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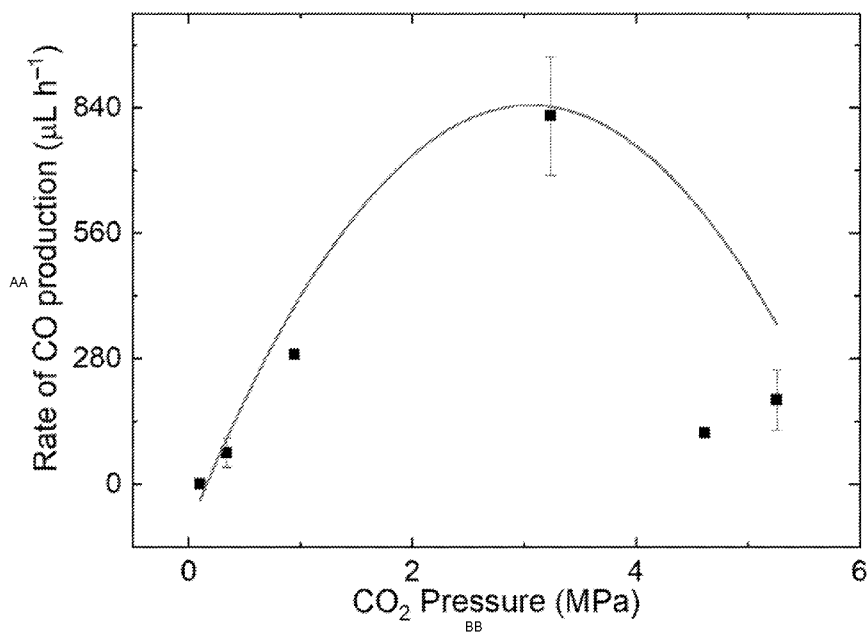


FIG. 8B

(57) Abstract: Processes for the electrochemical reduction of CO₂ are provided. In an embodiment, such a process comprises passing a current through a CO₂ expanded liquid medium under a pressure greater than 0.2 MPa and less than 7.4 MPa in the presence of a catalyst to reduce and convert CO₂ to one or more products, wherein the CO₂ expanded liquid medium comprises dissolved CO₂, a liquid solvent, and a dissolved electrolyte, and wherein the liquid solvent and the dissolved electrolyte are selected to provide a concentration of the dissolved CO₂ of at least 2 M at the pressure.



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ELECTROCATALYTIC CONVERSION OF CARBON DIOXIDE IN LIQUIDS EXPANDED BY CARBON DIOXIDE

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] The present application claims priority to U.S. Provisional Patent Application No. 62/694,627 that was filed July 6, 2018, the entire contents of which are hereby incorporated by reference.

REFERENCE TO GOVERNMENT RIGHTS

[0002] This invention was made with government support under grant number 1605524 awarded by the National Science Foundation. The government has certain rights in the invention.

BACKGROUND

[0003] Point sources are a major contributor to rising anthropogenic CO₂ emissions and account for roughly 25x10³ Mt/y. (Aresta, M., et al., *Dalton Transactions* 2007, (28), 2975-2992.) At present, CO₂ utilization in industrial processes (e.g., synthesis of urea, inorganic/organic carbonates, and methanol, etc.) represents less than 1% of these emissions. The development of technologies that utilize sequestered CO₂ to form products that help ‘fix’ carbon in fuels or chemicals is highly desirable to arrest and potentially reverse atmospheric CO₂ accumulation. However, a major hurdle confronting CO₂ reduction technology is that it must be done in a sustainable fashion, i.e., more CO₂ must be reduced than is produced from the energy that is consumed. This is a significant challenge because CO₂ is unreactive and typically requires high temperatures to produce active intermediates that can be used for producing fuels and chemicals via chemocatalysis. Electrocatalytic reduction on the other hand has been shown to reduce CO₂ to CO at ambient temperatures. However, reported rates are too low to be practically viable.

BRIEF DESCRIPTION OF THE DRAWINGS

[0004] Illustrative embodiments of the disclosure will hereafter be described with reference to the accompanying drawings, wherein like numerals denote like elements.

[0005] FIG. 1 shows increasing CO₂ concentration in a solution of acetonitrile and 0.4 M tetra(n-butylammonium) hexafluorophosphate (squares) and the extrapolated concentration profile of CO₂ in pure H₂O from Henry's law (dashed line).

[0006] FIG. 2 is a schematic showing an experimental set-up for studying the expansion of liquid media, such as acetonitrile, by CO₂.

[0007] FIG. 3 is a schematic of an illustrative electrochemical reactor which may be used to carry out the processes of the present disclosure.

[0008] FIG. 4 shows a cross-sectional view of an illustrative electrochemical reactor comprising (1) 50 mL Parr reaction vessel; (2) Teflon liner; (3) Stir Rod; (4) Custom reactor cap with PTFE O-ring seal; (5) Ceramtec electrical feedthrough; (6) Split-ring clamp; (7) Magnetic drive adaptor; and (8) Parr magnetic drive; which may be used to carry out the processes of the present disclosure.

[0009] FIGs. 5A-5C demonstrate the CO₂ expansion of electrolyte solution. FIG. 5A shows the change in volume of a 10 mL sample of MeCN (squares) and MeCN initially containing 0.4 M [ⁿBu₄N]⁺[PF₆]⁻ (triangles) upon CO₂ pressurization. FIG. 5B shows increasing CO₂ concentration as the volume expands with increasing pressure. MeCN (squares) and MeCN initially containing 0.4 M [ⁿBu₄N]⁺[PF₆]⁻ (triangles). The CO₂ concentration in the expanded liquid asymptotically approaches the concentration of liquid CO₂ (dashed line). FIG. 5C shows cyclic voltammetry of standard metallocene complexes in CO₂-expanded electrolyte solution (5.2 MPa CO₂) composed of 0.4 M [ⁿBu₄N]⁺[PF₆]⁻ present in acetonitrile. Redox couples of ferrocene (0 V, ΔE_p = 120 mV), decamethylferrocene (-0.5 V, ΔE_p = 109 mV) and cobaltocene (-1.34 V, ΔE_p = 100 mV) are shown. Working electrode was the basal plane of highly-oriented pyrolytic graphite (HOPG, 0.09 cm²).

[0010] FIGs. 6A-6B show cyclic voltammetry of the Fc⁺⁰ redox couple and estimated diffusivities as a function of CO₂ pressure in CXEs. FIG. 6A shows experimental (dashed lines) and simulated (solid lines) cyclic voltammetry of ferrocene conducted under various CO₂ pressures. Working electrode was the basal plane of highly-oriented pyrolytic graphite (HOPG, 0.09 cm²). Scan rate 100 mV/s. FIG. 6B shows diffusion coefficients of ferrocene as obtained from the cyclic voltammetry data and from COMSOL simulations (circled) as a function of CO₂ pressure. Curve is included to simply show trend.

[0011] FIGs. 7A-7D show electrochemical current response as a function of potential and pressure in CXE media. FIGs. 7A-7C show cyclic voltammetry conducted under variable

pressure of CO₂. 200 μm Au disk electrode, scan rate 100 mV/s. The control curves were obtained under 0.3 MPa of Ar. FIG. 7D shows steady state currents measured by chronoamperometry with the same electrode at $-2.5\text{ V vs Fc}^{+/0}$, under variable pressure of CO₂. Following initial agitation to achieve equilibrium CO₂ dissolution in the electrolyte phase, the agitation of the solution was stopped during the cyclovoltammetry experiments. The parabolic curve is included to display the trend.

[0012] FIGs. 8A-8C show enhancement of electrochemical CO₂ reduction in CXE media. FIG. 8A is a plot of charge passed and CO detected by gas chromatography for different bulk electrolysis times, using a 1.16 cm² Au coil electrode. Lines are included to guide the eye. Triangles are used to outline the data points showing the amount of CO detected. FIG. 8B shows the pressure dependence of CO formation from the Au coil during bulk electrolysis. Parabolic curve is to guide the eye. FIG. 8C shows Faradaic efficiency following variable bulk electrolysis times with respect to CO detected. Lines are linear fits provided assuming efficiency for CO production remains constant with time. All electrolyses were performed at $-2.5\text{ V vs Fc}^{+/0}$ without stirring.

DETAILED DESCRIPTION

[0013] The present disclosure provides processes for the electrochemical reduction of CO₂ using CO₂ expanded liquid media. By contrast to conventional methods, at least some embodiments of the present disclosure provide much higher selectivities and faradaic efficiencies under moderate conditions (e.g., pressure, temperature), thereby enabling a sustainable, commercially viable pathway to sequestering CO₂ and converting the pollutant to a variety of useful fuels and chemicals.

[0014] Conventional methods have made use of certain organic liquid solvents and certain electrolytes to electrocatalytically convert CO₂ under ambient temperature and atmospheric pressures. However, the present disclosure is based, in part, on the inventors' findings regarding the unexpected synergistic behavior of the organic liquid solvent and the electrolyte at elevated pressures (i.e., greater than atmospheric pressure). These findings reveal that the particular combination of organic liquid solvent and the electrolyte affects whether high CO₂ concentrations can be achieved and sustained in the resulting pressurized liquid medium without resulting in electrolyte precipitation while maintaining a single phase. These findings also reveal that the particular combination affects whether fast electron transfer can be achieved (and thus, fast CO₂ conversion) despite a drop in polarity in the resulting pressurized

liquid medium. Finally, these findings also reveal an unexpected, but critical pressure range for maximizing CO₂ conversion/CO selectivity. It is believed that these findings are important in rationally leveraging the behavior of the liquid media under pressure, including those comprising organic liquid solvents and electrolytes to realize commercially viable CO₂ conversion.

[0015] In embodiments, a process for the electrochemical reduction of CO₂ includes passing a current through a CO₂ expanded liquid medium containing CO₂ and a liquid solvent in the presence of a catalyst. The CO₂ is dissolved in the liquid solvent. By “CO₂ expanded liquid medium,” it is meant that the CO₂ and the liquid solvent are under a pressure which is sufficient to increase the solubility of the CO₂ in the liquid solvent and expand the volume of the liquid solvent. The particular pressure may depend upon the selected liquid solvent (as well as other components included in the CO₂ expanded liquid medium). The particular pressure may also depend upon the selected amount of CO₂ to be dissolved in the liquid solvent. In embodiments, the pressure is selected to achieve a concentration of CO₂ in the liquid solvent of at least 0.1 M. This includes embodiments in which the CO₂ concentration is at least 0.5 M, at least 1 M at least 5 M, at least 10 M, or in the range of from about 0.1 M to about 15 M. As further described below, whether a selected pressure can provide the desired concentration under homogeneous (single-phase) conditions depends upon the components of the liquid medium, e.g., the particular combination of organic liquid solvent and electrolyte. The particular pressure may also depend upon the selected temperature for the electrochemical reduction. In embodiments, the temperature is less than about 60 °C. In embodiments, the temperature is less than the critical temperature of CO₂ ($T_c = 31.1\text{ }^{\circ}\text{C}$). In embodiments, the temperature is in the range of from about 20 °C to about 60 °C, from about 20 °C to about 30 °C, or from about 20 °C to about 25 °C (i.e., room temperature).

[0016] The optimal pressure for a particular CO₂ expanded liquid medium may be determined from CO₂-expansion studies performed in a Jerguson® View cell procured from Clark Reliance Corporation. A schematic diagram of an illustrative experimental setup is shown in FIG. 2. The temperature of the cell is maintained with a water bath, and a transducer is used to monitor the pressure within the cell. A mixture of the selected liquid solvent (and optionally, including other additives such as an electrolyte) is expanded with CO₂ and equilibrated at specific additions of CO₂. The expansion of the mixture is recorded in terms of the increase in volume. The expansion factor is defined as the ratio of the expanded volume (at the equilibrated pressure and temperature) to the original CO₂-free liquid solvent volume

(at the initial pressure and temperature). The expansion volume where a second phase first appears is determined. The optimal pressure for the electrochemical reduction may be a pressure at which the CO₂ expanded liquid medium exists as a single phase. As noted above, whether a single phase can be achieved at a desired pressure depends upon the components of the liquid medium, e.g., the particular combination of organic liquid solvent and electrolyte. The pressure may be further optimized to provide a desired (e.g., maximum) conversion of CO₂ and/or selectivity of a particular product (e.g., CO). As further described below, it has been found that the relationship between pressure and CO₂ conversion is unexpectedly non-monotonic (e.g. see FIGs. 7D, 8B). Therefore, for a particular CO₂ expanded liquid medium, there can exist a critical pressure range for achieving a desired (e.g., maximum) CO₂ conversion.

[0017] In embodiments, the pressure is in the range of from greater than 1 atm (0.1 MPa) to 100 atm (10.1 MPa). This includes embodiments in which the pressure is in the range of from 2 atm (0.2 MPa) to 60 atm (6.1 MPa), from 5 atm (0.51 MPa) to 50 atm (5.1 MPa), or from 10 atm (1 MPa) to 40 atm (4.1 MPa). This includes embodiments in which the pressure is at least 2 atm (0.2 MPa), at least 5 atm (0.51 MPa), at least 10 atm (1 MPa), or at least 20 atm (2.0 MPa). This further includes embodiments in which the pressure is no greater than the critical pressure of CO₂ ($P_c = 72.9$ atm, 7.38 MPa).

[0018] The use of a CO₂ expanded liquid medium for the electrochemical reduction is by contrast to media in which CO₂ is bubbled through a solvent at atmospheric pressure. The use of the CO₂ expanded liquid medium has a number of other advantages, including enabling pressure-tunable, higher CO₂ concentrations and pressure-tunable, much higher CO₂ transfer rates to catalytic surfaces, both of which improve selectivities and faradaic efficiencies. It is also noted that electrochemical systems configured for CO₂ conversion at atmospheric pressure are generally not appropriate for CO₂ conversion using the elevated pressures described herein. This is true of the electrochemical system of WO2014164262.

[0019] The CO₂ may be derived from a variety of sources. An illustrative source includes a waste stream, e.g., from an industrial process such as an electricity generation facility or a chemical plant.

[0020] A variety of liquid solvents may be used. In embodiments, the liquid solvent is an organic liquid solvent. The organic liquid solvent may be selected on the basis of its ability to dissolve a selected electrolyte, including high concentrations of the selected electrolyte. The

organic liquid solvent may be selected on the basis of having a dielectric constant which is sufficient to fully dissociate the selected electrolyte. Illustrative organic liquid solvents include methanol, acetonitrile, ethyl acetate, toluene, and carbonates such as propylene carbonate, ethylene carbonate, and dimethyl carbonate. Combinations of different types of organic liquid solvents may be used. The use of the term “liquid” with respect to the solvent is meant to indicate that the solvent exists in the liquid state under the selected pressure and temperature of the electrochemical reduction.

[0021] Other additives may be included in the CO₂ expanded liquid medium. In embodiments, e.g., when using an organic liquid solvent, an electrolyte is also included in the CO₂ expanded liquid medium. A variety of electrolytes may be used. Illustrative electrolytes include tetrabutylammonium hexafluorophosphate, lithium perchlorate, tetraethylammonium tetrafluoroborate, potassium chloride, etc. Other similar salts may be used. Combinations of different types of electrolytes may be used. The concentration of electrolyte included in the CO₂ expanded liquid medium may be that which is sufficient to provide an electrochemical double layer on the surface of electrodes used in the electrochemical reduction but without precipitating out of the CO₂ expanded liquid medium at the selected pressure and temperature.

[0022] As noted above, although different organic liquid solvents and different electrolytes may be used, it has been found that not all combinations and not all supporting electrolyte concentrations are able to achieve/sustain high CO₂ concentrations and provide fast electron transfer as the properties of the CO₂ expanded liquid medium change under pressure (e.g., its polarity). By way of illustration, although the combination of acetonitrile and tetrabutylammonium hexafluorophosphate (TBAPF₆) was found to be suitable, the combination of acetonitrile and tetramethylammonium hexafluorophosphate (TMAPF₆) was not. This is despite the minor structural change from butyl to methyl. Specifically, when TBAPF₆ was dissolved in acetonitrile with an initial concentration of 0.4 M, it showed no visible sign of precipitation up to a CO₂ pressure of 740 psi (5.1 MPa) and the total volume expanded to ca. 200% of the initial volume. By contrast, when TMAPF₆ was dissolved in acetonitrile with an initial concentration of 0.4 M, it visibly precipitated at a CO₂ pressure of ca. 300 psi (2.1 MPa). Moreover, TBAPF₆ is not necessarily compatible with every organic liquid solvent. When TBAPF₆ was dissolved in dimethyl carbonate with an initial concentration of 0.4 M, it also visibly precipitated at a CO₂ pressure of ca. 480 psi (3.3 MPa) and a volume expansion of ca. 64%. As another example, it was found that when LiClO₄ was

dissolved in dimethyl carbonate with an initial concentration of 0.4 M, it visibly precipitated at a CO₂ pressure of ca. 350 psi (2.4 MPa) and a volume expansion of ca. 15%. Even at an initial LiClO₄ concentration of 0.2 M, it also visibly precipitated at a CO₂ pressure of ca. 430 psi (3 MPa) and a volume expansion of ca. 40%.

[0023] As an alternative to the organic liquid solvents described above, in embodiments, the liquid solvent is an ionic liquid. The terms “organic liquid solvent” and “ionic liquid” are distinguished from one another in the present disclosure. In this case, the particular ionic liquid and other components of the liquid medium also determine whether the medium can achieve/sustain high CO₂ concentrations and provide fast electron transfer as the properties of the CO₂ expanded liquid medium change under pressure. By “ionic liquid,” it is meant a salt existing in the liquid state under the selected pressure and temperature of the electrochemical reduction. A variety of ionic liquids may be used and combinations of different types of ionic liquids may be used. Illustrative ionic liquids include 1-n-butyl-3-methylimidazolium hexafluorophosphate and 1-n-butyl-3-methyl-imidazolium tetrafluoroborate. However, in embodiments, the CO₂ expanded liquid medium does not comprise and is not in contact with an ionic liquid.

[0024] In embodiments, a proton source may be included in the CO₂ expanded liquid medium. The proton source may be used to provide mass balance for the products of the electrochemical reduction. The use of a proton source also enables the tuning of the thermodynamics of the electrochemical reduction. A variety of proton sources may be used. Illustrative proton sources include water, alcohols such as methanol, ethanol, trifluoroethanol, and tertbutylethanol, and salts such as trialkylammonium and pyridinium salts. Combinations of different types of proton sources may be used. The proton source may be a different compound from the liquid solvent. Various amounts of the proton source may be used as determined by the selected catalyst, electrolyte, pressure, temperature, etc. The amount may be that which maximizes the yield of carbon-containing products or the yield of a selected carbon-containing product. However, in embodiments, the CO₂ expanded liquid medium comprises no more than 1 M of a proton source, e.g., water. In embodiments, the CO₂ expanded liquid medium does not comprise and is not in contact with a proton source such as water. In embodiments, the CO₂ expanded liquid medium may be considered to be nonaqueous and free of water.

[0025] A catalyst is included in the CO₂ expanded liquid medium. A variety of catalysts may be used, provided the catalyst is capable of catalyzing the electrochemical reduction of

CO₂. The catalyst may be one which is soluble in the CO₂ expanded liquid medium. Organometallic catalysts may be used, such as those based on complexes of rhenium, manganese, rhodium, cobalt, iron, and iridium. Illustrative catalysts include Re(bpy)(CO)₃Cl and Mn(bpy)(CO)₃Br, where bpy = 2,2'-bipyridyl. A variety of bidentate chelating ligands bearing imine, phosphine, or amine donors may be used, including fluorinated bipyridyl ligands. Other illustrative catalysts include catalysts bearing the pentamethylcyclopentadienyl ligand (designated generally as Cp*M catalysts), wherein M = Co, Rh, Ir and Cp* = pentamethylcyclopentadienyl.

[0026] Nanostructured metallic catalysts may be used. By “nanostructured” it is meant a solid material of the metallic catalyst in the form of distinct, distinguishable nanostructures having at least one dimension of about 1000 nm or less or about 100 nm or less. Otherwise, the particular shape and the dimensions of the nanostructures may vary. Nanoparticles, nanowires and nanodiscs are some illustrative shapes. Various metals may be used, including transition metals/post-transition metals such as Co, Rh, Ir, Ru, Mn, W, Ti, Cu, Ag, Au, Zn, In, Sn, Ni, Pt, Fe, Cr, Mo, Pd, Cd, and combinations thereof. Oxides or sulfides of such metals may be used, e.g., FeS₂ and In₂O₃.

[0027] The catalyst may be added directly to the CO₂ expanded liquid medium (e.g., soluble catalysts). Alternatively, the catalyst may be immobilized on a substrate, e.g., by being coated, impregnated, or otherwise incorporated into the substrate. A variety of substrates may be used. Illustrative substrates include carbon-based substrates such as glassy carbon and highly oriented pyrolytic graphite (HOPG). A HOPG substrate may be coated with carbon black, such as Vulcan or Ketjen black. Other illustrative substrates include platinum, gold, and fluorine-doped tin oxide. The nature of the immobilization may be via noncovalent interactions between the catalyst and the substrate (e.g., between pyrene groups on the catalyst and carbon-based substrates). Catalyst-treated substrates may be used as one of the electrodes in the electrochemical reduction, as further described below.

[0028] The conditions under which the electrochemical reduction takes place include, e.g., the pressure, temperature, and the applied electrochemical potential for passing the current through the CO₂ expanded liquid medium. The pressure and temperature have been described above. An electrochemical potential may be applied by applying a voltage across electrodes immersed in the CO₂ expanded liquid medium. The voltage may be applied, e.g., in linear sweep voltammetry or steady state polarization. Various voltages may be applied, e.g.,

in the range of from about -3 V to about 1 V versus the ferrocenium/ferrocene couple. Polarization pulses may be applied if needed.

[0029] The particular products produced by the electrochemical reduction depend upon the selected catalyst, additives, conditions, etc. Products include carbon monoxide, formate, methane, ethane, acetylene, ethylene, methanol, formaldehyde and ethanol. Higher products, e.g., C₃, C₄ compounds may also be formed. Product identification may be determined by use of gas-phase chromatography (GC), nuclear magnetic resonance (NMR), and the like. Products may be separated and collected or combined with other reactants. By way of illustration, the product carbon monoxide may be combined with a stream of O₂ for oxycarbonylation reactions. As another example, carbon monoxide may be separated and collected for use as a source in carbonylation reactions, Fischer Tropsch synthesis and hydroformylation reactions.

[0030] The processes of the present disclosure may be characterized by a faradaic efficiency and/or selectivity for a particular product at the selected conditions. By way of illustration, when using a molecular catalyst, the selectivity may be about 100% for CO production over the timescale of about an hour. When using a gold catalyst, a CO₂ pressure of about 450 psi (3.1 MPa), room temperature, and an applied potential of -2.5 V the faradaic efficiency may be at least about 80% and the selectivity of CO may be about 100% over the timescale of about two hours.

[0031] The processes of the present disclosure may be carried out in a variety of electrochemical reactor systems. However, as noted above, not all electrochemical reactor systems will be appropriate to withstand the pressures disclosed herein. The electrochemical reactor system includes an electrochemical reactor configured to contain the CO₂ expanded liquid medium and electrodes for the electrochemical reduction. An illustrative electrochemical reactor is shown in FIG. 3. The electrochemical reactor is based on a Parr Instruments pressure vessel which can accommodate elevated pressures and temperatures. As shown in FIG. 3, the head assembly of the pressure vessel is drilled and tapped to accept a pressure gauge, CO₂ port, thermocouple, head-space sampling port, and three electrode feedthroughs. The head assembly is sealed to the body of the reactor with a compression gasket.

[0032] The electrochemical reactor may be used to perform voltammetry experiments to quantify kinetic rate constants and diffusion coefficients. In that case, one of the electrodes

may be a small planar metallic electrode, e.g., a ~2 mm a metal disk, soldered to a 2 mm stainless steel conducting rod which passes through the electrode feedthrough on the head assembly. Various metals may be used, e.g., Cu, Ag, Au, Zn, In, Sn, Ni, Pt, Fe, Cr, Mo, Pd, Cd and combinations thereof. The conducting rod may be masked with epoxy and/or Teflon tape to prevent contact with the CO₂ expanded liquid medium.

[0033] For carrying out the electrochemical reduction of CO₂, two styles of larger electrodes may be used. First, planar metallic electrodes may be used, e.g., a 10 cm² metal flag electrode soldered to the sealed stainless-steel rod as described above. Second, for the catalytic electrochemical reduction of CO₂, a substrate, e.g., a 10 cm² HOPG substrate may be soldered to the sealed stainless-steel rod. Other substrates may be used as described above. A high surface area carbon (e.g., Vulcan or Ketjen black) may be coated on the substrate, followed by incorporation of any of the catalysts described above.

[0034] As shown in FIG. 3, a counter electrode, e.g., a Pt flag electrode of appropriate size, is also included in the head assembly. FIG. 3 also shows a reference electrode included in the head assembly. A silver wire coated with AgCl immersed directly in the CO₂ expanded liquid medium may be used as the reference electrode, particularly if utilizing a chloride electrolyte salt. Alternatively, a tungsten wire coated with an anodically formed oxide may be used as a quasi-reference electrode. Reporting potentials with respect to the ferrocenium/ferrocene couple may be used, as this is useful in the field of homogeneous electrocatalysis.

[0035] Although the electrochemical reactor shown in FIG. 3 is a single compartment reactor, two-compartment reactors separated by porous membranes, e.g., Nafion, may also be used.

[0036] The electrochemical reactor may be interfaced directly or indirectly with a variety of other devices, e.g., those for product identification or other studies, e.g., for performing *in situ* infrared spectroscopy for analyzing catalysts. For example, the electrochemical reactor of FIG. 3 may be interfaced with a GC device, an NMR device, or an *in situ* attenuated total reflectance (ATR) IR probe (Mettler Toledo Inc.).

[0037] Another suitable electrochemical reactor is shown in FIG. 4 and is further described in the Example, below.

EXAMPLE

[0038] This Example demonstrates the use of CO₂-rich electrolyte media for intensifying CO₂ conversion in electrochemical systems. The media are termed CO₂-eXpanded Electrolytes (CXEs). Pressurization of organic solvents such as acetonitrile with CO₂ (15-50 bar, 1.5 MPa – 5 MPa) at near-ambient temperatures leads to dissolution of significant amounts of CO₂ in the organic solvent. This increase in CO₂ solubility is related to its mild critical properties ($T_c = 31.1^\circ\text{C}$; $P_c = 73.8 \text{ bar}$, 7.38 MPa) and results in an exponential increase in CO₂ solubility with pressure. Such non-linear solubility behavior is shown in FIG. 1 (squares) and is differentiated from linear solubility (dictated by Henry's law). The increased CO₂ dissolution results in a pressure-tunable volumetric expansion of the liquid phase—hence the name “CO₂ expanded liquid.” CXEs represent a continuum of pressure-tunable electrochemical reaction media that can enable enhanced CO₂ concentrations at much milder pressures (tens of bars) than supercritical CO₂. Moreover, it has been found that through careful selection of liquid organic solvent and electrolyte, such enhanced CO₂ concentrations can be leveraged to achieve extremely fast CO₂ electrocatalytic conversion therein.

[0039] Specifically, this Example demonstrates that the cathodic polarization of a model polycrystalline gold electrocatalyst in a CO₂-expanded acetonitrile + tetra(n-butylammonium) hexafluorophosphate solution results in CO₂ → CO conversion rates that are nearly an order of magnitude faster than those previously reported. It is shown that the observed enhancement relates to increased CO₂ availability *and* diffusivity in CXEs.

[0040] Experimental

[0041] All manipulations were carried out in dry, N₂ filled gloveboxes (Vacuum Atmospheres Co., Hawthorne, CA) or under an Ar atmosphere in a glovebag (NPS Corp., Spilfyter) unless otherwise noted. All solvents were of commercial grade and dried over activated alumina using a PPT Glass Contour (Nashua, NH) solvent purification system prior to use, degassed and then stored over molecular sieves. All chemicals used were from major suppliers and used after extensive drying.

[0042] *Volumetric expansion studies*

[0043] The volumetric expansion studies of acetonitrile both with and without tetra(n-butylammonium) hexafluorophosphate (TBAPF₆) were carried out in a Jerguson view cell. (See FIG. 2.) The expansion was measured with a Digimatic Heightgauge (Mitutoyo).

[0044] *Electrochemical Studies*

[0045] All electrochemical experiments were conducted in a 50 mL reactor (Parr) with a custom lid outfitted with gas-tight electrical leads as well as a temperature probe and pressure transducer (see FIG. 4 and additional description below in “Electrochemical Reactor”). The supporting electrolyte used was 0.4 M tetra(n-butylammonium) hexafluorophosphate ($[\text{Bu}_4\text{N}]^+[\text{PF}_6]^-$; Oakwood Chemical) prior to expansion. Measurements were made with a Gamry Reference 3000 Potentiostat/Galvanostat using a standard three-electrode configuration. The working electrode used differed depending on the experiment run. CO_2 reduction experiments were either done with a 200 micron diameter gold microelectrode or with a gold wire with an area of 1.16 cm^2 (Alfa Aesar, 99.95%, 0.1mm diameter). Gold working electrodes were cleaned between experiments by soaking in hydrogen peroxide (52%, SUPPLIER) for one hour then rinsed with acetone and dried. Experiments with metallocene electrochemistry used the basal plane of highly oriented pyrolytic graphite (HOPG) (GraphiteStore.com, Buffalo Grove, Ill.; surface area 0.09 cm^2). A copper wire (Alfa Aesar, 99.9%, 1.5mm diameter) immersed in electrolyte was used as a pseudoreference and separated from the solution by a Vycor frit (Bioanalytical Systems, Inc.). The counter electrode was a platinum wire (Kurt J. Lesker, Jefferson Hills, PA; 99.99%, 0.5 mm diameter).

[0046] Electrolyte solution was loaded into the reactor under an Ar atmosphere in a glovebag. Prior to experiments, the reactor was purged three times by repeated pressurization and depressurization cycles (c.a. 100 psi to 20 psi) to exclude trace water and oxygen from the system. To achieve liquid expansion, the reactor was brought to the required pressure, stirred only until equilibrium was established, and then closed off from gas supply. No stirring was done during any electrochemical measurements.

[0047] *Sample preparation for gas chromatography*

[0048] Following electrolysis, gas contained within both the expanded liquid and reactor headspace was collected by expansion of the headspace into an evacuated steel cylinder. At low pressures ($<5 \text{ atm}$, 0.5 MPa) a 40 mL vessel was used and at high pressures a 1 L vessel was used. The connection of the larger volume reverses the expansion of the liquid allowing for a representative sample to be taken. The pressure and temperature of the system were allowed to equilibrate before closing the connection and removing the cylinder for analysis.

[0049] *Gas chromatography*

[0050] Analysis of gaseous samples was performed with a Shimadzu GC-2014 Custom-GC gas chromatograph with a thermal conductivity detector and dual flame-ionization detectors. A custom set of 8 columns and timed valves enabled quantitative analysis of the following gases: hydrogen, nitrogen, oxygen, carbon dioxide, carbon monoxide, methane, ethane, ethylene, and ethyne. Argon served as the carrier gas. The instrument was calibrated prior to experimental runs with a standard checkout gas mixture (Agilent 5190-0519) to obtain qualitative data for H₂ and CO. Calibration curves over a range of 100–10,000 ppm for H₂ and 90–9,000 ppm for CO were constructed with prepared mixtures of H₂ or CO in N₂ to allow for quantification. Quantification was done accounting for sample dilution during sample collection, assuming all gases behaved ideally.

[0051] Analysis of the liquid phase was achieved by injection of a sample of the electrolyte following electrolysis into an Agilent 6890 Gas Chromatograph fitted with a CP-Wax 58 (FFAP) CB column. The sample was filtered over silica to remove excess electrolyte and then analysis done using the FID detector on the instrument.

[0052] *Electrochemical Reactor*

[0053] A simple high pressure electrochemical cell was designed to lower the threshold of reactor design necessary to conduct high pressure experiments. The cell is shown in FIG. 4. The cell has been operated at up to 800 psi (5.5 MPa), however the design and the components are robust enough that higher operating pressures can be obtained.

[0054] An advantage of the reactor design is that all components except for the reactor cap are commercially available. The custom-built reactor cap contains seven threaded ports and an O-ring seal (PTFE, Parr). The seven threaded ports are to interface electrical connections, gas inlet/outlet, a thermocouple and pressure transducer, pressure release valve, and sampling ports. The reactor cap was designed to interface with a standard 50 mL reactor (Parr) and is clamped to the reactor with a split ring cover clamp (Parr). This custom reactor cap is easily fabricated by a machinist, especially utilizing a CNC mill.

[0055] The reaction vessel itself is composed of a 50 mL reactor (Parr) rated to 3000 psi (20.7 MPa) at 350 °C. It would be possible to use this vessel by itself to hold the electrolyte, however a Teflon insert is used inside to decrease the possibility of contamination. An advantage of using the Parr vessel as the pressure containment is that it is also possible to create specialized inserts for different experimental needs. For example, the construction of a fritted container to separate counter and working products would be much easier than if the

container had to withstand the pressure. A magnetically coupled drive (Parr) is used to provide agitation in the solution to speed equilibration or enhance mass transport to the electrodes. Pressure and temperature monitors share one port in the cap. The thermocouple extends down into the electrolyte solution for accurate temperature determination.

Temperature adjustments are made using an external aluminum heating block attached to a recirculating water bath (Fisher). The gas inlet line shares another port with a rupture disk for pressure safety. To pressurize this cell, high pressure gas from a commercially supplied tank is used with a needle valve to control flow and a normal two stage pressure regulator to establish the pressure required. All gas lines were built using standard components (Swageloc). A check valve is used to prevent any solvent from the reactor from contaminating the gas in the cylinder. A syringe pump could be inserted in this system if higher pressures were required, however, as the requirements for this Example did not exceed the pressures available in commercial cylinders, this option was not utilized.

[0056] A key change from a typical three electrode setup is the use of the last four ports for electrical leads into the cell. Many electrodes have a specific voltage window, outside of which they experience degradation or other redox events. The inclusion of the fourth electrode allows the use of a different electrode material to establish the potential of a reference compound and to calibrate the pseudoreference electrode outside of the voltage window of interest for the electrode being studied. The fourth electrode also allows a faster throughput of high pressure experiments for screening of catalysts. The most time-consuming part of the experimentation is allowing sufficient time to ensure complete equilibrium of the gas and the liquid. Having a second working electrode can double the rate of experiments completed for a given pressure.

[0057] An additional advantage is the ease of changing electrodes in the cell. The feedthroughs are threaded into the cap and so can be pressure tested once and are not a possible point of loss of pressure thereafter. The electrical feedthroughs used (CeramTec) in the cell are rated to 4000 psi (27.6 MPa). Using this type of feedthrough also eliminates the possibility of ejecting a swaged or shear forced feedthrough. The electrodes are then attached to the leads using gold plated clips. Thus, instead of needing to create a new pressure tight electrode each time a new material needs to be tested, the electrodes can be identical to electrodes used in typical experiments at ambient pressures.

[0058] *COMSOL Modeling*

[0059] COMSOL (COMSOL Multiphysics v. 5.3) simulations were performed to obtain the diffusion coefficient of ferrocene as a function of CO₂ pressure. The COMSOL geometry utilized a 2D axial-symmetric domain with the electrode size (100 μm radius) and reactor dimensions exactly as they were in the experiments described above. To create the mesh, a free triangular mesh with COMSOL's built-in “fine” element size was used for the bulk of the reactor, with an “extra fine” mesh used for 1 cm x 1 cm around the electrode. To create a fine mesh around the electrode surface, an edge mesh was incorporated with a minimum mesh element of $2 \times 10^{-5} \text{ cm}^2$ and a maximum mesh element of $2 \times 10^{-4} \text{ cm}^2$.

[0060] The electrode current was simulated via the COMSOL Electroanalysis module. This module obtains the concentration of the oxidized and reduced species in solution and the current on the electro-active boundary as a function of applied potential by coupling the Butler-Volmer Equation with Fick's Law of Diffusion. An electron-transfer rate constant of 1 cm s^{-1} and a transfer coefficient, $\alpha = 0.5$ were used for the $\text{Fc}^{0/+}$ redox reaction. The bulk concentration of ferrocene was determined using the volumetric expansion data obtained for the electrolyte media at the relevant pressures. The diffusion coefficient was determined by obtaining a best fit between the experimental data and the simulation.

[0061] Results and Discussion

[0062] This Example reports electrochemical studies in CO₂-expanded acetonitrile. To begin, the volumetric expansion of 10 mL of dry acetonitrile was measured upon CO₂ pressurization at 20 °C up to 800 psi (5.5 MPa). Volumetric expansion of up to 300% (i.e., tripling of the liquid phase volume) was observed upon pressurization at 800 psi (5.5 MPa, see FIGs. 5A, 5B). This expansion is caused by a large increase in CO₂ solubility (by up to ca. 15 M at 52 bars, 5.2 MPa) in the liquid phase.

[0063] For electrochemical studies, a supporting electrolyte is needed to establish the double layer charging region and a suitable electrode-electrolyte interface. Tetrabutylammonium hexafluorophosphate (TBAPF₆) was added to the acetonitrile. It was found that the volumetric expansion of the acetonitrile phase containing dissolved electrolyte ([TBAPF₆]₀ = 0.4 M) was only slightly decreased (compared to acetonitrile alone) over the CO₂ pressure range (FIG. 5A) with a virtually undetectable change in the CO₂ mole fraction in the liquid phase (FIG. 5B). Thus, acetonitrile containing sufficient supporting electrolyte for electrochemical work undergoes CO₂ expansion, and can attain concentrations of CO₂ in the liquid phase of up to 15 M.

[0064] To perform electrochemical reaction in CXEs, a high-pressure reaction vessel (Parr Instrument Co.) was fitted with a custom cap featuring ports for multiple electrodes, gas input and sampling, and a mechanical stirrer (as described above). As electrochemical reactions have not been previously reported in CO₂-expanded media, the thermodynamic potentials for common redox reactions in these media as well as the behavior of redox reagents as a function of CO₂ concentration were investigated. The 1e⁻ ferrocenium/ferrocene couple (denoted hereafter as Fc⁺⁰) is the most common reference potential used for electrochemical studies in acetonitrile. Hence this convention has been adopted here. It is found that the cobaltocenium/cobaltocene couple at -1.34 V vs. Fc⁺⁰ and decamethylferrocene at -0.5 V vs. Fc⁺⁰. (See FIG. 5C.) These results compare well with literature values for the reversible potentials of these metallocenes in acetonitrile (-1.33 V and -0.48 V, respectively) (N. G. Connelly, W. E. Geiger, Chemical Redox Agents for Organometallic Chemistry. *Chemical Reviews* **96**, 877-910 (1996)). Considering the known polarity dependence of metallocene redox potentials, it is anticipated that CO₂ expansion results in a slightly less polar liquid phase compared to pure acetonitrile. Indeed, liquid-phase electronic absorption measurements carried out with Re(CO)₃(bpy)Cl as a function of CO₂ pressure are consistent with the progressively decreasing polarity of the CO₂-expanded liquid phase upon CO₂ pressurization (data not shown).

[0065] A key advantage of utilizing gas-expanded liquids in homogenous chemocatalysis includes improved mass transfer rates compared to the neat solvent medium. To determine if the CO₂-expanded electrolyte medium also permits higher diffusion coefficients for electroactive species, voltammetry was performed on the Fc⁺⁰ redox couple as a function of CO₂ pressure, and the results simulated using COMSOL Multiphysics simulation software (see details above). The experimental voltammograms showed very good agreement with the simulations, except for a slight attenuation of the reduction wave in the experimental data compared to the simulations (FIG. 6A). The ferrocene diffusion coefficients from the voltammetry simulations showed a 40% increase in the CXE media in the same pressure range where volumetric expansion occurs upon CO₂ pressurization (FIG. 6B). This shows that the solute diffusivity is also tuned favorably with CO₂ pressure.

[0066] Following characterization of the electrochemical properties of CO₂-expanded electrolyte solution, CO₂ electroreduction in CXEs as a function of CO₂ pressure was investigated next. Polycrystalline gold was chosen as the electrode material, as it reliably produces CO selectivity upon CO₂ reduction under most conditions, including in the presence

of acetonitrile. Cyclic voltammetry carried out on a polycrystalline gold electrode in contact with acetonitrile under a headspace CO₂ pressure of 1 atm (0.1 MPa) shows onset of an irreversible, catalytic response near -2.5 V vs. Fc⁺⁰. (See FIG. 7A, showing similar data at 0.3 MPa.) Notably, catalytic current is enhanced as the headspace CO₂ pressure is increased to 3.2 MPa. (See FIG. 7B.) At 3.2 MPa, the voltammogram appears relatively sharp, and the current density does not reach a plateau as observed at the lower pressure. This behavior suggests increased catalysis as the electrode is polarized to increasingly negative potentials. The current profile displays little hysteresis, consistent with no electrode poisoning, product inhibition, and reduced CO₂ diffusion limitations under the CO₂-rich conditions. This contrasts with the voltammogram obtained at the lower pressure (FIG. 7A), which displays a plateauing catalytic current characteristic of modest catalysis attributed to diffusion-limited current flow and low CO₂ concentration (ca. 0.08 M) available near the electrode.

[0067] For typical outer-sphere electron transfer processes, one would predict that the current flowing would increase linearly with the concentration of the redox active species available in the liquid phase. In sharp contrast, during electrocatalytic CO₂ reduction in CXE media, a maximum in the electrocatalytic current was observed. (See FIG. 7D.) The CO₂ conversion rate (i.e., current density) was found to decrease at CO₂ pressures beyond ca. 450 psi (3.1 MPa), trending toward values measured at the lowest CO₂ pressure. However, the voltammetric response obtained at higher pressures (for example, 5.2 MPa as shown in FIG. 7C) shows a very different profile than the data obtained at the lowest CO₂ pressure (FIG. 7A). Specifically, the response is very sharp, showing little hysteresis and no discernable plateau in the current density. This suggests that even though the current densities are similar, the underlying CO₂ reduction mechanism at 5.2 MPa is different than at 1 atm (0.1 MPa) pressure.

[0068] Analytical experiments were carried out to confirm the production of CO and any other products following electrolysis on a polycrystalline Au coil electrode. Quantitative gas chromatography showed that CO was the only major product with an estimated faradaic efficiency of ca. 40% at 35 psi (0.24 MPa) CO₂ pressure and 80% at 450 psi (3.1 MPa) CO₂ pressure. Time dependent measurements of CO production and faradaic efficiency show that the media is stable during CO production. (FIG. 8A, 8C.) The amounts of CO produced as a function of CO₂ pressure show analogous trends to the voltammetry data, i.e., a volcano-type profile. (FIG. 8B.) At low CO₂ pressures, the amount of CO produced is c.a. 25 μ mol. However, at pressures where appreciable CO₂ expansion occurs (i.e. 450 psi, 3.1 MPa) the

amount of CO produced increases by one order of magnitude to c.a. 250 μmol . This is concomitant with the one order of magnitude increase in the current density between 35 psi (0.24 MPa) and 450 psi (3.1 MPa) as measured in the voltammetry experiment (FIG. 7D). At higher CO₂ pressures, the CO production progressively decreases to levels observed at ambient pressure, again consistent with the volcano-type current density profile with CO₂ pressure. These results clearly show that CO production can be sensitively tuned in CXE media with CO₂ pressure. Further, the optimal CO₂ pressures for maximizing CO production are relatively mild (tens of bars), favoring process economics.

[0069] Regarding the volcano-type profiles described above, at progressively higher CO₂ concentrations at the higher pressures, the observed rate inhibition could be due to several factors such as active site limitation, intermediate product adsorption/desorption dynamics and the decreased polarity of the CXE medium. The facile pressure-tunability of CXE media helps to simultaneously optimize CO₂ concentrations at the electrode surface and media conductivity in order to maximize the CO₂ electroreduction rates. Further, by providing ultra-high CO₂ concentrations to electrode surfaces, CXEs not only unlock the potential of conventional electroreduction catalysts but also open up new vistas for designing catalysts that can take advantage of such media to convert CO₂ into value-added chemical precursors at intensified rates that approach practical viability.

[0070] The word "illustrative" is used herein to mean serving as an example, instance, or illustration. Any aspect or design described herein as "illustrative" is not necessarily to be construed as preferred or advantageous over other aspects or designs. Further, for the purposes of this disclosure and unless otherwise specified, "a" or "an" means "one or more".

[0071] The foregoing description of illustrative embodiments of the disclosure has been presented for purposes of illustration and of description. It is not intended to be exhaustive or to limit the disclosure to the precise form disclosed, and modifications and variations are possible in light of the above teachings or may be acquired from practice of the disclosure. The embodiments were chosen and described in order to explain the principles of the disclosure and as practical applications of the disclosure to enable one skilled in the art to utilize the disclosure in various embodiments and with various modifications as suited to the particular use contemplated. It is intended that the scope of the disclosure be defined by the claims appended hereto and their equivalents.

WHAT IS CLAIMED IS:

1. A process for the electrochemical reduction of CO₂, the process comprising passing a current through a CO₂ expanded liquid medium under a pressure greater than 0.2 MPa and less than 7.4 MPa in the presence of a catalyst to reduce and convert CO₂ to one or more products, wherein the CO₂ expanded liquid medium comprises dissolved CO₂, a liquid solvent, and a dissolved electrolyte, and wherein the liquid solvent and the dissolved electrolyte are selected to provide a concentration of the dissolved CO₂ of at least 2 M at the pressure.
2. The process of claim 1, wherein the concentration of the dissolved CO₂ is in a range of from at least 2 M to 12 M.
3. The process of claim 1, wherein the liquid solvent is an organic liquid solvent.
4. The process of claim 3, wherein the organic liquid solvent is selected from methanol, acetonitrile, ethyl acetate, toluene, propylene carbonate, ethylene carbonate, dimethyl carbonate, and combinations thereof.
5. The process of claim 1, wherein the dissolved electrolyte is selected from tetrabutylammonium hexafluorophosphate, lithium perchlorate, tetraethylammonium tetrafluoroborate, potassium chloride, and combinations thereof.
6. The process of claim 1, wherein the organic liquid solvent is acetonitrile and the dissolved electrolyte is tetrabutylammonium hexafluorophosphate.
7. The process of claim 1, wherein the CO₂ expanded liquid medium does not comprise an ionic liquid and is not in contact with an ionic liquid.
8. The process of claim 1, wherein the CO₂ expanded liquid medium does not comprise water and is not in contact with water.
9. The process of claim 1, wherein the CO₂ expanded liquid medium exists as a single phase.
10. The process of claim 1, wherein the dissolved electrolyte is present at a concentration in a range of from 0.1 M to 0.5 M.

11. The process of claim 1, wherein the CO₂ expanded liquid medium further comprises a proton source.
12. The process of claim 11, wherein the proton source is selected from water, an alcohol, a salt, or combinations thereof.
13. The process of claim 11, wherein the proton source is present at an amount of no more than 1 M.
14. The process of claim 1, wherein the selected liquid solvent and the dissolved electrolyte provide a faradaic efficiency of 80% and a selectivity of CO of 100% using a pressure of 3.1 MPa, room temperature, a timescale of two hours, a gold catalyst, and an applied potential of -2.5 V.
15. The process of claim 1, wherein the pressure is in a range of from 1 to 5 MPa.
16. The process of claim 1, wherein the CO₂ expanded liquid medium is at a temperature in the range of from 20 °C to 60 °C.
17. The process of claim 16, wherein the CO₂ expanded liquid medium is at room temperature.
18. The process of claim 1, wherein the current is passed by applying a voltage across electrodes in direct contact with the CO₂ expanded liquid medium.
19. The process of claim 1, wherein the liquid solvent is an organic liquid solvent; the CO₂ expanded liquid medium exists as a single phase; the dissolved electrolyte is present at a concentration in a range of from 0.1 M to 0.5 M; the pressure is in a range of from 1 to 5 MPa; and the CO₂ expanded liquid medium is at a temperature in the range of from 20 °C to 60 °C.

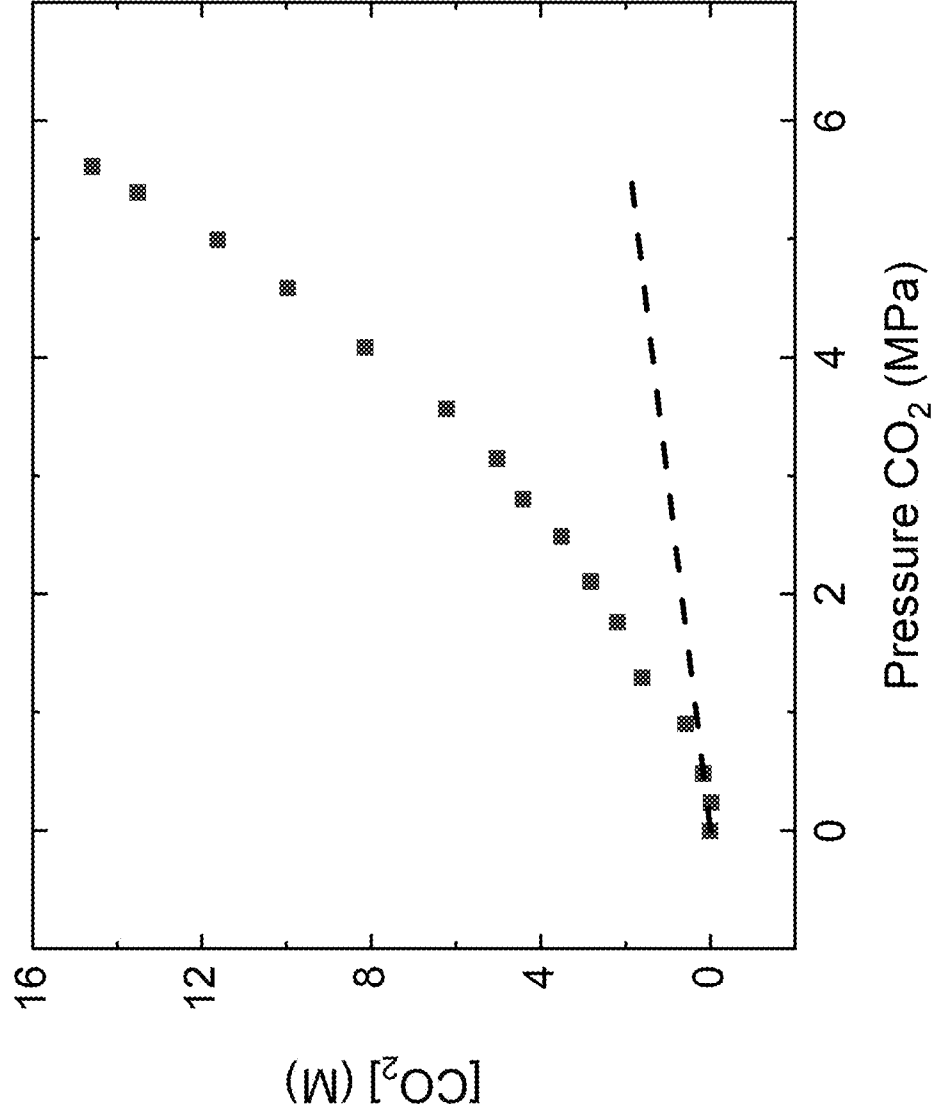


FIG. 1

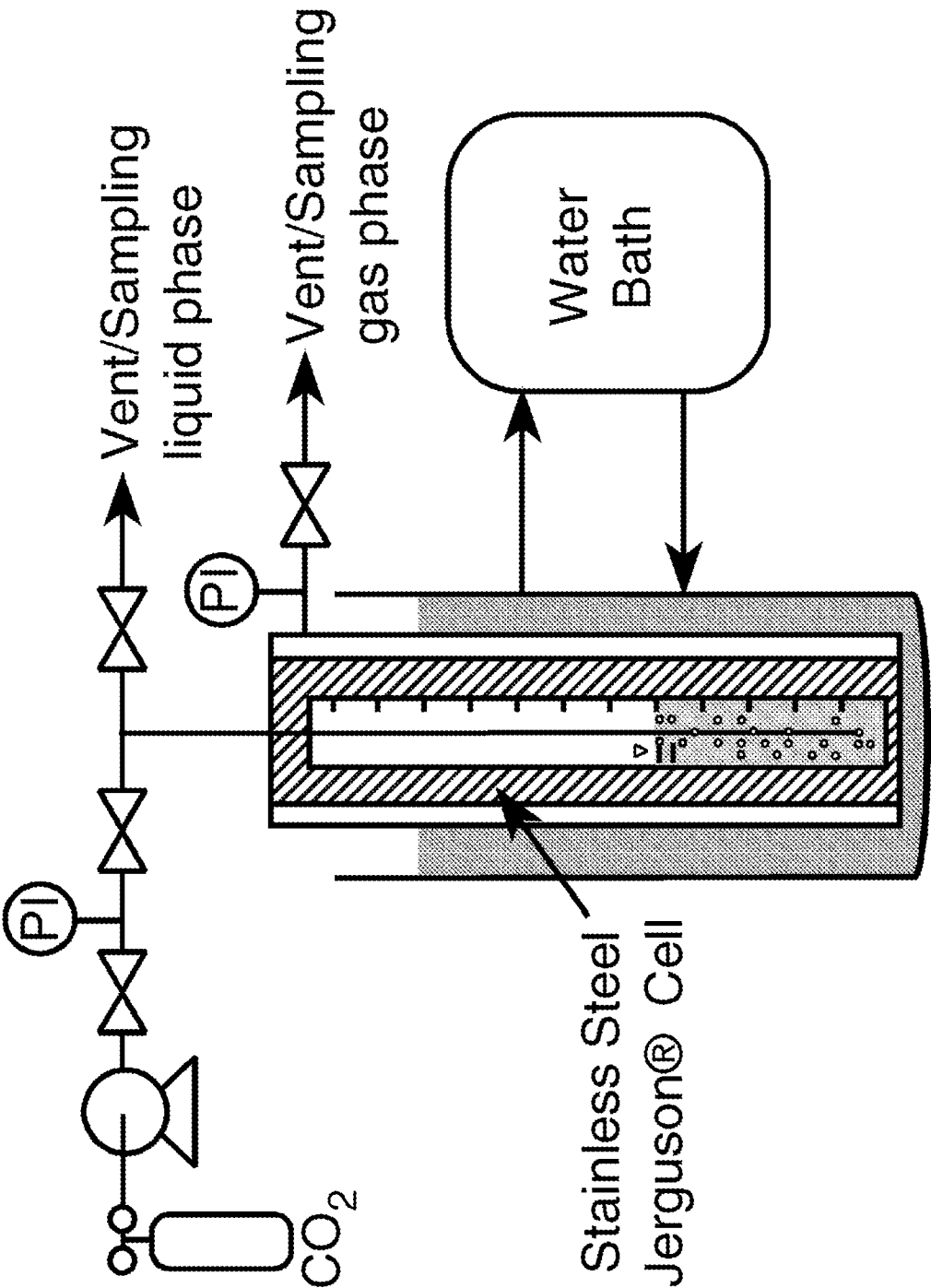


FIG. 2

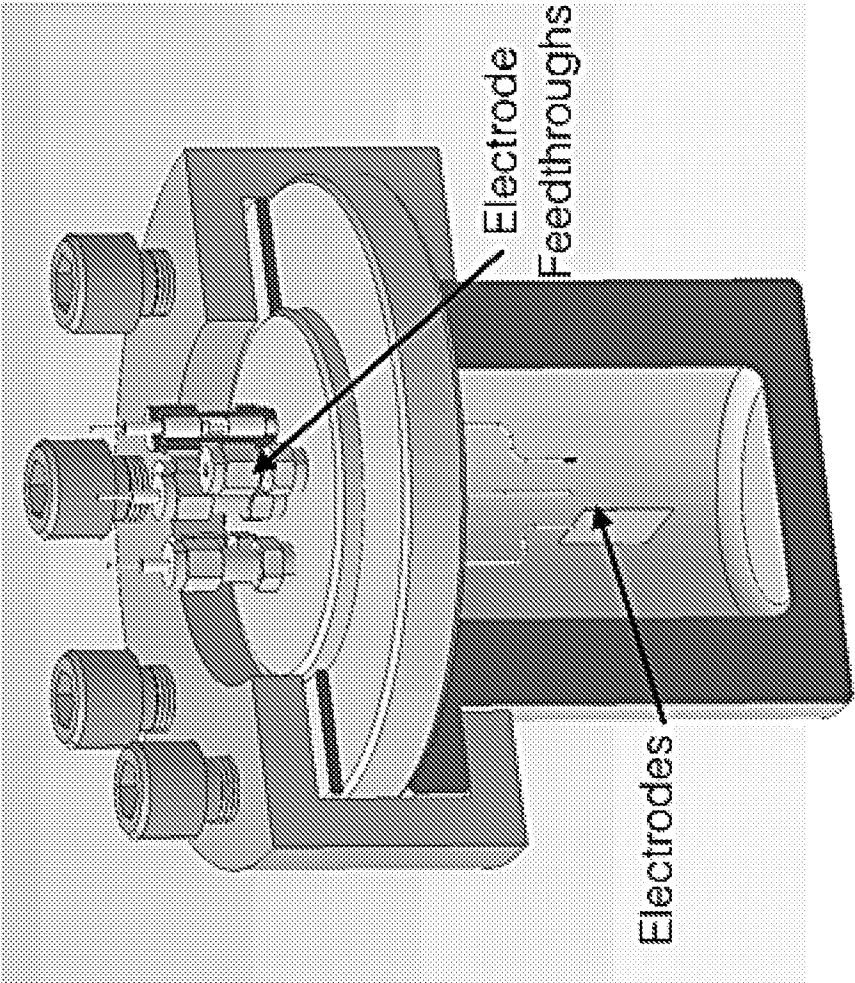


FIG. 3

4/13

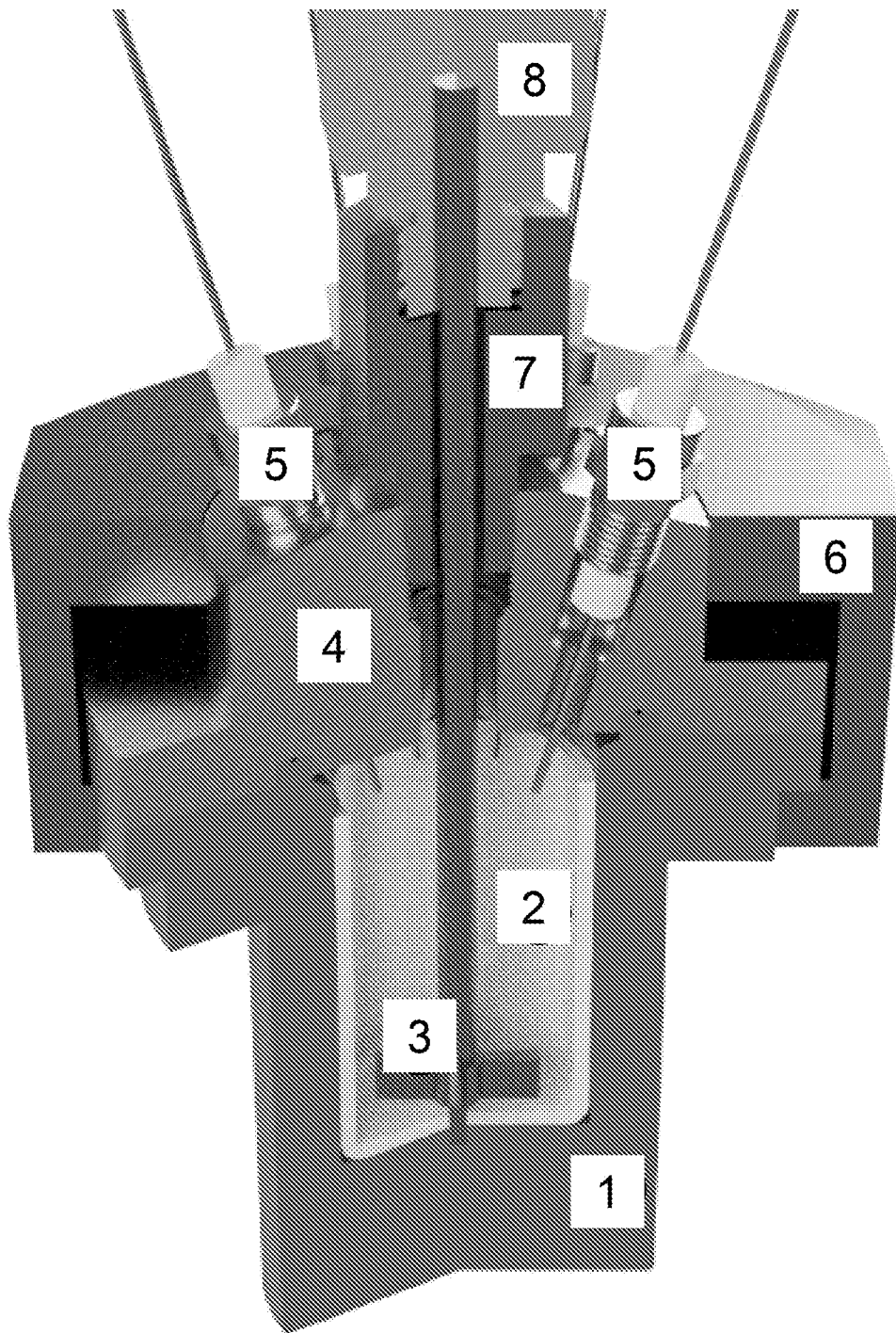
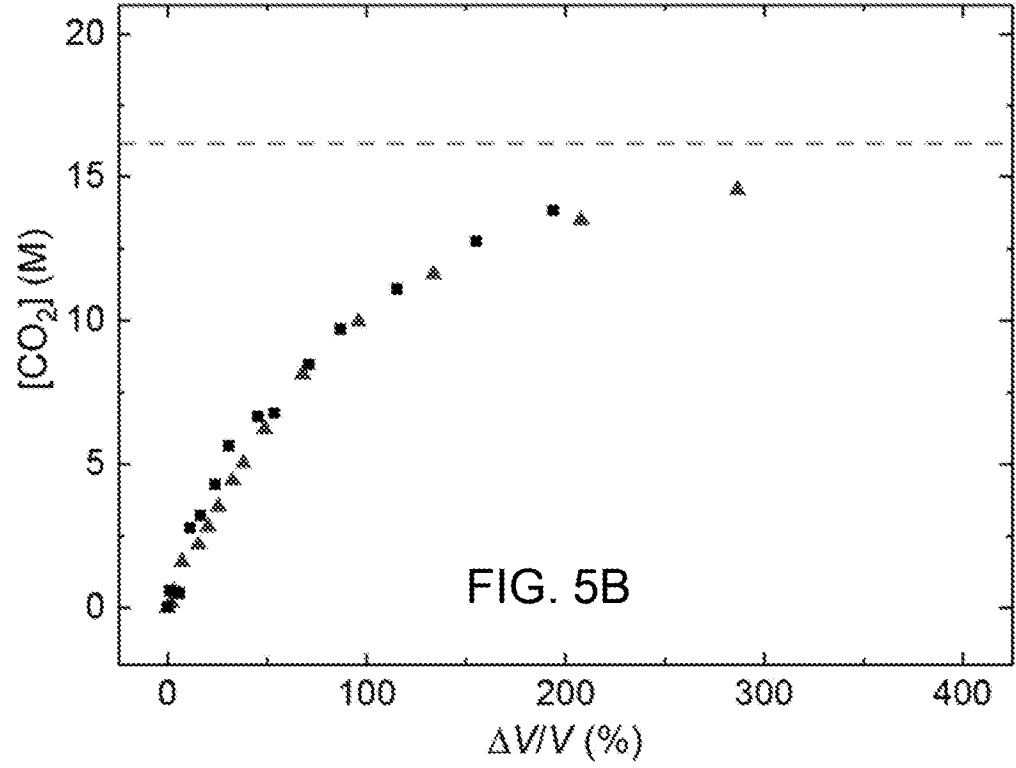
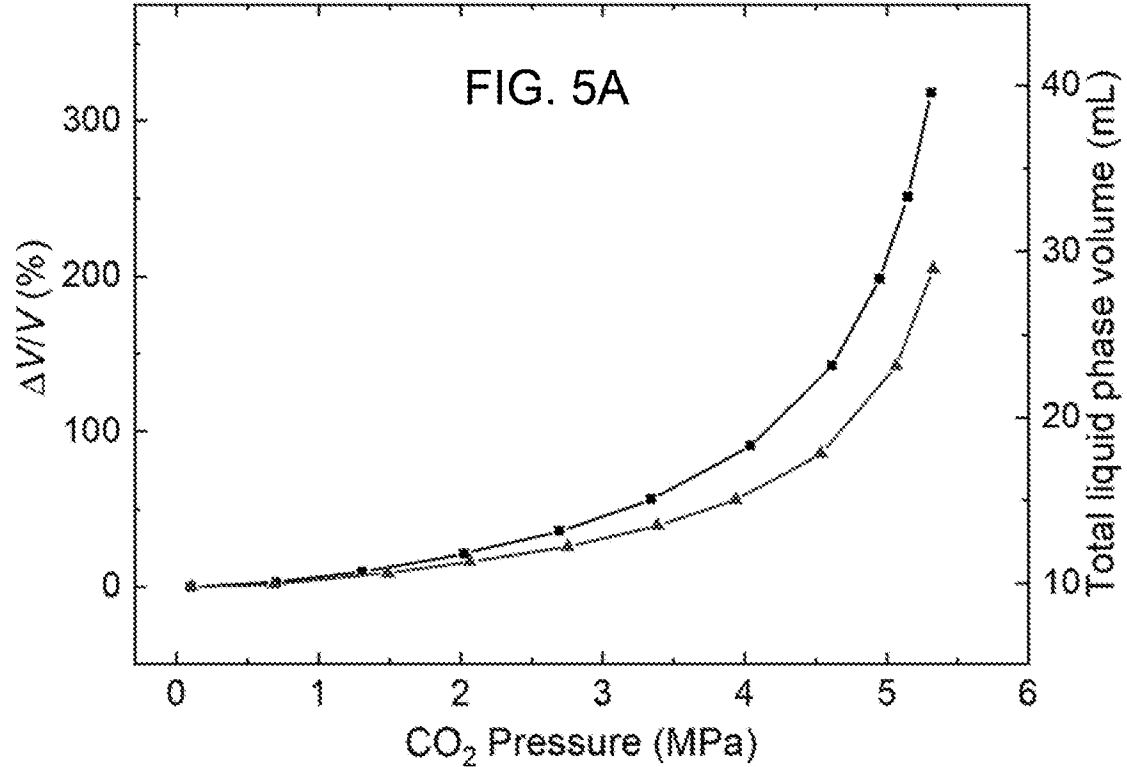


FIG. 4



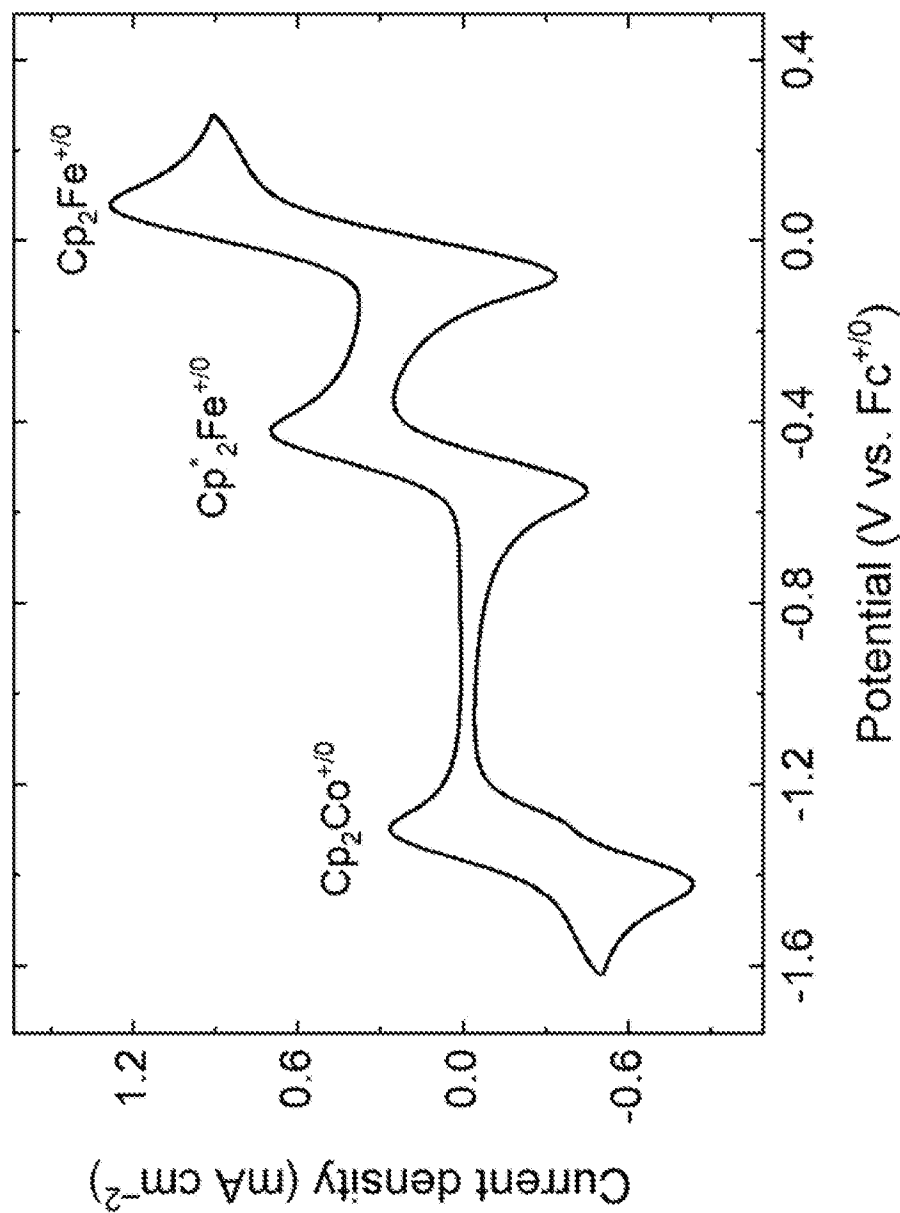


FIG. 5C

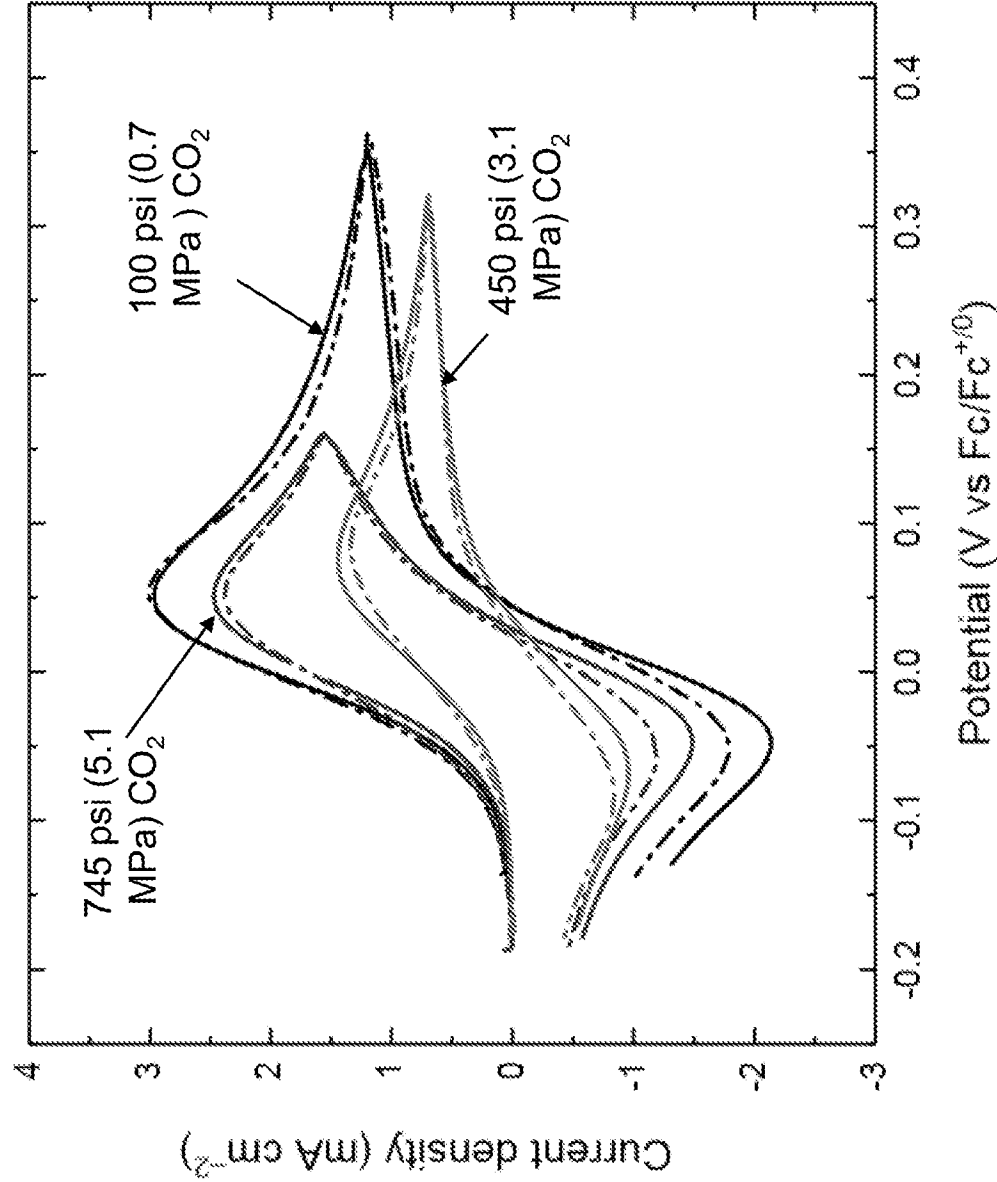


FIG. 6A

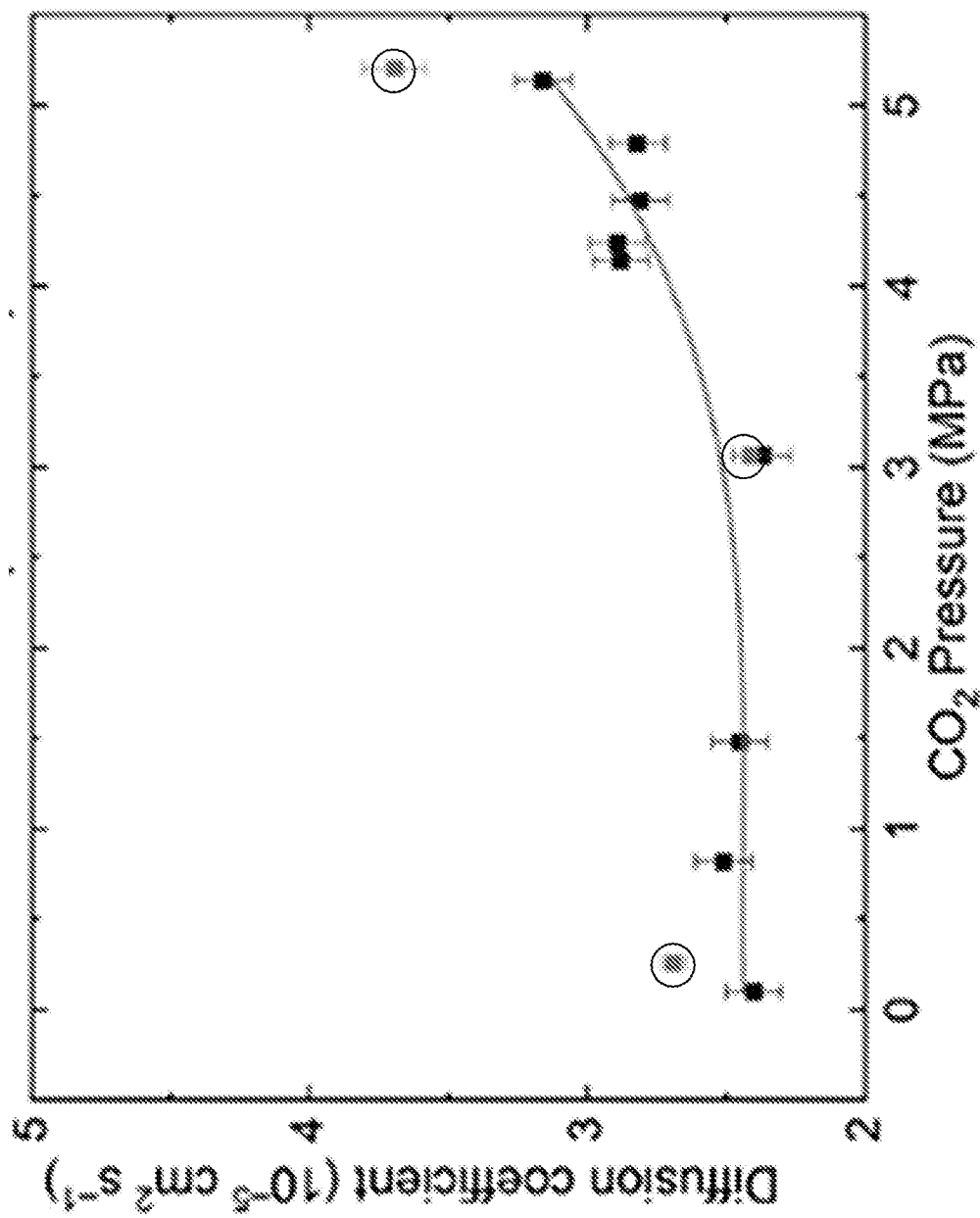
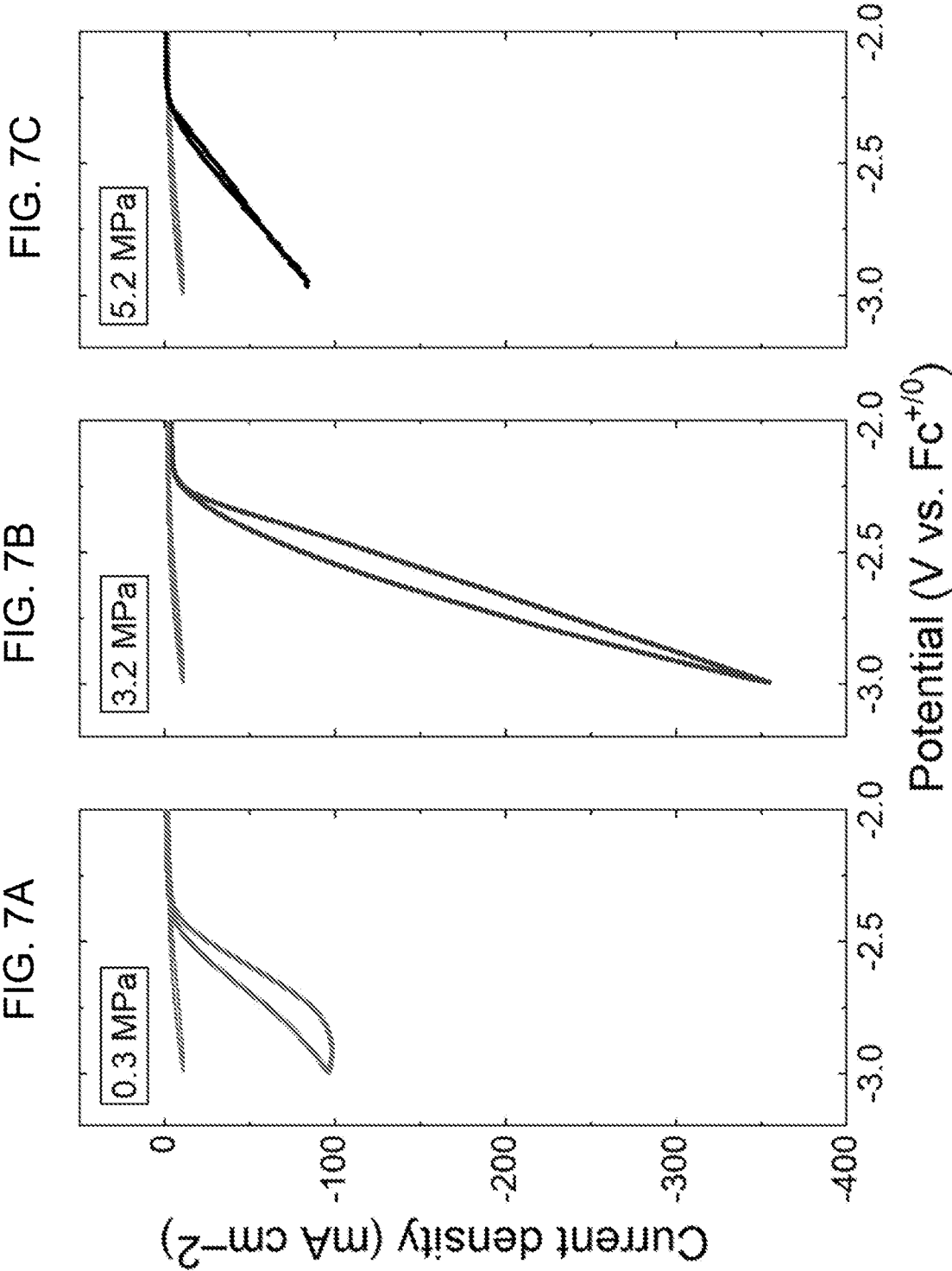


FIG. 6B



10/13

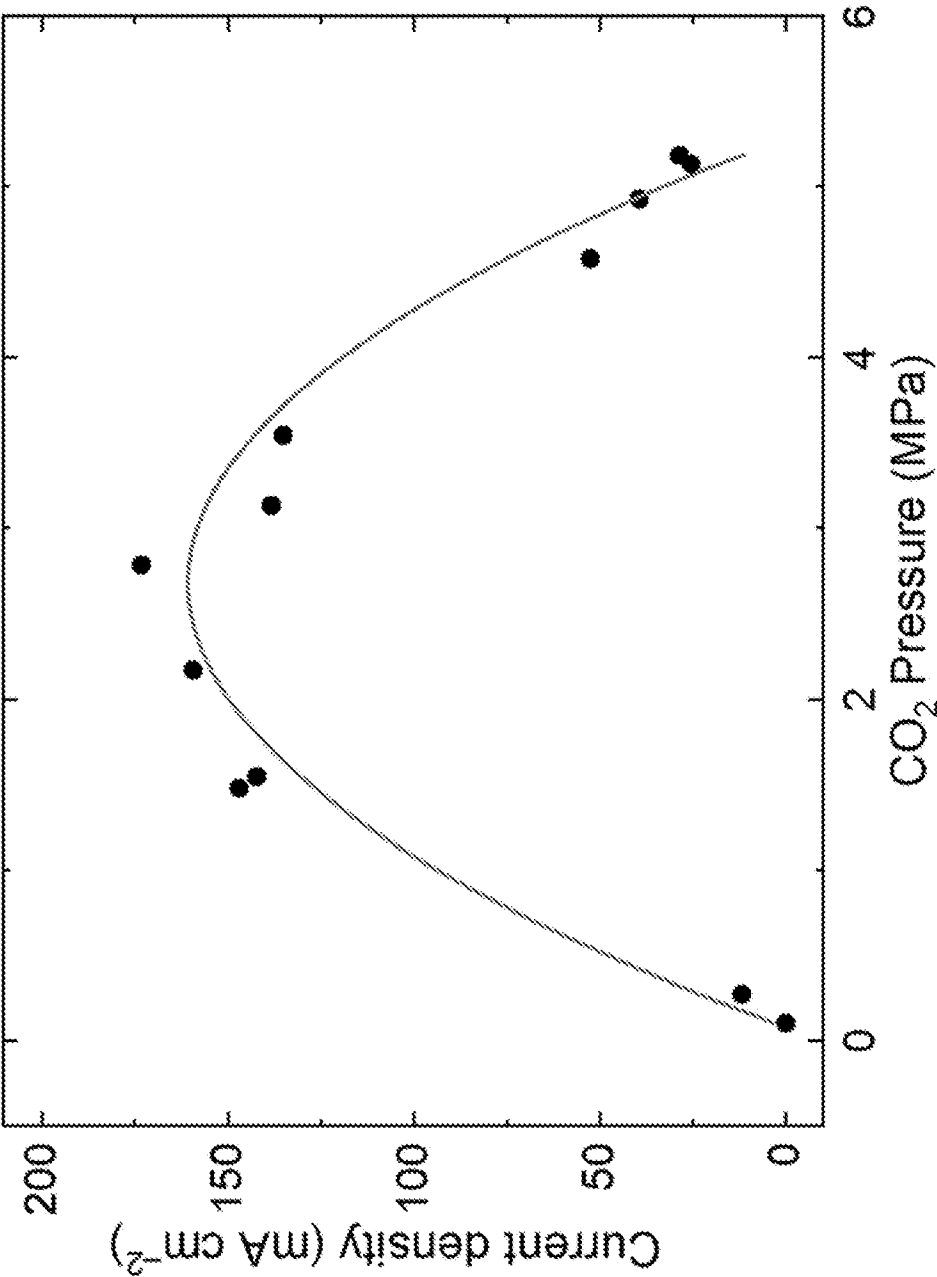


FIG. 7D

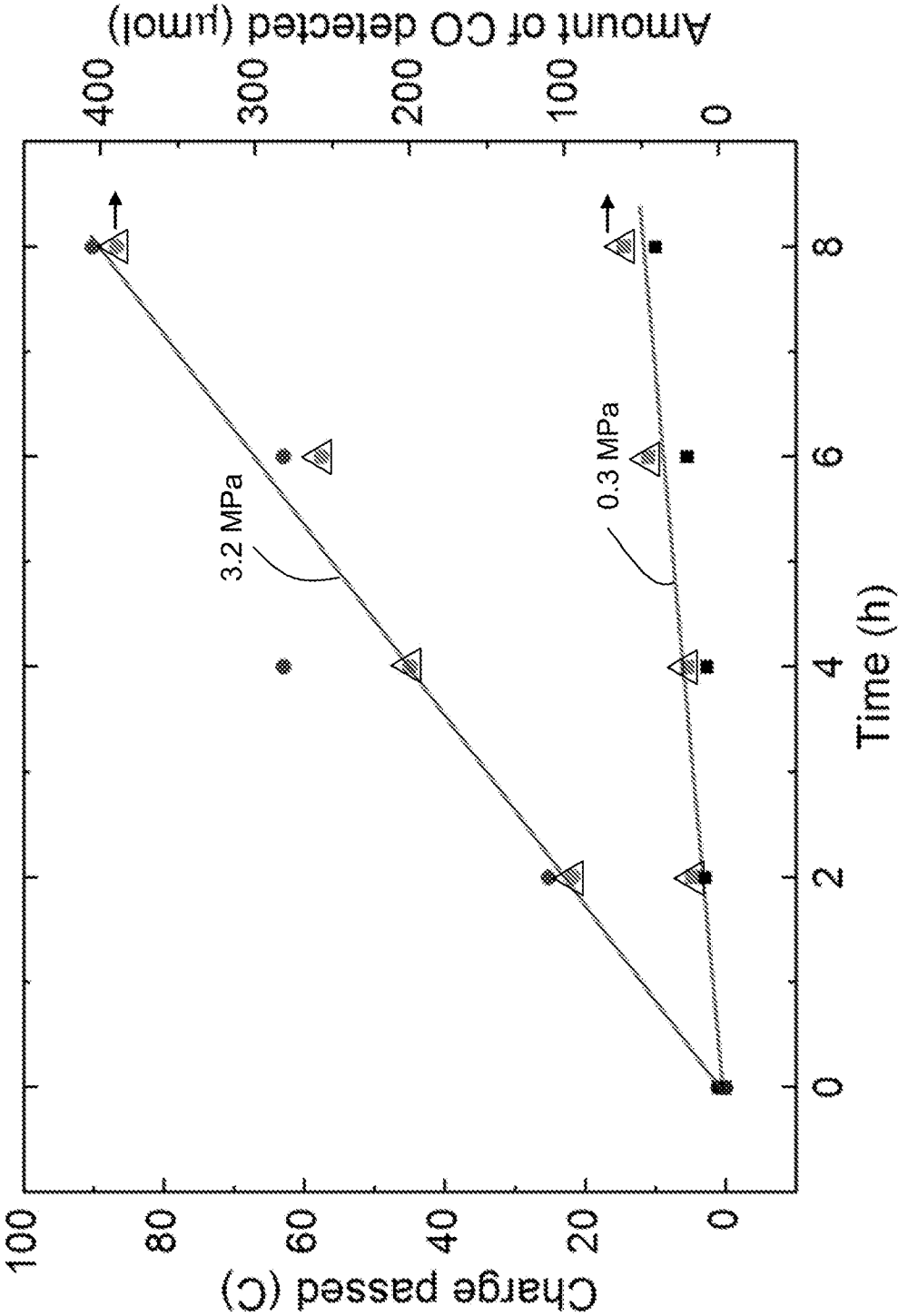


FIG. 8A

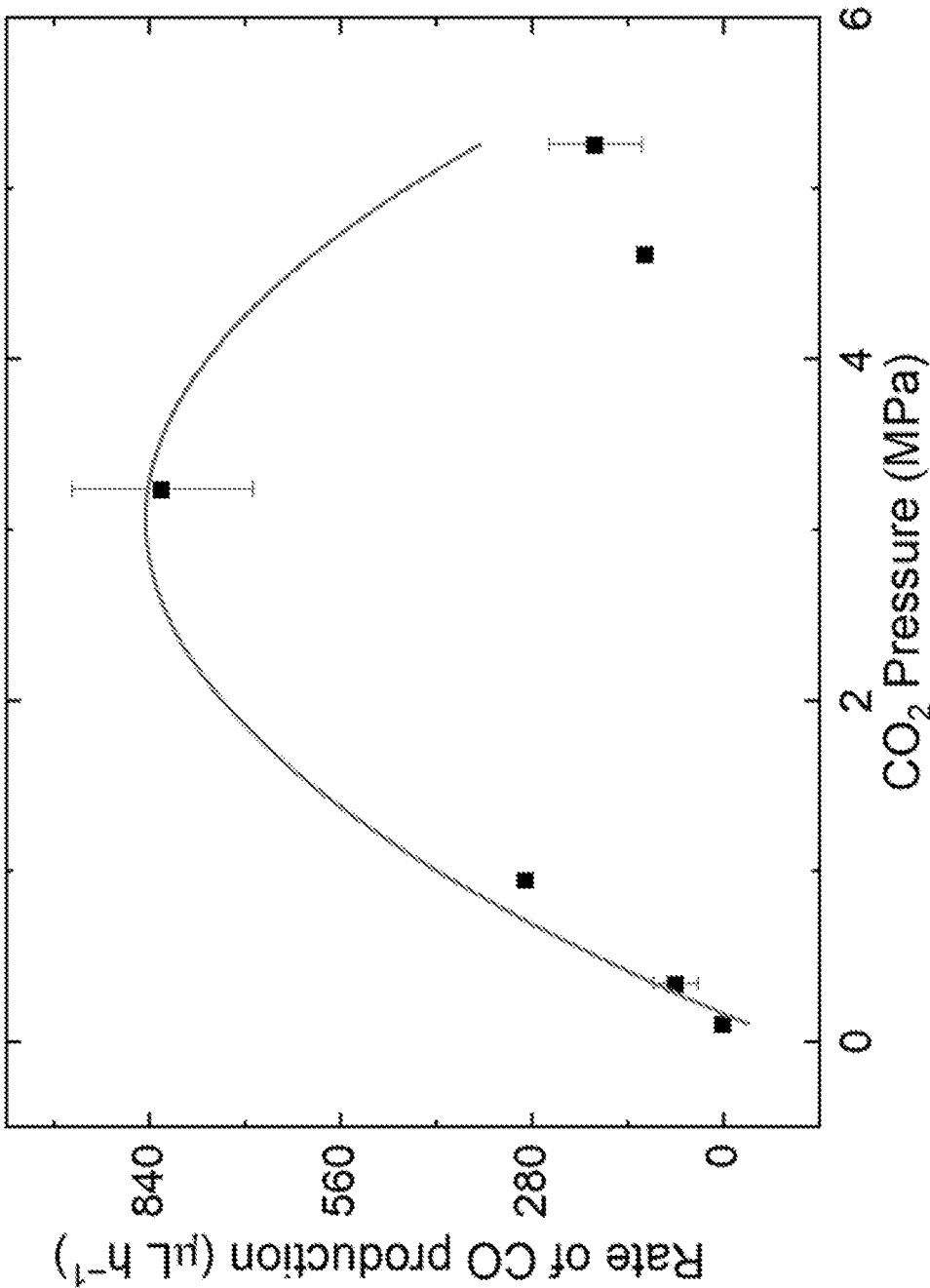


FIG. 8B

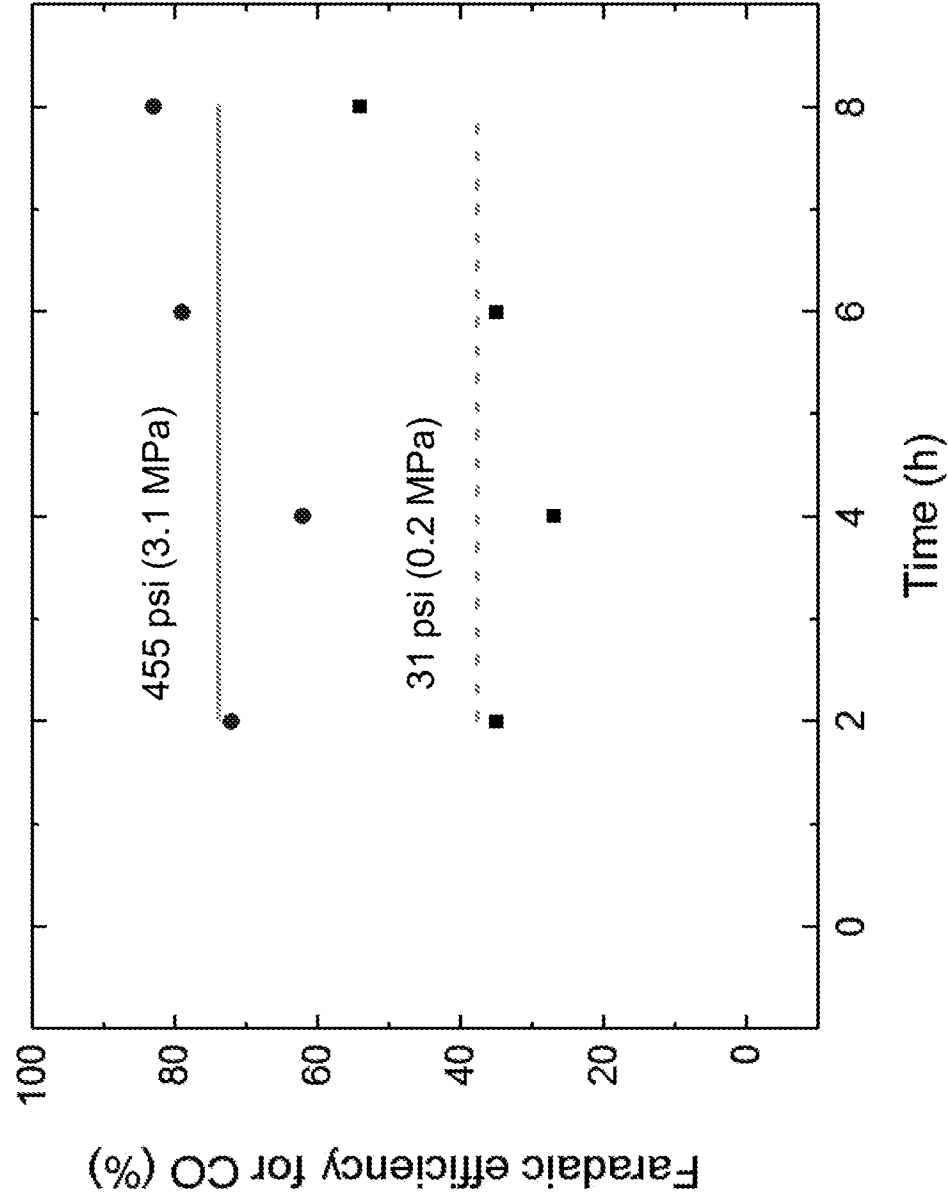


FIG. 8C

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US19/40671

A. CLASSIFICATION OF SUBJECT MATTER

IPC - C25B 1/00, 3/04; B01D 53/32; B01J 31/02 (2019.01)

CPC - C25B 1/00, 3/04; B01D 53/326, 53/32; B01J 31/02

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)

See Search History document

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

See Search History document

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

See Search History document

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 2016/178590 A1 (OMNIDEA, LDA.) 10 November 2016; abstract; page 18, lines 580-591; claim 1	1
A	WEI, M et al. CO ₂ -Expanded Solvents: Unique and Versatile Media for Performing Homogeneous Catalytic Oxidations. J. AM. CHEM. SOC. 16 February 2002. Vol. 124. No. 11. DOI: 10.1021/ja0114411; pages 2514-2516, table 1	1
A	SUBRAMANIAM, B. Exploiting Neoteric Solvents for Sustainable Catalysis and Reaction Engineering: Opportunities and Challenges. Ind. Eng. Chem. Res. 2010. Vol. 49, page 10221	1
P, X	SHAUGHNESSY, CI et al. Intensified Electrocatalytic CO ₂ Conversion in Pressure-Tunable CO ₂ -Expanded Electrolytes. ChemSusChem. 06 June 2019. Vol 12. DOI: 10.1002/cssc.201901107; abstract; pages 2-3	1

☐ Further documents are listed in the continuation of Box C.

☐ See patent family annex.

* Special categories of cited documents:

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"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

20 August 2019 (20.08.2019)

Date of mailing of the international search report

13 SEP 2019

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