the overall FE for HCO2H for the polycrystalline Cu electrode and several of the annealed electrodes with progressively thicker initial C40 layers at -0.5 V vs the reversible hydrogen electrode.

FIG. 4F shows the average FE for CO vs the amount of charge required to reduce the C40 layer per electrode area.

FIGS. 5A-F show the scanning electron microscopy (SEM) images, X-ray diffraction (XRD) patterns, and high-resolution Cu 2p X-ray photoelectron spectroscopy (XPS) spectra for a Cu electrode after annealing procedure and after subsequent CO2 reduction electrolysis.

FIGS. 6A-C show the total current densities and faradaic efficiencies for the major products for a Cu electrode annealed at 500 °C for 12 h and for polycrystalline Cu.

FIG. 7 shows Tafel data for a Cu electrode annealed at 500 °C for 12 h and Tafel data for polycrystalline Cu.

FIG. 8 is a high level flow chart of an embodiment of the invention.

FIGS. 9A-B are enlarged cross-sectional views of part of a conductive substrate with a metal coating, forming part of a cathode.

FIG. 10 is a schematic view of an electrolyzer that may be used in an embodiment of the invention.

FIG. 11 is a high level flow chart of another embodiment of the invention.
FIG. 12 is a schematic view of an electrolyzer that may be used in another embodiment of the invention.

DETAILED DESCRIPTION OF ILLUSTRATED EMBODIMENTS

Tin

Metal electrodes have been the focus of extensive C(¾ electroreduction studies in aqueous solutions at ambient temperature. Sn has attracted considerable interest because it is one of the most active metals and its low cost is amenable to large-scale use. Despite its appeal relative to other electrodes, the energy efficiency of Sn is too low for practical electrolysis. Sn is reported to require at least 0.86 V of overpotential to attain a CO₂ reduction partial current density of 4-5 mA/cm² in an aqueous solution saturated with 1 atm of C(¾. It is generally assumed that the bare Sn surface is the catalytically active surface for CO₂ reduction. The large overpotential required for CO₂ reduction is thought to result from the barrier associated with the initial e⁻ transfer to form a CO₂⁻ intermediate that is poorly stabilized by the Sn surface. This mechanistic scenario is commonly invoked for many metal electrodes.

In an embodiment of the invention, SnO²⁻ is essential to CO₂ reduction catalysis on Sn. This may be shown by demonstrating that removal of SnO²⁻ from a Sn electrode results in nearly exclusive ¾ evolution activity. This insight is subsequently applied to prepare a composite Sn/SnO²⁻ thin film catalyst that exhibits greatly enhanced CO₂ reduction activity relative to a typical Sn electrode.

To evaluate the importance of SnOₓ on the surface of Sn in CO₂ reduction, we compared the activity of Sn electrodes that had been etched in strong acid to the activity of untreated electrodes. In both cases, new pieces of high purity Sn foil (99.998%) were used. The surface of the untreated foil was examined by XPS to characterize the native SnOₓ layer. FIG. 1A shows the XPS spectra of untreated Sn foil before and after electrolysis (left) and Sn foil after etching in HBr (right). The curves are combinations of two Gaussian/Lorentzian curves at 486.5 eV and 484.7 eV. FIG. 1B is a plot of total current density vs time (indicated by the line), CO faradaic efficiency vs time (indicated by the ■ points) and overall HCO₃⁻ faradaic efficiency for untreated Sn at -0.7 V vs RHE in CO₂-saturated 0.5 M NaHCO₃ for unetched Sn. FIG. 1C is a plot of total current density vs time (indicated by the line), CO faradaic efficiency vs time (indicated
by the ■ points) and overall HCO$_2$H faradaic efficiency for untreated Sn at -0.7 V vs RHE in CO$_2$-saturated 0.5 M NaHC0$_3$ for etched Sn.

The high resolution Sn 3d$_{5/2}$ spectrum was fit to two peaks at 486.5 eV and 484.7 eV that correspond to Sn$^{4+/2+}$ (SnO$_x$) and Sn°, respectively. The ratio of corrected peak areas for SnO$_x$ to Sn° is 95:5, indicating the presence of a > 5 nm native SnO$_x$ layer.

Etched electrodes were prepared by immersing the Sn foil in 24% HBr at 90° C for 10 min. An XPS spectrum of the etched electrode taken immediately after removal from the HBr solution exhibited a SnO$_x$:Sn° ratio of 17:83 (FIG. 1A). The residual oxide observed on this electrode is likely due to oxide regrowth in the brief exposure to air upon transferring to the XPS chamber, as assessed by independent XPS experiments with a sputtered electrode. For electrolysis experiments, etched electrodes were rinsed with deionized water at the conclusion of the etching procedure and used immediately to minimize oxide regrowth.

The electrolyses were performed in an H-cell in 0.5 M aqueous NaHC0$_3$ saturated with CO$_2$ ("NaHC0$_3$/CO$_2$") at a potential of -0.7 V vs the reversible hydrogen electrode (RHE; all potentials are referenced to this electrode). The headspace of the cathodic compartment was continuously purged with CO$_2$ into the sampling valve of a gas chromatograph (GC), enabling periodic quantification of the gas phase products. FIG. 1B shows the total geometric current density $j_{tot}$ vs time and the faradaic efficiency for CO production at various time points for an untreated Sn electrode. The electrode exhibits a current density of 0.4-0.6 mA/cm$^2$ and a steady-state faradaic efficiency for CO of 5-10%. NMR analysis of the electrolyte at the conclusion of the experiment indicates 19% faradaic efficiency for HCO$_2$H; the remainder of the current is accounted for by ¾ formation. This CO$_2$ reduction activity is consistent with the best reported activity for Sn at -1.06 V, taking into account the difference in overpotential. An electrode examined by XPS after a 12 h electrolysis at -0.7 V exhibited a SnO$_x$:Sn° ratio of 89:11, indicating that the native SnO$_x$ layer is stable to the reduction conditions (FIG. 1A).

Strikingly, an etched Sn electrode exhibits a much higher $j_{tot}$ of 3-4 mA/cm$^2$, but very low faradaic efficiency for CO (0.5%) and HCO$_2$H production (0.3%) (FIG. 1C). The higher $j_{tot}$ likely reflects a larger electrochemical surface area due to etching. Despite the higher surface area, the geometric partial current density for CO$_2$ reduction is lower for the etched Sn electrode (24-32 µA/cm$^2$) than the untreated Sn electrode (92-
140 μA/cm²) due to the much lower faradaic efficiency. Very low (< 1%) CO₂ reduction faradaic efficiencies on etched Sn are also observed over a range of potentials from -0.5 V to -1.0 V. Thus, etched Sn is a moderately efficient 3/4 evolution catalyst, but is essentially inactive for CO₂ electroreduction. Similar results were obtained if Sn electrodes were etched by polarizing at -3 V in HCl solution instead of treating with hot HBr solution.

Together, the XPS and electrolysis results indicate that removal of the native SnOₓ layer from a Sn electrode suppresses CO₂ reduction activity such that H₂ evolution accounts for > 99% of the current density. The small residual CO₂ reduction activity observed on etched Sn likely reflects the growth of a small amount of SnOₓ on the etched electrode before the start of electrolysis.

Based on these results, we hypothesized that the simultaneous deposition of Sn⁰ and SnOₓ on an electrode surface would result in a material with enhanced Sn-SnOₓ contact that is consequently a more active catalyst for CO₂ reduction than a typical Sn foil electrode with a native SnOₓ layer. Accordingly, we sought electrodeposition conditions in which the hydrolysis of Sn²⁺ by cathodically generated OH⁻ would take place concurrently with the reduction of Sn²⁺ to Sn⁰ (E° = -0.1375 V vs NHE). As described below, deposition on Ti electrodes under the same conditions used for CO₂ electroreduction proved to be particularly effective.

FIG. 2A depicts the bulk electrolysis trace at -0.7 V in NaHCO₃/C0₂ electrolyte for a Ti cathode before and after the addition of 1 mM SnCl₂ to the electrolyte. Prior to the addition of Sn²⁺, the Ti electrode exhibits a current density of -10 μA/cm² with very little detectable CO₂ reduction. Addition of Sn²⁺ results in a sharp rise in the current density to a steady-state value of -1.8 mA/cm² and the formation of a grey deposit on the electrode surface. The current density is stable for > 10 h and corresponds to > 85% CO₂ reduction with the remainder accounted for by 3/4 evolution. Nearly identical results are obtained if Sn(OTf)₂ is used instead of SnCl₂, indicating that Cl⁻ is not necessary for catalyst formation.

The composition and structure of the electrodeposited catalyst were characterized by a combination of scanning electron microscopy (SEM), XPS and powder x-ray diffraction (XRD). A catalyst was prepared via in situ deposition as described above and removed from the electrolyte 30 min after the addition of Sn²⁺. FIG. 2B shows SEM images of a Ti electrode before (left) and after (right) deposition.
showing the formation of a porous, particulate film with ~100 nm-diameter pieces atop a more uniform layer. FIG. 2C is a high resolution Sn 3d_{5/2} XPS of a Sn/SnOₓ catalyst removed 30 min (left) or 12 h (right) after the addition of Sn²⁺. XPS analysis indicates a SnOₓ:Sn⁺ ratio of 93:7, similar to the ratio observed for Sn foil electrodes with a native SnOₓ layer. FIG. 2D provides graphs of XRD patterns showing Sn⁺ (■), SnO₂ (*) and Ti (▲) peaks after 30 min or 12 h. In the XRD pattern of this electrode, strong Sn⁺ peaks are observed along with small peaks that correspond to SnO₂. The latter are absent for a Sn foil electrode with a native SnOₓ layer. For comparison, a separate catalyst film was prepared and removed for analysis 12 h after the addition of Sn²⁺. The XPS spectrum, shown in FIG. 2C, and XRD pattern for this electrode are very similar to those of the sample removed after 30 min. Together, these results indicate that a composite Sn/SnOₓ material is formed under the deposition conditions.

[0037] The electrodeposited catalyst (hereafter referred to as "Sn/SnOₓ") exhibits greatly enhanced CO₂ reduction catalysis compared to a typical Sn foil electrode with a native SnOₓ layer. For both electrodes, CO, HCO₂H and 3⁄4 together account for >99% of the reduction products in NaHCO₃/C₂O₂ electrolyte. To compare the activities of Sn foil and Sn/SnOₓ, we measured their partial current densities for CO and HCO₂H at selected potentials between -0.5 and -0.7 V. Comparison of CO₂ reduction catalysis for Sn foil and in situ deposited Sn/SnOₓ thin film electrodes are illustrated in FIGS. 3A-C.

FIG. 3A shows Tafel plots for HCO₂H production. FIG. 3B shows Tafel plots for CO production. FIG. 3C is a bar graph showing Faradaic efficiencies for HCO₂H and CO at various potentials. These data were obtained by performing stepped-potential electrolyses with periodic quantification of the gaseous products by GC and removal of aliquots after each step for NMR analysis.

[0038] For Sn foil, approximate Tafel slopes of 74 mV/dec and 72 mV/dec are observed for HCO₂H and CO production, respectively. Similar Tafel slopes are observed for HCO₂H (67 mV/dec) and CO (77 mV/dec) production on Sn/SnOₓ, however the geometric partial current densities are 7-8-fold higher than for Sn foil. The higher geometric current densities on Sn/SnOₓ are not simply the result of greater electroactive surface area, as indicated by cyclic voltammetry and the dramatic differences in faradaic efficiencies for Sn foil and Sn/SnOₓ. Over the range of potentials used for Tafel analysis, the CO faradaic efficiencies are 4-fold higher and the HCO₂H faradaic efficiencies are 2-3-fold higher on Sn/SnOₓ than on untreated Sn foil.
The Tafel slopes for HC\(_2\)H and CO production on both Sn foil and Sn/SnO\(_x\) are inconsistent with CO\(_2\) reduction mechanisms that proceed through an initial rate-determining 1 e\(^-\) transfer to CO\(_2\). Such a mechanism would result in a 118 mV/dec slope. The observed slopes are instead much closer to 59 mV/dec, which supports mechanisms in which there is a reversible 1 e\(^-\) transfer to CO\(_2\) to form CO\(_2\)\(^{\cdot\cdot\cdot}\) prior to a chemical rate-determining step. Possibilities for the chemical rate-determining step include protonation of CO\(_2\)\(^{\cdot\cdot\cdot}\) or migration to an alternative site on the electrode surface. Competing rate-determining steps, such as protonation at C vs O of CO\(_2\)\(^{\cdot\cdot\cdot}\), may determine the HCO\(_2\)H vs CO selectivity.

The Tafel slopes, combined with the absence of appreciable CO\(_2\) reduction activity on etched Sn, suggest that SnO\(_x\) enables CO\(_2\) reduction to occur by stabilizing CO\(_2\)\(^{\cdot\cdot\cdot}\). At present, we cannot determine whether reduction takes place at the interface between Sn\(^n\) and SnO\(_x\) or on the SnO\(_x\) surface directly. In the absence of SnO\(_x\) to stabilize CO\(_2\)\(^{\cdot\cdot\cdot}\), Sn\(^n\) only catalyzes \(\frac{3}{4}\) evolution because the 1 e\(^-\) transfer to CO\(_2\) is prohibitively slow. The higher CO\(_2\) reduction partial current density and faradaic efficiency on Sn/SnO\(_x\) relative to Sn foil with a native SnO\(_x\) layer are therefore indicative of a greater density of active sites for CO\(_2\) reduction and a higher ratio of these sites to \(\frac{3}{4}\) evolution sites for the in situ deposited catalyst.

The CO\(_2\) reduction activity of Sn/SnO\(_x\), as indicated by the Tafel plots and faradaic efficiencies in FIGS. 3A-C, compares favorably to all polycrystalline metal electrodes in aqueous electrolytes with the exception of Au, which is comparably active initially, but subject to rapid deactivation. Improving CO\(_2\) and ion mass transport by incorporating Sn/SnO\(_x\) in a flow cell and/or a gas diffusion electrode may enable increasing the current density by 1-2 orders of magnitude without large overpotential increases. Elucidating the detailed mechanistic role of SnO\(_x\) in mediating electron transfer to CO\(_2\) is an important objective toward this goal. Moreover, the importance of SnO\(_x\) to CO\(_2\) reduction on Sn surfaces raises the possibilities that metal oxides may be involved in CO\(_2\) reduction pathways on other metal electrodes and that the preparation of alternative metal/metal oxide composites may yield additional CO\(_2\) reduction catalysts with superior activity.

**Copper**
Polycrystalline Cu has been the focus of most CO2 reduction studies because it is one of the best available catalysts and is capable of producing hydrocarbon products. Although mechanistic studies have yielded valuable insights into the CO2 reduction pathways on Cu, the principal shortcomings of this electrode have not been addressed. Most significantly, the energetic efficiency of Cu is limited by the large overpotential (> 0.7 V) required for CO2 reduction to outcompete ½ O reduction. In addition, Cu electrodes rapidly lose their CO2 reduction activity unless stringently purified electrolytes are used, a requirement that is not compatible with scalable fuel synthesis.

Achieving efficient Cu-catalyzed CO2 reduction requires preparing Cu particles whose surfaces have active sites that are different from those on the surface of a polycrystalline Cu electrode. Electrochemical reduction of metal oxides provides one possible route to metal particles with altered surface structures. Researchers have previously used electrochemical methods including potential cycling and anodic pulses to form and subsequently reduce oxides on Cu electrodes. These treatments have resulted in increased hydrogen evolution activity in alkaline electrolytes and altered product selectivity at high overpotential in CO2 reduction electrolyses. While these studies provide evidence of altered electrocatalytic properties, substantial improvements to the energetic efficiency of CO2 reduction have not been observed. Researchers have also used copper oxide electrodes in CO2 reduction electrolyses. The oxides were reduced to Cu° in situ during CO2 reduction catalysis, but only transient changes in the CO2 product distribution attributed to oxide catalysis were observed. Here we show that the CO2 reduction properties of Cu° electrodes resulting from copper oxide reduction vary widely depending on the properties of the initial oxide layer. Reduction of thick Cu2O layers formed by high temperature annealing results in electrodes that catalyze energy-efficient CO2 reduction and are stable to the deactivation phenomena that plague bulk metal electrodes.

Electrodes were prepared by electropolishing pieces of polycrystalline Cu foil (99.9999%) in 85% phosphoric acid and subsequently annealing the electrodes in air at selected temperatures for variable amounts of time. The activities of these electrodes were compared to that of a polycrystalline Cu electrode in controlled potential electrolyses performed in CO2-saturated 0.5 M NaHCO3 electrolyte (“NaHCO3/CO2”) in a two-compartment electrolysis cell. The headspace of the cathodic chamber was continuously purged with CO2 into the sampling loop of a gas chromatograph (GC) to enable periodic
quantification of the gas-phase products. The solution-phase products were quantified by NMR analysis of the electrolyte at the conclusion of the electrolyses.

[0045] FIGS. 4A-E shows the total geometric current density \( j_{\text{tot}} \) vs time, the faradaic efficiency (FE) for CO vs time and the overall FE for HCO\(_2\)H for the polycrystalline Cu electrode (FIG. 4A) and several of the annealed electrodes (FIG. 4B-E) with progressively thicker initial C\%0 layers at -0.5 V vs the reversible hydrogen electrode (RHE; all potentials are referenced to this electrode). The polycrystalline Cu electrode exhibited a \( j_{\text{tot}} \) of -100 \( \mu \)A/cm\(^2\), a FE for CO that declined from 10% at the start of the electrolysis to < 2% over the course of 7 h and a FE for HCO\(_2\)H of 3%. The majority of the current, > 90%, was due to CO evolution. These values are consistent with the previously measured activity for Cu in KHCO\(_3\) electrolytes. Annealing Cu at 130° C, the temperature used to prepare C\%0 electrodes for most previous studies, had very little effect on the activity under these conditions. The electrode annealed at 130° C for 12 h (FIG. 4B) exhibited a \( j_{\text{tot}} \) of 10 mA/cm\(^2\) during the first 4 s in which the thin Cu\(_2\)O layer was reduced. Subsequently, the \( j_{\text{tot}} \) and FE values were very similar to those of the polycrystalline electrode.

[0046] In contrast to these results, the electrodes annealed at higher temperatures exhibited larger \( j_{\text{tot}} \) values and improved CO\(_2\) reduction FE values upon reduction of the C\%0 layer. The electrode annealed at 300° C for 30 min exhibited an initial \( j_{\text{tot}} \) of 10 mA/cm\(^2\) for 2 min as the C\%0 was reduced and subsequently a stable \( j_{\text{tot}} \) of 1.0 mA/cm\(^2\). The FE for CO was 25% during the first hour of electrolysis before declining to 10% over 7 h; the FE for HCO\(_2\)H on the reduced electrode was 5%. Further improvements were obtained by starting with a thicker Cu\(_2\)O layer. After C\%0 reduction of the electrode annealed at 300° C for 5 h, \( j_{\text{tot}} \) reached a stable value of 1.3 mA/cm\(^2\), the FE for CO reached 35% and the FE for HCO\(_2\)H was 24% (FIG. 4D). Annealing at 500° C for 12 h resulted in an even thicker Cu\(_2\)O layer and a stable \( j_{\text{tot}} \) of 2.7 mA/cm\(^2\). This electrode produced CO with \(-40\%\) FE and HCO\(_2\)H with \(33\%\) FE. Notably, the FE for CO was maintained at \(40\%\) throughout the electrolysis, indicating not only efficient but also stable activity for CO\(_2\) reduction on this surface.

[0047] A plot of the average CO FEs for the annealed electrodes vs the amount of charge passed per electrode area (Q) in the Cu\(_2\)O reduction is shown in FIG. 4F. The FEs increased with the amount of charge passed until reaching a plateau at 30-40% for Q > -5 C/cm\(^2\). Assuming bulk density of C\%0 on the electrode, 5 C/cm\(^2\) corresponds to a -3
µηι-thick layer. Together, these results demonstrate that a threshold thickness of the initial CuO layer is required to achieve both efficient and stable CO₂ reduction catalysis for the electrode resulting from Cu₂O reduction.

Based on these results, electrodes prepared by annealing Cu at 500 °C for 12 h were selected for further characterization and CO₂ reduction studies. FIGS. 5A-F show the scanning electron microscopy (SEM) images (FIGS. 5A, D), X-ray diffraction (XRD) patterns (FIGS. 5B, E), and high-resolution Cu 2p X-ray photoelectron spectroscopy (XPS) spectra (FIGS. 5C, F) for a Cu electrode after this annealing procedure (FIGS. 5A-C) and after subsequent CO₂ reduction electrolysis (FIGS. 5D-F). After annealing, the SEM showed a dense array of rods with 100-1000 nm diameters on the electrode surface. These rods are the outermost portion of a thick CuO layer coating the electrode, as evidenced by the large CuO peaks and the near complete suppression of the Cu° peaks in the XRD pattern. The characteristic Cu²⁺ satellite peaks in the XPS spectrum are consistent with the presence of a thin (< 10 nm) CuO layer coating the Cu₂O. Following CO₂ reduction electrolysis, SEM indicated that the rod morphology was intact, but smaller particles (~20 nm) were embedded within the rods (FIG. 5D and Figure S3). Only Cu° peaks were observed in the XRD pattern, FIG. 5F. The Cu 2p XPS spectrum indicated the presence of Cu° or Cu⁺, but the peaks associated with Cu²⁺ in the spectra prior to electrolysis were absent. Together, these results indicate the complete reduction of the CuO layer, although we cannot rule out the presence of a thin, metastable CuO layer or other surface-bound Cu⁺ species during electrocatalysis.

[0048] The electrochemically active surface area of a reduced electrode that had been annealed at 500 °C for 12 h was determined by measuring the double layer capacitance in 0.1 M HClO₄ after CO₂ reduction electrolysis. The capacitance was 13.9 mF/cm², which is 475x larger than the capacitance of 29 μF/cm² measured for a polycrystalline Cu electrode. This roughness factor is considerably larger than the difference in juc between the two electrodes (~30x), consistent with the difference in FEs between the two electrodes.

[0049] The presence of 100-1000 nm rods observed in FIG. 5D is not necessary for efficient CO₂ reduction. Electrodes annealed at temperatures >500 °C for variable amounts of time exhibited very different morphological features on this length scale, but nonetheless comparable FEs for CO₂ reduction at -0.5 V. These results suggest that the CO₂ reduction efficiency of electrodes annealed at high temperatures is associated with a
Cu particle surface or grain boundary structure that forms when suitably thick C\textsubscript{3}/O layers are electrochemically reduced.

[0050] To further characterize the effect of high temperature annealing on the CO\textsubscript{2} reduction activity of Cu, we measured the partial current densities for the reduction products at a variety of potentials between -0.2 V and -1.0 V in NaHCO\textsubscript{3}/CO\textsubscript{2} using an electrode that had been annealed at 500 °C for 12 h (hereafter referred to as "annealed Cu"). The total current densities and faradaic efficiencies for the major products are shown in FIGS. 6A-C, which provides comparisons of electrocatalytic activities of polycrystalline Cu and Cu annealed at 500 °C for 12 h. FIG. 6A is a graph of total current density vs. potential. FIG. 6B is a graph of faradaic efficiencies for CO and HCO\textsubscript{2}H vs potential. FIG. 6C is a graph of faradaic efficiencies for CH\textsubscript{4}, C2H\textsubscript{4} and C2H\textsubscript{6} vs potential. Attempts to collect the corresponding data under identical conditions with polycrystalline Cu were unsuccessful due to the rapid degradation of catalytic activity. Instead, optimal data from previous studies with polycrystalline Cu at several potentials in 0.1 M KHCO\textsubscript{3} are included for comparison.

[0051] The annealed Cu electrode exhibits a high efficiency for CO\textsubscript{2} reduction at remarkably low overpotentials. A peak faradaic efficiency of -45% for CO production is obtained at potentials ranging from -0.3 V to -0.5 V, corresponding to 0.19 V to 0.39 V of overpotential for this product (FIG. 6B). By comparison, essentially no CO\textsubscript{2} reduction to CO is observed for polycrystalline Cu in this potential range; the maximum efficiency for CO with polycrystalline Cu is 20%, which requires -0.8 V (\(\eta = 0.69\) V). Similarly, annealed Cu attains a peak faradaic efficiency for HCO\textsubscript{2}H production of 30% at potentials ranging from -0.45 V to -0.65 V (\(\eta = 0.25\) V to 0.45 V), whereas polycrystalline Cu requires -0.7 V to -0.9 V (\(\eta = 0.5\) V to 0.7 V) to attain a comparable faradaic efficiency (FIG. 6B).

[0052] At relatively negative potentials (< -0.6 V), annealed Cu catalyzes the reduction of CO\textsubscript{2} to ethylene and ethane (FIG. 6C). In contrast, polycrystalline Cu produces only ethylene and methane at high overpotential. Previous work on Cu single crystals has shown that the ratio of ethylene to methane can be boosted by introducing (111) steps in the (100) basal plane, i.e. by using single crystal Cu electrodes with a high index face exposed to the solution. However, methane was never fully suppressed and no ethane was observed in these studies. These results indicate that the surface structures of the Cu particles produced by C\textsubscript{3}/O reduction are distinct from the structures of the high
index faces of Cu. We also note that no methanol was detected among the reduction products for annealed Cu at any potential examined here, in contrast to what has been reported for CO$_2$ reduction catalysis with Cu electrodes annealed at lower temperatures.

[0053] The faradaic efficiencies for the hydrocarbon products on annealed Cu are low and $\frac{3}{4}$ is the major product at high overpotentials. This difference relative to the lower overpotential regime most likely reflects the mass transport limitations at the high current densities observed ($> 10$ mA/cm$^2$) rather than the intrinsic selectivity of the electrode. Improvements in mass transport by using a flow cell or gas diffusion electrode are expected to enable substantially higher CO$_2$ reduction current densities without large overpotential increases.

[0054] To obtain insight into the mechanistic pathway(s) for CO$_2$ reduction with annealed Cu, a plot of overpotential vs the log of the partial current density for CO production (a Tafel plot) was extracted from the data described above. The data are shown in FIG. 7 along with Tafel data for polycrystalline Cu. The plot for annealed Cu is linear over the range of overpotentials from 0.05 V to 0.3 V with a slope of 116 mV/decade. This slope is consistent with a rate-determining initial electron transfer to CO$_2$ to form a surface-adsorbed CO$_2^+$ intermediate, a mechanism that is commonly invoked for metal electrodes. A similar slope is evident in the plot for polycrystalline Cu. The dramatic difference in FE between the two electrodes suggests that the Cu surfaces formed by reducing thick Cu$_{20}$ layers enable formation of the CO$_2^+$ intermediate while suppressing H$_2$O reduction.

[0055] In summary, our results show that Cu particles prepared by reducing μm-thick Cu$_{20}$ films catalyze the reduction of CO$_2$ to CO and HCO$_2$H with high faradaic efficiencies at exceptionally low overpotentials and produce C2 hydrocarbons to the exclusion of CH$_4$ at high overpotentials. Electrodes with these characteristics can readily be prepared with high surface areas, enabling $> 1$ mA/cm$^2$ geometric current densities for CO$_2$ reduction at $< 0.4$ V overpotential and measurable CO$_2$ reduction current densities at $< 0.1$ V overpotential, levels of activity that were previously inaccessible with metal electrodes under comparable conditions. Furthermore, CO$_2$ reduction with these electrodes is resistant to deactivation for at least several hours, a marked improvement over the rapid deactivation of polycrystalline Cu under identical conditions. We anticipate that elucidation of the surface structures of the Cu particles formed by reducing thick Cu$_{20}$ layers will provide crucial insights into the structural requirements for preferential
CO₂ reduction and the formation of C₂ products. In addition, this synthetic approach may prove useful for preparing additional electrocatalysts for CO₂ reduction.

**Embodiments of Implementation**

[0056] To facilitate understanding of the invention, FIG. 8 is a high level flow chart of an embodiment of the invention. In this embodiment, a cathode with a catalyst metal is provided (step 804). A metal oxide coating is formed on the catalyst metal (step 808). The metal oxide coating and the catalyst metal form a metal and metal oxide coating, which may comprise a metal oxide coating over a metal coating or a single coating with both metal oxide particles and metal particles. An anode is spaced apart from the cathode (step 812). An ionic transport is provided between the anode and cathode (step 816). The cathode is exposed to CO₂ and H₂O (step 820). The anode is exposed to H₂O (step 824). A voltage is provided between the cathode and anode (step 828). The voltage causes CO₂ and H₂O to be reduced to CO, ¾ ¾, and ¾. The CO and ¾ may be converted to hydrocarbon or alcohol products.

[0057] In a specific embodiment of the invention, the cathode is formed by providing a conductive substrate (step 804) with a catalyst metal coating (step 808). FIG. 9A is an enlarged cross-sectional view of part of a conductive substrate 904 with a metal coating 908, forming part of a cathode 912. In this example, the conductive substrate 904 is steel. The metal coating 908 is copper. The conductive substrate may be in the form of a net over which the metal coating is applied. In other embodiments, the conductive substrate and metal coating may be a single piece of the same material, such as a copper wire. In such a case, the metal coating may be considered an outer layer of the metal substrate.

[0058] A metal oxide coating is formed on the catalyst metal (step 808). FIG. 9B shows the part of the cathode 912 after the metal oxide coating 916 is formed. In this example, part of the copper catalyst metal coating 908 is formed into copper oxide by heating the cathode to at least 300 °C for at least 15 minutes. Preferably, the metal oxide coating is thicker than a native oxide layer. For example, the metal oxide coating has a thickness of at least twice the thickness of a native metal oxide layer. More preferably, the metal oxide coating is at least 50 nm thick. In other embodiments, the metal oxide coating 916 may be provided by a deposition process to deposit the metal oxide coating on the catalyst metal coating. In this example the copper catalyst metal coating 908 and the metal oxide coating 916 form a metal and metal oxide coating. In other embodiment,
metal particles and metal oxide particles may form a single layer to form the metal and metal oxide coating.

[0059] In some embodiments, some or all of the native metal oxide layer may be reduced before or during usage as a cathode. In the specification and claims, the term "oxidized cathode" will apply to a cathode on which an oxide layer is formed on the cathode by a process that increases the thickness of the metal oxide beyond that of a native metal oxide, whether the metal oxide coating remains or is subsequently reduced. Therefore the oxidized cathode is a cathode with an oxidized cathode layer, which is a metal and metal oxide coating where the metal oxide either remains or is reduced back to metal, and wherein the metal oxide is at least twice as thick as native metal oxide.

[0060] An anode is spaced apart from the cathode (step 812). FIG. 10 is a schematic view of an electrolyzer 1000 that may be used in an embodiment of the invention. An anode is formed by a conductive anode substrate 1004 covered with an anode material 1008. In this example, the anode material 1008 is nickel. An anode electrolyte compartment 1012 is adjacent to the anode and holds an anode electrolyte. The anode electrolyte is provided from an anode electrolyte source 1016, which may continuously circulate anode electrolyte through the anode electrolyte compartment 1012. A cathode electrolyte compartment 1020 holds a cathode electrolyte. The cathode electrolyte is provided from a cathode electrolyte source 1024, which may continuously circulate cathode electrolyte through the cathode electrolyte compartment 1020. Alternatively, the cathode electrolyte may flow to a tank where the solution-phase products are collected. A separator 1028 is placed between the anode electrolyte compartment 1012 and the cathode electrolyte compartment 1020. The separator 1028 may be a porous frit or membrane that may allow certain ions to pass through the separator 1028. As described above, a cathode comprising a conductive substrate 904 with an oxidized cathode layer 1032 forms a cathode adjacent to the cathode electrolyte compartment 1020. In this embodiment, a gas chamber 1036 is placed on the backside of the cathode. A CO₂ source 1040 provides a flow of CO₂ into the gas chamber 1036. A product collector 1044 collects gas-phase products and unused CO₂ from the gas chamber 1036. Product in the product collector 1044 may be isolated and the remaining CO₂ may be recycled back to the CO₂ source 1040. A voltage source 1048, such as a battery, provides a voltage between the anode and cathode.
In operation, the anode electrolyte source 1016 flows electrolyte through the anode electrolyte compartment 1012. The cathode electrolyte source 1024 flows electrolyte through the cathode electrolyte compartment 1020. CO$_2$ is flowed from the CO$_2$ source 1040 into the gas chamber 1036. The voltage source 1048 applies a positive voltage to the anode substrate 1004 and a negative voltage to the cathode substrate 904 with the anode connected to a positive terminal and the cathode connected to a negative terminal. The process provides electrolysis of the C(3/4). Various chemical reactions may occur during the electrolysis of CO$_2$, depending on the metal cathode and other factors. One chemical reaction is C(O)$_2$+H$_2$O $\rightarrow$CO+H$_2$O$_2$. Other chemical reactions provide products of HCO$_2$H, CH$_3$OH or C$_2$H$_4$. In a preferred embodiment, the product collector 1044 provides the product to another system that converts CO, O$_2$, and 3/4 and possibly other products to methanol or some other fuel or usable chemical.

It has been unexpectedly found that by providing a metal oxide layer on a cathode that is thicker than the native oxide layer and subsequently reducing the metal oxide layer, the reduction of CO$_2$ is improved. Without being bound by theory, it is believed that the reduction of the thick metal oxide layer results in metal particles that have unique structures that result in improved CO$_2$ reduction, however, the reason for the improvement is currently unknown. It has also been unexpectedly found that for some cathodes having a metal and metal oxide interface improves CO$_2$ reduction. Preferably, the metal and metal oxide use the same metal material. However, in an embodiment using cerium oxide, the metal is something other than cerium such as tin or copper. Since cerium would turn to cerium oxide during electrolysis, tin is used to provide a native metal for an enhanced metal oxide metal interface, which provides improved CO$_2$ reduction.

As demonstrated above, copper cathodes that are annealed at 130 °C to grow the oxidation layer do not provide the desired improvement. Annealing copper at 300 °C provides some improvement. It has been found that annealing copper at over 500 °C provides the preferred improvement. Anodization at a constant potential for several hours can also be used to obtain a thick C(3/4) layer on Cu and results in improved CO$_2$ reduction.

In the case of some metals such as gold, neither annealing in air or O$_2$ or anodization at a constant potential is effective for preparing a thick oxide layer. Instead, a square wave potential routine is preferred to obtain the metal oxide layer. In the case of
gold, a thick, hydrous \( \text{Au}^{3/4} \) layer can be formed on the Au electrode by applying a square wave potential alternating between 2.7 V and 0.45 V vs Hg/HgSO\(_4\) at a frequency of 1 kHz for 30-60 min. Subsequent reduction of this \( \text{Au}^{3/4} \) layer results in a Au electrode with greatly improved \( \text{CO}_2 \) reduction activity and resistance to catalyst deactivation. Similarly, growth of a silver oxide on silver electrodes by application of a square wave potential routine, followed by electrochemical reduction, results in an Ag electrode with greatly improved \( \text{C}^{3/4} \) reduction activity and resistance to catalyst deactivation.

FIG. 11 is a high level flow chart of another embodiment of the invention. In this embodiment, a cathode with a catalyst metal is provided (step 1104). A metal oxide coating is formed on the catalyst metal (step 1108). The metal oxide coating and the catalyst metal form a metal and metal oxide coating, which may comprise a metal oxide coating over a metal coating or a single coating with both metal oxide particles and metal particles. An anode is spaced apart from the cathode (step 1112). An ionic transport is provided between the anode and cathode (step 1116). The cathode is exposed to \( \text{CO} \) and \( \text{H}_2\text{O} \) (step 1120). The anode is exposed to \( \text{\%27}0 \) (step 1124). A voltage is provided between the cathode and anode (step 1128). The voltage causes \( \text{CO} \) and \( \%270 \) to be reduced to \( \text{CH}_3\text{CH}_2\text{OH} \).

In a specific embodiment of the invention, the cathode is formed by providing a conductive substrate (step 1104) with a catalyst metal coating (step 1108). In this example, the conductive substrate is steel. The metal coating is copper. The conductive substrate may be in the form of a net over which the metal coating is applied. In other embodiments, the conductive substrate and metal coating may be a single piece of the same material, such as a copper wire. In such a case, the metal coating may be considered an outer layer of the metal substrate.

A metal oxide coating is formed on the catalyst metal (step 1108). In this example, part of the copper catalyst metal coating is formed into copper oxide by heating the cathode to at least 300 °C for at least 15 minutes. Preferably, the metal oxide coating is thicker than a native oxide layer. For example, the metal oxide coating has a thickness of at least twice the thickness of a native metal oxide layer. More preferably, the metal oxide coating is at least 50 nm thick. In this example the copper catalyst metal coating and the metal oxide coating form a metal and metal oxide coating.
[0068] An anode is spaced apart from the cathode (step 1112). FIG. 12 is a schematic view of an electrolyzer 1200 that may be used in an embodiment of the invention. An anode is formed by a conductive anode substrate 1204 covered with an anode material 1208. In this example, the anode material 1208 is nickel. An anode electrolyte compartment 1212 is adjacent to the anode and holds an anode electrolyte. The anode electrolyte is provided from an anode electrolyte source 1216, which may continuously circulate anode electrolyte through the anode electrolyte compartment 1212. A cathode electrolyte compartment 1220 holds a cathode electrolyte. The cathode electrolyte is provided from a cathode electrolyte source 1224, which may continuously circulate cathode electrolyte through the cathode electrolyte compartment 1220. In this embodiment, the cathode electrolyte flows to a product collector 1244 where the solution-phase products are collected. A separator 1228 is placed between the anode electrolyte compartment 1212 and the cathode electrolyte compartment 1220. The separator 1228 may be a porous frit or membrane that may allow certain ions to pass through the separator 1228. As described above, a cathode comprising a conductive substrate 1230 with an oxidized cathode layer 1232 forms a cathode adjacent to the cathode electrolyte compartment 1220. In this embodiment, a gas chamber 1236 is placed on the backside of the cathode. A CO source 1240 provides a flow of CO into the gas chamber 1236. The product collector 1244 collects products and unused CO from the gas chamber 1236. Product in the product collector 1244 may be isolated and the remaining CO may be recycled back to the CO source 1240. A voltage source 1248, such as a battery, provides a voltage between the anode and cathode.

[0069] In operation, the anode electrolyte source 1216 flows electrolyte through the anode electrolyte compartment 1212. The cathode electrolyte source 1224 flows electrolyte through the cathode electrolyte compartment 1220. In this example, the electrolyte is KOH in an aqueous solution. CO is flowed from the CO source 1240 into the gas chamber 1236. The voltage source 1248 applies a positive voltage to the anode substrate 1204 and a negative voltage to the cathode substrate 1230 with the anode connected to a positive terminal and the cathode connected to a negative terminal. The process provides electrolysis of the CO. Various chemical reactions may occur during the electrolysis of CO, depending on the metal cathode and other factors. If the reduction uses an acidic aqueous solution for ion transport, in one embodiment, the following reaction occurs: $2\text{CO} + 8e^- + 8\text{H}^+ \rightarrow \text{C}_2\text{H}_4 + 4\text{H}_2 + 3\text{O}$. If the reduction uses a basic
aqueous solution for ion transport, in another embodiment, the following reaction occurs:

\[ 2\text{CO} + 8e^- + 7\text{H}_2\text{O} \rightarrow \text{CH}_3\text{CH}_2\text{OH} + 8\text{OH}^- \]. Since the product is \( \text{CH}_3\text{CH}_2\text{OH} \), may be produced in liquid phase, the product may diffuse through the conductive substrate 1230 and the oxidized cathode layer 1232 to the cathode electrolyte compartment 1220. In such a case, the product collector 1244 would need to remove the product from the cathode electrolyte.

[0070] In one embodiment, the product collector 1044 for a \( \text{CO}_2 \) reduction system may provide CO for the CO source 1240 for the CO reduction system. In another embodiment, another source of CO may be used. In another embodiment, a source of a mixture of CO and \( \text{CO}_2 \) may provide both CO and \( \text{CO}_2 \) to a reduction system. In some embodiments, the pressure of the CO from the CO source 1240 is provided at a pressure greater than 1 atm. The higher pressure increases the solubility of CO in an aqueous solution. The use of an oxide-derived Cu catalyst in embodiments of the invention proved CO reduction with a high energetic efficiency without requiring \( \text{H}_2 \). In another embodiment of the invention, CO is converted to acetate according to the equation 2CO + 4e^- + 3H^+ → CH\(_3\)CO\(_2\)^-. In another embodiment of the invention, CO is converted to ethylene according to the equation 2CO + 8e^- + 8H^+ → C\(_2\)H\(_4\) + 2H\(_2\)O. In other embodiments, the electrolytic reduction reduces CO to other hydrocarbons or alcohols. In other embodiments, the electrolytic reduction reduces \( \text{CO}_2 \) to hydrocarbons or alcohols.

[0071] While this invention has been described in terms of several preferred embodiments, there are alterations, permutations, modifications and various substitute equivalents, which fall within the scope of this invention. It should also be noted that there are many alternative ways of implementing the methods and apparatuses of the present invention. It is therefore intended that the following appended claims be interpreted as including all such alterations, permutations, modifications, and various substitute equivalents as fall within the true spirit and scope of the present invention.
CLAIMS

What is claimed is:

1. A method for electrochemically reducing CO₂, comprising:
   - providing a cathode, wherein the cathode comprises a conductive substrate with a
   - catalyst of a metal and a metal oxide based coating on a side of the cathode;
   - providing an anode spaced apart from the cathode;
   - providing an ionic transport between the anode and cathode;
   - exposing the cathode to CO₂ and H₂O;
   - exposing the anode to H₂O;
   - providing a voltage between the cathode and anode.

2. The method, as recited in claim 1, wherein the metal oxide is tin oxide, copper oxide, silver oxide, palladium oxide, gold oxide, molybdenum oxide, lead oxide, platinum oxide, nickel oxide, bismuth oxide, antimony oxide or cerium oxide.

3. The method, as recited in any of claims 1 or 2, wherein the metal oxide is thicker than the native oxide.

4. The method, as recited in any of claims 1-3, wherein the providing the cathode comprises:
   - providing a conductive substrate with a metal coating; and
   - providing on the conductive substrate a metal oxide coating that is thicker than a native oxide layer by either annealing the metal coating, electrochemically oxidizing the metal coating, chemically oxidizing the metal coating or depositing a metal oxide layer.

5. The method, as recited in any of claims 1-4, further comprising reducing metal oxide in the metal and metal oxide based coating to the metal 0 oxidation state.

6. The method, as recited in any of claims 1-5, where the metal oxide in the metal and metal oxide based coating has a thickness that is greater than 50 nm.

7. The method, as recited in any of claims 1-6, where the metal oxide in the metal and metal oxide based coating has a thickness that is greater than twice a thickness of a native oxide layer.

8. The method, as recited in any of claims 1-7, wherein the metal oxide and metal are of the same metal material.

9. The method, as recited in any of claims 1-8, wherein the metal and metal oxide containing coating provide a metal and metal oxide interface.

10. The method, as recited in any of claims 1-9, wherein the exposing the cathode to
CO₂ and H₂O, comprises:

exposing a first side of the cathode to ¾₀; and
flowing CO₂ past a second side of the cathode.

11. The method, as recited in any of claims 1-10, wherein the providing the cathode,
comprises:

providing a conductive substrate with a metal coating; and
applying an anodic square wave potential to the metal coating to form an oxide layer.

12. The method, as recited in claim 11, wherein the metal coating is gold or silver.

13. The method, as recited in any of claims 1-12, wherein the exposing the cathode to CO₂ and H₂O further exposes the cathode to CO.

14. The method, as recited in claim 13, wherein the metal oxide is copper oxide.

15. The method, as recited in any of claims 13-14, further comprising flowing CO past the second side of the cathode from a CO source.

16. A method for electrochemically reducing CO₂, comprising:

providing on a cathode a coating formed by heating a metal layer of the cathode in air, electrochemically oxidizing the metal layer of the cathode, chemically oxidizing the metal layer or by a metal oxide deposition to form a metal and metal oxide interface;
providing a conductive substrate with a metal coating; and
providing an ionic transport between the anode and cathode;
exposing the coating to CO₂ and ¾₀;
exposing the anode to H₂O ; and
providing a voltage between the cathode and anode.

17. The method, as recited in claim 16, wherein the cathode is copper and the coating is formed by heating the cathode to a temperature of at least 500 °C for at least 15 minutes.

18. The method, as recited in claim 16, wherein the cathode is copper and the coating is formed by heating the cathode to a temperature of at least 300 °C for at least 15 minutes.

19. The method, as recited in any of claims 16-18, further comprising reducing the metal oxide to metal.

20. The method, as recited in any of claims 16-19, where the metal oxide has a thickness that is greater than 50 nm.
21. The method, as recited in any of claims 16-20, where the metal oxide has a thickness that is greater than twice a thickness of a native oxide layer.

22. The method, as recited in any of claims 16-21, wherein the providing on a cathode a coating, comprises applying an anodic square wave potential to the metal layer to form an oxide layer.

23. The method, as recited in claim 22, wherein the metal layer is gold or silver.

24. The method, as recited in any of claims 16-23, wherein the exposing the cathode to CO₂ and H₂O further exposes the cathode to CO.

25. The method, as recited in claim 24, wherein the metal oxide is copper oxide.

26. The method, as recited in any of claims 24-25, further comprising flowing CO past the second side of the cathode from a CO source.

27. An apparatus, for electrochemically reducing CO₂, comprising:
   an anode;
   an oxidized cathode spaced apart from the anode;
   a chamber for exposing the anode and oxidized cathode to at least one electrolyte adjacent to the anode and oxidized cathode;
   a gas chamber for exposing the oxidized cathode to CO₂ adjacent to the oxidized cathode; and
   a CO₂ source for providing CO₂ to the gas chamber, connected to the gas chamber.

28. The apparatus, as recited in claim 27, wherein the oxidized cathode comprises:
   a conductive substrate; and
   an oxidized layer over the conductive substrate.

29. The apparatus, as recited in claim 28, wherein the oxidized layer, comprises:
   a metal layer formed over the conductive substrate; and
   a metal oxide layer formed over the conductive substrate and forming a metal layer metal oxide layer interface.

30. The apparatus, as recited in claim 29, wherein the oxidized layer is subsequently reduced.

31. The apparatus, as recited in claim 27, wherein the oxidized cathode comprises a metal layer that has been oxidized using an anodic square wave potential.

32. The apparatus, as recited in claim 31, wherein the metal layer is gold or silver.

33. The apparatus, as recited in any of claims 27-32, further comprising a CO source for providing CO to the gas chamber.
34. The apparatus, as recited in claim 33, wherein the oxide layer is copper oxide.

35. A method for electrochemically reducing CO, comprising:
providing a cathode, wherein the cathode comprises a conductive substrate with a
catalyst of a metal and a metal oxide based coating on a side of the cathode;
providing an anode spaced apart from the cathode;
providing an ionic transport between the anode and cathode;
exposing the cathode to CO and H₂O;
exposing the anode to H₂O; and
providing a voltage between the cathode and anode.

36. The method, as recited in claim 35, wherein the metal oxide is copper oxide.

37. The method, as recited in any of claims 35 or 36, wherein the metal oxide is
thicker than the native oxide.

38. The method, as recited in any of claims 35-37, wherein the providing the cathode
comprises:
providing a conductive substrate with a metal coating; and
providing on the conductive substrate a metal oxide coating that is thicker than a
native oxide layer by either annealing the metal coating, electrochemically oxidizing the
metal coating, chemically oxidizing the metal coating or depositing a metal oxide layer.

39. The method, as recited in any of claims 35-38, further comprising reducing metal
oxide in the metal and metal oxide based coating to the metal 0 oxidation state.

40. The method, as recited in any of claims 35-39, where the metal oxide in the metal
and metal oxide based coating has a thickness that is greater than 50 nm.

41. The method, as recited in any of claims 35-40, wherein the metal oxide and metal
are of the same metal material.

42. The method, as recited in any of claims 35-41, wherein the metal and metal oxide
containing coating provide a metal and metal oxide interface.

43. The method, as recited in any of claims 35-42, wherein the exposing the cathode
to CO₂ and H₂O, comprises:
exposing a first side of the cathode to ¾O; and
flowing CO₂ past a second side of the cathode.

44. The method, as recited in any of claims 35-43, wherein the providing the cathode,
comprises:
providing a conductive substrate with a metal coating; and
applying an anodic square wave potential to the metal coating to form an oxide layer.

45. The method, as recited in any of claims 35-44, wherein the metal coating is copper or copper alloy.

46. The method, as recited in any of claims 45-46, wherein the metal coating is copper or copper alloy.

47. A method for electrochemically reducing CO, comprising:
    providing on a cathode a coating formed by heating a metal layer of the cathode in air, electrochemically oxidizing the metal layer of the cathode, chemically oxidizing the metal layer or by a metal oxide deposition to form a metal and metal oxide interface;
    providing an anode spaced apart from the cathode;
    providing an ionic transport between the anode and cathode;
    exposing the coating to CO and ¾0; and
    providing a voltage between the cathode and anode.

48. The method, as recited in claim 47, wherein the cathode is copper and the coating is formed by heating the cathode to a temperature of at least 500 °C for at least 15 minutes.

49. The method, as recited in claim 47, wherein the cathode is copper and the coating is formed by heating the cathode to a temperature of at least 300 °C for at least 15 minutes.

50. The method, as recited in any of claims 47-49, further comprising reducing the metal oxide to metal.

51. The method, as recited in any of claims 47-50, where the metal oxide has a thickness that is greater than 50 nm.

52. The method, as recited in any of claims 47-51, where the metal oxide has a thickness that is greater than twice a thickness of a native oxide layer.

53. The method, as recited in any of claims 47-52, wherein the providing on a cathode a coating, comprises applying an anodic square wave potential to the metal layer to form an oxide layer.

54. The method, as recited in any of claims 47-53, wherein the metal layer is copper or copper alloy.

55. The method, as recited in any of claims 47-54, wherein the metal oxide is copper
oxide.

56. The method, as recited in any of claims 47-55, wherein the ionic transport is an aqueous basic solution.

57. An apparatus, for electrochemically reducing CO, comprising:

an anode;
an oxidized cathode spaced apart from the anode;
a chamber for exposing the anode and oxidized cathode to at least one electrolyte adjacent to the anode and oxidized cathode;
a gas chamber for exposing the oxidized cathode to CO$_2$ adjacent to the oxidized cathode; and
a CO source for providing CO to the gas chamber, connected to the gas chamber.

58. The apparatus, as recited in claim 57, wherein the oxidized cathode comprises:
a conductive substrate; and
an oxidized layer over the conductive substrate.

59. The apparatus, as recited in claim 58, wherein the oxidized layer, comprises:
a metal layer formed over the conductive substrate; and
a metal oxide layer formed over the conductive substrate and forming a metal layer metal oxide layer interface.

60. The apparatus, as recited in claim 59, wherein the oxidized layer is subsequently reduced.

61. The apparatus, as recited in claim 57, wherein the oxidized cathode comprises a metal layer that has been oxidized using an anodic square wave potential.

62. The apparatus, as recited in any of claims 57-61, wherein the metal layer is copper or copper alloy.

63. The apparatus, as recited in any of claims 59-62, wherein the metal oxide layer is copper oxide.
FIG. 1A

(a) Before / After Electrolysis

Etched in HBr

Binding Energy / eV

95%  5%  89%  11%  17%  83%

492 488 484 492 488 484 492 488 484

FIG. 1B

(b) Untreated Sn Foil

$\text{HCO}_2\text{H Faradaic efficiency: 19\%}$

$\dot{j}_{\text{tot}} / \text{mA cm}^{-2}$

0 0.5 1.0 1.5 2.0

Time / h

0 1 2 3 4 5

CO Faradaic Efficiency / %

0 5 10 15 20

FIG. 1C

(c) Etched Sn Foil

$\text{HCO}_2\text{H Faradaic efficiency: 0.3\%}$

$\dot{j}_{\text{tot}} / \text{mA cm}^{-2}$

0 1.0 2.0 3.0 4.0

Time / h

0 2 4 6 8 10 12

CO Faradaic Efficiency / %

0 0.5 1.0 1.5 2.0
FIG. 7
START

PROVIDE CATHODE WITH CATALYST METAL

FORM METAL OXIDE COATING ON CATALYST METAL

PLACE ANODE SPACED APART FROM CATHODE

PROVIDE IONIC TRANSPORT BETWEEN ANODE AND CATHODE

EXPOSE CATHODE TO CO₂ AND H₂O

EXPOSE ANODE TO H₂O

PROVIDE VOLTAGE BETWEEN CATHODE AND ANODE

STOP

FIG. 8
FIG. 10
START

PROVIDE CATHODE WITH CATALYST METAL 1104

FORM METAL OXIDE COATING ON CATALYST METAL 1108

PLACE ANODE SPACED APART FROM CATHODE 1112

PROVIDE IONIC TRANSPORT BETWEEN ANODE AND CATHODE 1116

EXPOSE CATHODE TO CO AND H₂O 1120

EXPOSE ANODE TO H₂O 1124

PROVIDE VOLTAGE BETWEEN CATHODE AND ANODE 1128

STOP  FIG. 11
INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2013/025791

A. CLASSIFICATION OF SUBJECT MATTER
C25B 3/04(2006.01)i, C01B 31/18(2006.01)i, C25B 11/06(2006.01)i

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED
Minimum documentation searched (classification system followed by classification symbols)
C01B31/00, C01B 31/18, C25B1/02, C25B3/04, C25B1 1/06, H01M8/10, H01M8/12

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
Korean utility models and applications for utility models
Japanese utility models and applications for utility models

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
eKOMPASS(KIPO internal) & Keywords: C02 reduction, CO reduction, electrolysis, electrochemical, catalyst, coating, metal, metal oxide, cathode

C. DOCUMENTS CONSIDERED TO BE RELEVANT

<table>
<thead>
<tr>
<th>Category</th>
<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
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<td>X</td>
<td>JP 07-188961 A (HITACHI LTD et al.) 25 July 1995 See abstract ; paragraphs [0005] , [0026] ; claims 1-2 ; figure 2.</td>
<td>27, 28, 33, 34, 57, 58 .62</td>
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<td>A</td>
<td>US 5064733 A (KRIST, K. et al.) 12 November 1991 See column 7 , lines 44-54 ; claim 1 ; figures 1-2 .</td>
<td>47-50 , 57-62</td>
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Further documents are listed in the continuation of Box C. See patent family annex.

Date of the actual completion of the international search 27 May 2013 (27.05.2013)
Date of mailing of the international search report 02 June 2013 (02.06.2013)

Name and mailing address of the ISA/KR
Korean Intellectual Property Office
189 Cheongsapo-ro, Seo-gu, Daejeon Metropolitan City,
302-701 Republic of Korea
Facsimile No. 82-42-472-7140

Authorized officer
KM, Dong Seok
Telephone No. 82-42-481-8647

Form PCT/ISA/210 (second sheet) (July 2009)
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<td>☐ Claims Nos.: because they relate to subject matter not required to be searched by this Authority, namely:</td>
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<tr>
<td>2.</td>
<td>☒ Claims Nos.: 12,14,23,25 because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically: The above claims directly or indirectly refer to claim(s) which is/are not drafted in accordance with the second and/or third sentence of Rule 6.4(a). Thus, no meaningful search could be carried out.</td>
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<td>3.</td>
<td>☒ Claims Nos.: 4-1,13,15,20-22,24,26,38-46,51-56,63 because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).</td>
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<th>Observations where unity of invention is lacking (Continuation of item 3 of first sheet)</th>
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<td>This International Searching Authority found multiple inventions in this international application, as follows:</td>
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<td>1.</td>
<td>☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.</td>
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<tr>
<td>2.</td>
<td>☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.</td>
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<td>3.</td>
<td>☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:</td>
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<td>4.</td>
<td>☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:</td>
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**Remark on Protest**

☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.

☒ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.

☒ No protest accompanied the payment of additional search fees.
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<th>Publication date</th>
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