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(54) Title: ELECTROCHEMICAL CAPTURE AND RELEASE OF CO_2 USING INORGANIC SORBENT MATERIALS

(57) Abstract: An electrochemical method and associated system for adsorption and desorption of CO_2. The system comprises a porous inorganic oxide electrode and a non-aqueous solution comprising a dissolved electrolyte. The method comprises contacting the electrode with a gaseous input comprising CO_2 wherein the CO_2 saturates the electrolyte, and applying a negative voltage wherein the CO_2 is adsorbed to the electrode. Once saturated, desorption of the CO_2 from the inorganic oxide electrode is achieved by applying a positive voltage.

ELECTROCHEMICAL CAPTURE AND RELEASE OF CO_2 USING INORGANIC SORBENT MATERIALS

CROSS-REFERENCE TO RELATED APPLICATIONS

Priority is hereby claimed to U.S. provisional application Ser. No. 63/611,459, filed December 18, 2023, which is incorporated herein by reference.

BACKGROUND

Worldwide energy consumption is estimated to increase to 850 QBtu by 2050. (Raimi, D. et al., Global energy outlook 2022: Turning points and tension in the energy transition. *Resources for the Future: Washington, DC, USA* **2022**.) Fossil fuels are projected to remain the dominant source of energy and are predicted to cause more than 50 Gigatons of CO_2 emissions per year. (*Id.*) To limit the impact of CO_2 on global climate patterns, the development of efficient methods to capture and convert CO_2 to useful chemicals is of paramount importance. At the heart of this challenge is the effective adsorption of CO_2 to surfaces. See, for example, Alsarhan, L. M. et al., Circular carbon economy (CCE): A way to invest CO_2 and protect the environment, a review. *Sustainability* **2021**, 13 (21), 11625.

Current technology for CO_2 capture uses nucleophilic sorbent materials that can selectively bind to CO_2 molecules from dilute streams. Upon reaction of CO_2 with inorganic materials such as calcium hydroxide and organic materials such as amines and supported amines, temperature or pressure is applied to transfer the CO_2 to reservoirs of higher CO_2 concentration, while the sorbent material is regenerated and reused for further CO_2 absorption in subsequent capture cycles.

An example of this technology uses alkaline carbonates to remove CO_2. In this system, K_2CO_3 reacts with water and CO_2 to form $KHCO_3$. See Smith, K. et al., Demonstration of a concentrated potassium carbonate process for CO_2 capture. *Energy & fuels* **2014**, 28 (1), 299-306. The shortcoming of this approach is the high thermal energy required for regeneration (130 to 220 kJ mol^{-1}) and the slow absorption kinetics. (Hu, G. et al., Carbon dioxide absorption into promoted potassium carbonate solutions: A review. *International Journal of Greenhouse Gas Control* **2016**, 53, 28-40.) Temperature swing approaches are commonly applied to capture CO_2 via amines such as alkanolamines and alkanamines. Carbamate and protonated amine pairs or bicarbonates are formed after the CO_2 absorption process, followed by regeneration through application of both heat and vacuum. Typically, the thermal energies required for regeneration are around 100 to 180 kJ mol^{-1}, but inefficiencies in the plant design decrease the efficiency by 20 to 25 %. Unfortunately, the amines are prone to decomposition under typical operating

temperatures as well as forming carcinogenic products when reacting with contaminants in the CO_2 gas streams, such as NO_x and SO_x. See Chen et al., Emerging N-nitrosamines and N-nitramines from amine-based post-combustion CO_2 capture–a review. *Chemical Engineering Journal* **2018**, 335, 921-935.

Current progress in designing electrochemical CO_2 capture methods has involved the use of redox active quinones as carriers for CO_2. The current systems, however, are not stable in the presence of O_2, resulting in the formation of superoxide that destructively reacts with the electrolyte, solvent, and quinones. See Jeziorek, D. et al., Theoretical and electrochemical study of the mechanism of anthraquinone-mediated one-electron reduction of oxygen: the involvement of adducts of dioxygen species to anthraquinones. *Journal of the Chemical Society, Perkin Transactions 2* **1997**, (2), 229-236. For example, when using 2,3,5,6-tetrachloro-p-benzoquinone for electrochemical CO_2 capture under a mix of 87:10:3 of N_2:CO_2:O_2, quinones only survived a single adsorption-release cycle. (Barlow, J. M. et al., Oxygen-stable electrochemical CO_2 capture and concentration with quinones using alcohol additives. *Journal of the American Chemical Society* **2022**, 144 (31), 14161-14169.) Poly(1,4-anthraquinone) supported on carbon was more energy efficient (40 to 90 kJ mol^{-1}) and lost about 30 % capacity after 7000 adsorption/desorption cycles under anaerobic conditions. (Voskian, S. et al., Faradaic electro-swing reactive adsorption for CO_2 capture. *Energy & Environmental Science* **2019**, 12 (12), 3530-3547.) Typically, the use of organics in electrochemical CO_2-capturing processes, such as electrochemically mediated amine regeneration and proton-coupled electron transfer-mediated CO_2 capture involves expensive membranes. (Renfrew, S. E. et al., Electrochemical approaches toward CO_2 capture and concentration. *ACS Catalysis* **2020**, 10 (21), 13058-13074.) Thus, there remains a long-felt and unmet need to develop economical CO_2 capture systems that address both the efficiency and stability challenges.

SUMMARY

Disclosed herein is an electrochemical method and associated system / apparatus for the adsorption/desorption of CO_2. The system includes a porous inorganic oxide electrode (*e.g.*, TiO_2) disposed in a non-aqueous solution comprising a dissolved electrolyte (*e.g.*, tetrabutylammonium hexafluorophosphate ($TBAPF_6$)). In operation, a gaseous input comprising CO_2 is introduced whereupon it saturates the electrolyte with CO_2. A negative voltage is applied to the electrode to generate nucleophilic sites on the surface of the inorganic oxide electrode which subsequently adsorbs the CO_2 from the electrolyte solution. Once the electrode is saturated with CO_2, the adsorbed CO_2 is desorbed from the electrode by applying a positive

voltage. In an exemplary system shown herein, a voltage sweep of –1.7 V to 0.6 V was sufficient to adsorb and desorb the CO_2.

Thus, disclosed herein is a method of adsorbing CO_2 in a gaseous input, the method comprising:

contacting the gaseous input with a non-aqueous solution comprising a dissolved electrolyte and having disposed therein

a working electrode comprising a porous inorganic oxide, and

a counter electrode; and

applying a negative voltage across the electrodes wherein at least a portion of the CO_2 in the gaseous input is adsorbed to the working electrode.

Preferably, the inorganic oxide comprises at least one reducible oxide. Non-limiting examples of suitable reducible oxides include TiO_2, WO_3, SnO_2, Sb-SnO_2, In-SnO_2, and the like. In certain versions, the inorganic oxide comprises TiO_2.

The electrolyte may comprise $TBAPF_6$. In certain versions, the electrolyte may comprise $TBAPF_6$ and 1-ethyl-3-methylimidazolium tetrafluoroborate ($EMIMBF_4$).

Preferably, the negative voltage applied to the electrode to adsorb CO_2 ranges from about -1.2 to about -1.8 V. Voltages above and below this range are explicitly within the scope of the disclosed method.

The method may further comprise sparging the electrolyte with a noble gas after applying the negative voltage.

The method may further comprise applying a positive voltage across the electrodes to desorb the CO_2. The positive voltage can be applied by a positive sweep of potential from the negative voltage.

Also disclosed herein is a system configured to adsorb and desorb CO_2, the system comprising:

a working electrode comprising a porous inorganic oxide;

a counter electrode; and

a non-aqueous solution comprising a dissolved electrolyte.

The inorganic oxide of the working electrode comprises at least one reducible oxide. In certain versions, the inorganic oxide comprises one or more of TiO_2, WO_3, SnO_2, Sb-SnO_2, and In-SnO_2. In certain versions, the inorganic oxide comprises TiO_2.

The electrolyte may comprise $TBAPF_6$. In certain versions, the electrolyte may comprise $TBAPF_6$ and $EMIMBF_4$.

The method and system described herein address both the efficiency and stability challenges associated with current CO_2 capture systems (*e.g.*, energy intensive desorption

processes and degradation of organic materials via radical formation). Instead of applying substantial amounts of heat, the present method relies on the application of current at select voltages. In addition, the use of reducible inorganic oxides as electrosorbents (*e.g.*, TiO_2) addresses both the energy and stability limitations described above. Further, an electrochemical approach has the potential to be agnostic to the CO_2 concentration in the source gas. The method can also be run entirely on renewable electricity, thereby avoiding CO_2-generating externalities.

The objects and advantages of the disclosure will appear more fully from the following detailed description of the preferred embodiment of the disclosure made in conjunction with the accompanying drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1: A schematic illustration of the electrochemical adsorption and desorption process of CO_2 on TiO_2 as described herein.

Fig. 2: A scanning electron microscopic image of porous TiO_2.

Fig.3: A graph showing the current caused by CO_2 desorption by running a CV scan from −1.7 V to 0.6 V.

Fig. 4: A GC chromatogram showing signals of CO_2 desorbed from a porous TiO_2 electrode after an oxidative cyclovoltammetry scan from −1.5 V to 0.6 V vs Ag/AgCl (10), and signals of CO_2 remaining in acetonitrile solution after Ar sparging but before the oxidative desorption (12).

Fig. 5: A histogram showing maximum (white) and minimum (black) energies required to capture 1 mol of CO_2 under flue gas conditions. GM NPQ (glyme-modified naphthoquinone) derivative was tested under anaerobic conditions. The porous TiO_2 system according to the present disclosure is circled. Abbreviations: MCDI: membrane capacitive deionization; PCET: proton-coupled electron transfer; BPMED: bipolar membrane electrodialysis; EMAR: electrochemically mediated amine regeneration; Co-SAC PSE: cobalt single atom catalyst porous solid electrolyte; GM NPQ: glyme-modified naphthoquinone; PAQ-CNT: Polyanthraquinone carbon nanotubes.

Fig. 6: Cyclic voltammetry scans of porous TiO_2 electrode after holding potentials in saturated CO_2 acetonitrile, 0.1 M $TBAPF_6$ (2000 seconds) at −1.7 V (26), −1.6 V (22) and −1.5 V (18). The dashed lines 24 (−1.7 V), 20 (−1.6 V), and 16 (−1.5 V) are cyclic voltammetry scans performed under the corresponding potential conditions but under saturated CO_2 solutions for 800 seconds, then followed by 1200 seconds of argon sparging while maintaining the potential hold. The solid line 14 is the cyclic voltammetry scan of argon-saturated solution.

Fig. 7: Cyclic voltammetry scans of porous TiO_2 electrode after holding potentials in saturated CO_2 acetonitrile, 0.1 M $TBAPF_6$ and varying $EMIMBF_4$ concentrations. The solid "Ar" line at bottom is a cyclic voltammetry scan of argon-saturated solution.

Fig. 8: Cyclic voltammetry scans of porous TiO_2 after holding potentials (−1.7 V, 600 seconds) in CO_2 saturated acetonitrile, 0.1 M $TBAPF_6$ and 0.02 M $EMIMBF_4$ concentrations. Cyclic voltammetry scans of porous TiO_2 electrode, placed in the same electrolyte concentrations and holding potential value, but for 600 seconds in saturated CO_2 solution and 1200 seconds under argon sparging. The cyclic voltammetry scan of argon-saturated solution is shown in the solid "Ar" line at bottom.

DETAILED DESCRIPTION

Abbreviations and Definitions

ATO = Antimony-doped Tin Oxide (Sb-SnO_2).

$EMIMBF_4$ = 1-Ethyl-3-methylimidazolium tetrafluoroborate.

ITO = Indium tin oxide (In-SnO_2).

$TBAPF_6$ = Tetrabutylammonium hexafluorophosphate.

"Non-aqueous solvent" is used broadly herein to denote solvents other than water. Non-aqueous polar aprotic solvents are generally preferred, including but not limited to acetone, acetonitrile, dichloromethane, dimethylformamide, dimethyl sulfoxide, ethyl acetate, pyridine, sulfolane, tetrahydrofuran, and the like. Additionally, carbonate solvents may also be used, including, but not limited to ethylene carbonate, diethyl carbonate. ethyl methyl carbonate, vinylene carbonate, and the like. Halogenated benzenes, such as fluorobenzenes, may also be used. Ionic liquids such as imidazoles and their cations (imidzaoliums) may also be used – *e.g.*, ethylmethylimidazolium, dimethylimidazolium, etc. Also included within the definition are stable anions such as tetrafluorborate, perchlorate, and the like. Also included are halogenated acids such as trifluoromethanesulfonic acid.

Numerical ranges as used herein are intended to include every number and subset of numbers contained within that range, whether specifically disclosed or not. Further, these numerical ranges should be construed as providing support for a claim directed to any number or subset of numbers in that range. For example, a disclosure of from 1 to 10 should be construed as supporting a range of from 2 to 8, from 3 to 7, from 1 to 9, from 3.6 to 4.6, from 3.5 to 9.9, and so forth.

All references to singular characteristics or limitations of the present disclosure shall include the corresponding plural characteristic or limitation, and vice-versa, unless otherwise specified or clearly implied to the contrary by the context in which the reference is made. The

indefinite article "a" means "one or more," unless explicitly specified to the contrary. The word "or" is used inclusively and should be read as "and/or."

All combinations of method or process steps as used herein can be performed in any order, unless otherwise specified or clearly implied to the contrary by the context in which the referenced combination is made.

The methods of the present disclosure can comprise, consist of, or consist essentially of the essential elements and limitations of the method described herein, as well as any additional or optional ingredients, components, or limitations described herein or otherwise useful in electrochemistry. The disclosure provided herein may be practiced in the absence of any element or step which is not specifically disclosed herein.

Overview

To inhibit the exponential increase of atmospheric CO_2 concentrations and their negative effects in changing global climate patterns, the development of efficient methods to capture and convert CO_2 to useful chemicals is of paramount importance. Current technologies for CO_2 capture rely on changes in pressure and temperature to adsorb and release CO_2. Typically, the thermal energy required for CO_2 release is high (around 100 to 180 kJ mol^{-1}) and the adsorbents suffer from poor stability. Hope for better energy efficiencies was raised by the advent of electrochemical capture techniques. These approaches utilize electron transfer to an adsorbent (often a substituted quinone), which leads to the generation of negatively charged nucleophilic sites that reversibly bind to CO_2. Carbonates are formed in the process. Yet, like thermal sorbents, these electrochemical sorbents continue to suffer from poor energy efficiency and stability, often lasting for only a few cycles of adsorption / desorption.

In the present method, these shortcomings are addressed by directly linking the CO_2 adsorption site to the Fermi level of the electrode surface while avoiding the use of organic chemicals in the electrochemical CO_2 sorption. This is possible when using inorganic reducible oxides as electrosorption materials. Like quinones, these materials can take up electrons under reducing conditions, forming nucleophilic sites that bind CO_2. Because reducible oxides are only weakly able to promote the electrocatalytic transformation of CO_2 to other products, applying oxidizing conditions afterwards allows for the release of CO_2 from the material. Oxides are inorganic materials with very high mechanical, thermal, and electronic stability, thus the approach overcomes the major shortcomings of organic CO_2 electrosorbents.

The Method and System

To inhibit the exponential increase of atmospheric CO_2 concentrations and their negative effects in changing global climate patterns, the development of efficient methods to capture and convert CO_2 to useful chemicals is of paramount importance. Current technology for CO_2 capture relies on changes in pressure and temperature to adsorb and release CO_2. Typically, the thermal energy required for CO_2 release is high (around 100 to 180 kJ mol^{-1}) and the adsorbents suffer from poor stability. Commercial CO_2 capture plants from Climeworks (Zurich, Switzerland) use amine-functionalized sorbents such as 3-aminopropylmethyldiethoxysilane in thermal vacuum swings. They achieve relative stability only up to about 20 capture and release cycles. (Sim, Y. and Ruhaimi, A. Recent progress on (3-Aminopropyl) triethoxysilane (APTES) functionalized-adsorbent for CO_2 capture. In *Journal of Physics: Conference Series*, **2022**; IOP Publishing: Vol. 2259, p 012008.) However, even the 20-cycle limit was achieved under non-realistic conditions. Hope for better energy efficiencies was raised by the advent of electrochemical capture techniques using substituted quinones. Yet, like thermal sorbents, these electrochemical sorbents continue to suffer from poor stability and energy efficiency

Disclosed herein is a novel electrochemical method to adsorb and desorb carbon dioxide molecules on porous inorganic oxide electrodes. The method achieves better energy efficiency and far greater stability than the conventional organic sorbents. The method disclosed herein uses titanium dioxide (TiO_2) as a model compound inorganic oxide electrode. This is for brevity only. The method can be easily implemented using other reducible oxides. Non-limiting examples of the reducible oxides that can be used include WO_3, SnO_2, Sb-SnO_2 (ATO), In-SnO_2 (ITO), etc.

The present method rests on the property of TiO_2 (and other reducible inorganic oxides) to form nucleophilic sites upon reduction. These nucleophilic sites serve as adsorption sites for CO_2. Electrochemical reduction of TiO_2, transforms some Ti^{4+} sites to Ti^{3+}, which possess nucleophilic character. In the presence of H^+ or Li^+, for example, the charge on these reduced Ti centers is compensated by cation intercalation. This effect is used in some Li-ion batteries for energy storage ("LTO anodes"), where Li-intercalation and deintercalation can be carried out for thousands of cycles. This phenomenon confirms the robust stability of TiO_2-based electrodes. In absence of such ions, however, the negative charge can be stabilized through its transfer to CO_2, which leads to its binding in the form of a carbonate ion. Surprisingly, this effect has not been exploited for CO_2 capture. TiO_2 is shown herein to be an equally efficient and stable sorbent material for the electrochemical capture and release of CO_2.

As shown in **Fig. 1**, the designed system involves the use of a non-aqueous solution (*e.g.*, acetonitrile) with dissolved electrolytes as a medium for CO_2 capture, a surface of porous titania

as the working electrode, a counter electrode, a reference electrode, and a potentiostat. Mesoporous TiO_2 was prepared by deposition of a titania paste dispersed in ethanol, which was subsequently calcined at 500 °C for 30 minutes. The surface morphology of the porous TiO_2 surface is shown in **Fig. 2**, compared the morphology of the polished TiO_2 surface, the "rough" surface of the porous material is expected to accommodate adequate amount of CO_2 adsorption.

Through analysis via cyclic voltammetry (CV), linear sweep voltammetry (LSV) and gas chromatography (GC), it was demonstrated successful electrochemical adsorption and subsequent desorption of CO_2 in acetonitrile containing 0.1 M of tetrabutylammonium hexafluorophosphate ($TBAPF_6$) as supporting electrolyte. To adsorb CO_2, the electrolyte was saturated with CO_2 and a potential of -1.7 V *vs* Ag/AgCl was applied for up to 14 min. (The Ag/AgCl electrode was a "leakless electrode" acquired commercially from eDAQ Pty Ltd, Denistone East, NSW, Australia) While still applying the same potential, CO_2 was subsequently removed by sparging the electrolyte with argon. This step was followed by a positive sweep of the potential from -1.7 V to 0.6 V at 100 mV sec^{-1}. During this sweep, a current was observed corresponding to the desorption of CO_2, demonstrating that TiO_2 surfaces can be employed as an inorganic electrochemical CO_2 capture medium as shown in **Fig. 3**.

In **Fig. 4**, line 10 shows the released CO_2 dissolved in 1 mL of acetonitrile after adsorbing CO_2 at – 1.5 V *vs* Ag/AgCl followed by sparging the solvent with Ar to remove excess CO_2 in the solution. The amount of captured CO_2 is calculated to be 1.15 µmol from a 0.20 cm^2 TiO_2 surface. The total number of charges passing through the electrode during the adsorption process is 144 mC, thus if assuming CO_2 adsorption is a one electron process, the Faradaic efficiency is 90 %.

For efficient CO_2 capture, the potential gap between the onsets of desorption and adsorption should be as small as possible since this voltage difference represents a loss in energy between the potential at which adsorption takes place and the one at which CO_2 can be desorbed. The method demonstrates the onset of CO_2 adsorption is at slightly below -1.4 V. As the adsorption of CO_2 mostly occurred by holding the electrode under -1.7 V and the onset of desorption is at approximately 60 mV more positive or 6 kJ mol^{-1}, this is less than the 16 kJ mol^{-1} energy loss for the best sorbent material known to date, which is 4,4′-azopyridine. Even more, since the electrosorbent is an inorganic solid, it features substantially better stability than existing adsorbent materials. For example, a test was performed for 210 cycles; a capacity fade of only 3% was observed.

Table 1, below, compares results of the method and system disclosed herein to notable literature reports.

Table 1. Comparison to Conventional CO_2 Capture Methods

Material	**Captured CO_2 capacity**	**Energy consumed *per* mol CO_2**	**Efficiency**	**Cycle stability**	**Reference**
Porous TiO_2 (anaerobic)	5.75 μmol cm^{-2}	6 kJ mol^{-1}	90 %	210 cycles	Disclosed method and system
Polyanthraquinone on carbon nanotubes (PAQ-CNT) (anaerobic)	1.2 mmol $mmol^{-1}$	40 - 90 kJ mol^{-1}	~50% post	30 % capacity	1
4,4′–azopyridine	n/a	Theoretically 16 kJ mol^{-1}. flue gas 120 kJ mol^{-1}.	~87% average Coulombic efficiency	Stable within 14 cycles.	2
Glyme–modified naphthoquinone derivative (anaerobic)	~1.9 mmol $mmol^{-1}$	50 - 200 kJ mol^{-1}	~ 90% average Coulombic efficiency	Stable within 10 cycles.	3
Amine functionalized nanofibrated cellulose	~0.87 mmol g^{-1}	n/a	n/a	4 % decrease post 100 cycles	4
PAQ-CNT aqueous media	~ 5.46 mmol $mmol^{-1}$	56 kJ mol^{-1}	95.5% average Coulombic efficiency	10 % capacity loss after 75 cycles.	5

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2. Li, X.; Zhao, X.; Liu, Y.; Hatton, T. A.; Liu, Y. Redox-tunable Lewis bases for electrochemical carbon dioxide capture. *Nature Energy* **2022**, *7* (11), 1065-1075.
3. Diederichsen, K. M.; Liu, Y.; Ozbek, N.; Seo, H.; Hatton, T. A. Toward solvent-free continuous-flow electrochemically mediated carbon capture with high-concentration liquid quinone chemistry. *Joule* **2022**, *6* (1), 221-239.

4. Gebald, C.; Wurzbacher, J. A.; Tingaut, P.; Steinfeld, A. Stability of amine-functionalized cellulose during temperature-vacuum-swing cycling for CO_2 capture from air. *Environmental science & technology* **2013**, *47* (17), 10063-10070.

5. Liu, Y.; Ye, H; Diederichsen, K. M.; Van Voorhis, T.; Hatton, T. A. Electrochemically mediated carbon dioxide separation with quinone chemistry in salt-concentrated aqueous media. *Nature Communications* **2020**, 11, 2278.

As shown in **Fig. 5**, the maximum (white) and minimum (black) energies required to capture 1 mol of CO_2 under flue gas conditions were also compared. A GM NPQ (glyme-modified naphthoquinone) derivative was tested under anaerobic conditions. The porous TiO_2 system (circled) requires much less energy to capture 1 mol of CO_2 compared to other technologies.

Mechanistic Investigation

To gain insight into the electrochemical adsorption of CO_2 to TiO_2, a series of experimental investigations were performed, the results of which are displayed in **Fig. 6**. At 100 mV sec^{-1}, the largest desorption peak occurs at ca. –1.4 V. Secondary CO_2 desorption peaks appear at about –0.3 V and +0.2 V *vs* Ag/AgCl. These peaks have a much larger potential gap from the adsorption onset; therefore they are considered to have higher binding energies. The desorption peaks attributed to the higher binding energy sites decrease with increasing time of Ar sparging. Furthermore, none of the more strongly bound CO_2 was observed when adsorption of CO_2 was carried out at potentials below –1.6 V.

From a practical standpoint, CO_2 desorption from the higher binding energy sites is less useful (because it requires more energy). Therefore, the Ar sparging does not significantly affect the CO_2 binding at the preferred lower energies (preferred because of the small or non-existent adsorption/desorption potential gap). It also demonstrates that CO_2 is chemisorbed strongly enough that sparging in noble gases will not remove the adsorbed CO_2 on the TiO_2 surface.

When testing the impact of the electrolyte, a rise in the absolute quantity of CO_2 adsorbed was seen when adding $EMIMBF_4$, to the base $TBAPF_6$ electrolyte. This phenomenon was observed while keeping the porous TiO_2 electrode under the same conditions as mentioned above. **Fig. 7** shows this effect when increasing the concentration of $EMIMBF_4$ from 0 M to 0.04 M in 0.01 M intervals. Most importantly, much of the increase in desorption peak intensity is in the voltage range between –1.7 V to –1.2 V, which is the preferred desorption site due to the adsorption potentials being in the same region. The improved binding of CO_2 is due to improved stabilization of CO_2^- at the electrode surface. As shown in **Fig. 8**, with Ar sparging

applied, there is no evident loss of CO_2 adsorption on the TiO_2 surface compared to that without Ar sparging.

Advantages and Use of the System

The present disclosure addresses both the efficiency and stability challenges of current electrochemical CO_2 capture systems. The system works using very inexpensive materials, such as TiO_2, which is widely available and commonly used in white paint, coatings, ink and even toothpaste. Electrochemical CO_2 capture/release on inorganic oxides offers the ability to control the nucleophilicity of the electrode surface. Defining the difference of the onset potential at the desorption peak and the negative potential at which the electrode was held at during adsorption of CO_2, then the energy of releasing the captured low-binding energy CO_2 is calculated to be approximately 6 kJ mol^{-1} for when CO_2 was captured at -1.7 V. This energy is lower than that for typical pressure, temperature swings, and systems using quinones. Also, the present method and system does not require the membranes that are required when using organic compounds in electrochemical CO_2 capturing processes. Electrochemically mediated amine regeneration and proton-coupled electron transfer-mediated CO_2 capture requires such membranes to function.

The system disclosed herein can be used as a device to electrochemically capture CO_2 under ambient conditions. The method has a substantially smaller energy gap between the adsorption and desorption potential. The adsorbent material is entirely inorganic and can thus be expected to feature substantially higher stability than the commonly used organic sorbents which are notoriously unstable.

The system disclosed herein can be used as a component in enclosed spaces that require scrubbing of CO_2 from the local atmosphere, such as in high-altitude aircraft, spacecraft, and submarines. It can also be used to remove CO_2 from flue gas. The system disclosed herein will play a crucial part in the effort of using cheap and renewable electricity to capture and store CO_2, hence leaving investment opportunities for companies that wish to earn carbon credits or to avoid emission penalties.

CLAIMS

What is claimed is:

1. A method of adsorbing CO_2 in a gaseous input, the method comprising:

contacting the gaseous input with a non-aqueous solution comprising a dissolved electrolyte and having disposed therein

a working electrode comprising a porous inorganic oxide, and

a counter electrode: and

applying a negative voltage across the electrodes wherein at least a portion of the CO_2 in the gaseous input is adsorbed to the working electrode.

2. The method of claim 1, wherein the inorganic oxide comprises at least one reducible oxide.

3. The method of any one of claims 1-2, wherein the inorganic oxide comprises one or more of TiO_2, WO_3, SnO_2, Sb-SnO_2, and In-SnO_2.

4. The method of any one of claims 1-3, wherein the inorganic oxide comprises TiO_2.

5. The method of any one of claims 1-4, wherein the electrolyte comprises hexafluorophosphate ($TBAPF_6$).

6. The method of any one of claims 1-5, wherein the electrolyte comprises $TBAPF_6$ and 1-ethyl-3-methylimidazolium tetrafluoroborate ($EMIMBF_4$).

7. The method of any one of claims 1-6, wherein the CO_2 saturates the electrolyte upon contacting the gaseous input with the electrolyte.

8. The method of any one of claims 1-7, wherein the negative voltage ranges from about -1.2 to about -1.8 V.

9. The method of any one of claims 1-8, further comprising sparging the electrolyte with a noble gas after applying the negative voltage.

10. The method of any one of claims 1-9, further comprising applying a positive voltage across the electrodes to desorb the CO_2.

11. The method of claim 10, wherein the positive voltage is applied by a positive sweep of potential from the negative voltage.

12. A system configured to adsorb and desorb CO_2, the system comprising:
a working electrode comprising a porous inorganic oxide;
a counter electrode; and
a non-aqueous solution comprising a dissolved electrolyte.

13. The system of claim 12, wherein the inorganic oxide comprises at least one reducible oxide.

14. The system of any one of claims 12-13, wherein the inorganic oxide comprises one or more of TiO_2, WO_3, SnO_2, Sb-SnO_2, and In-SnO_2.

15. The system of any one of claims 12-14, wherein the inorganic oxide comprises TiO_2.

16. The system of any one of claims 12-15, wherein the electrolyte comprises $TBAPF_6$.

17. The system of any one of claims 12-16, wherein the electrolyte comprises $TBAPF_6$ and $EMIMBF_4$.

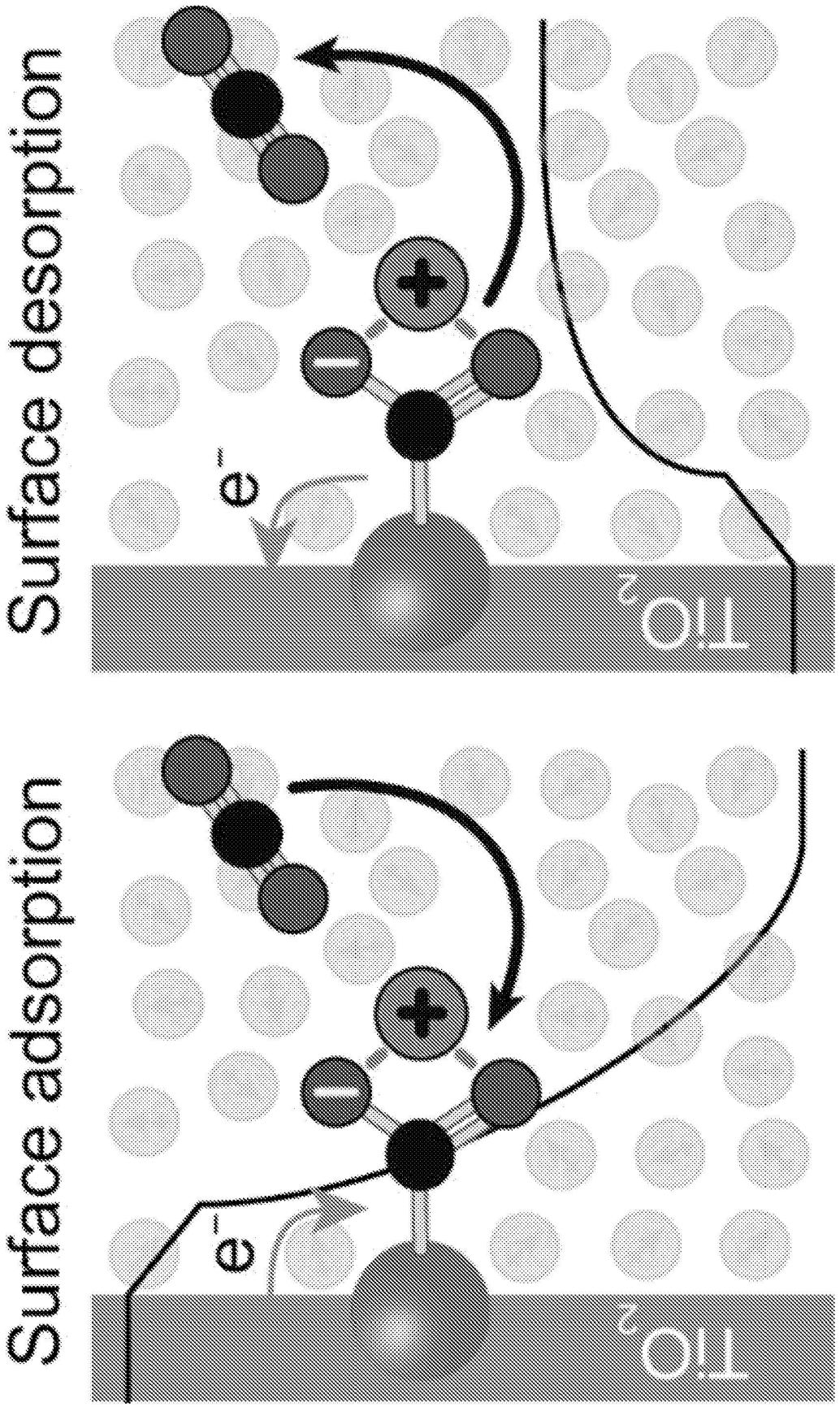

Fig. 1

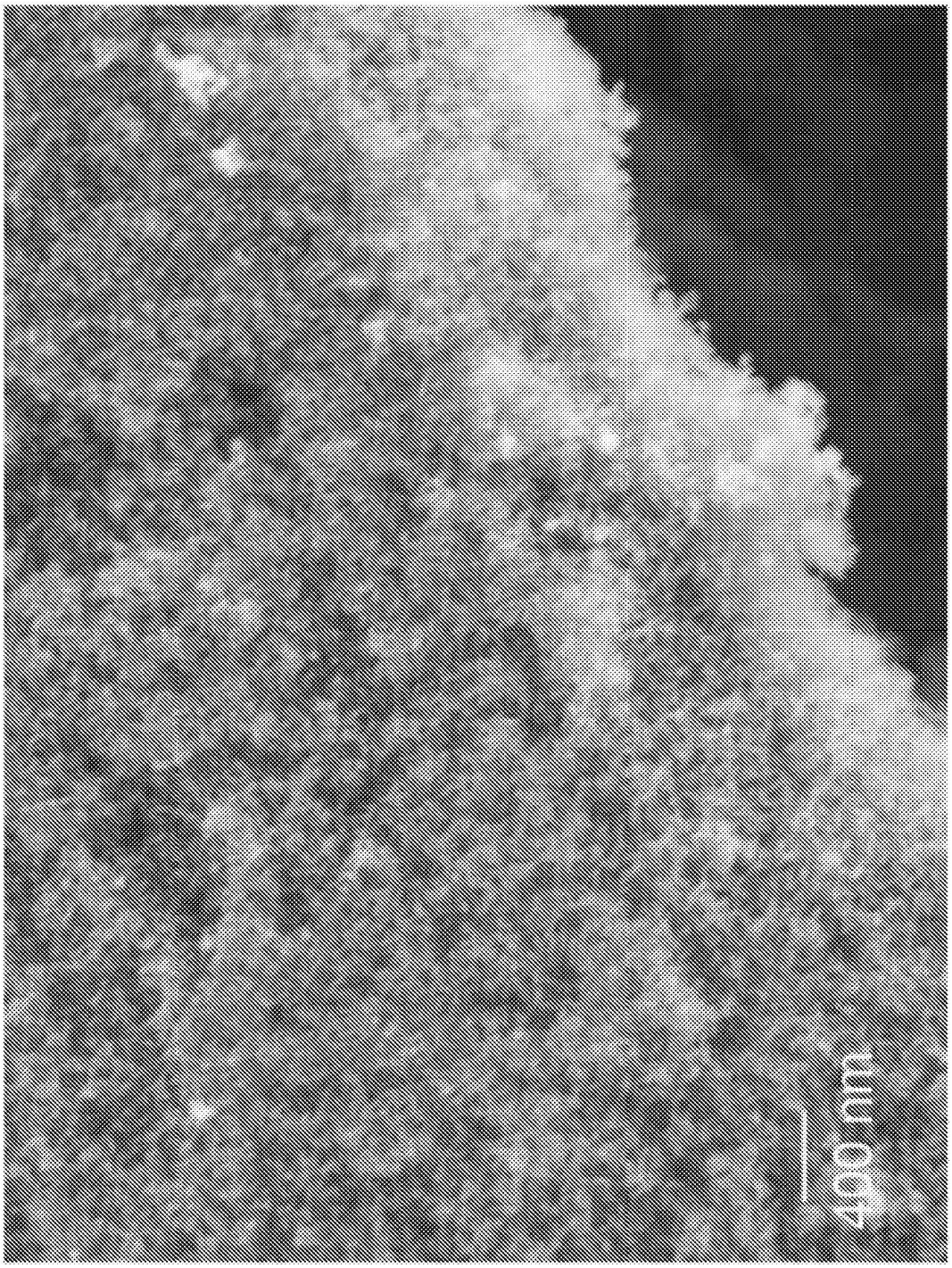

Fig. 2

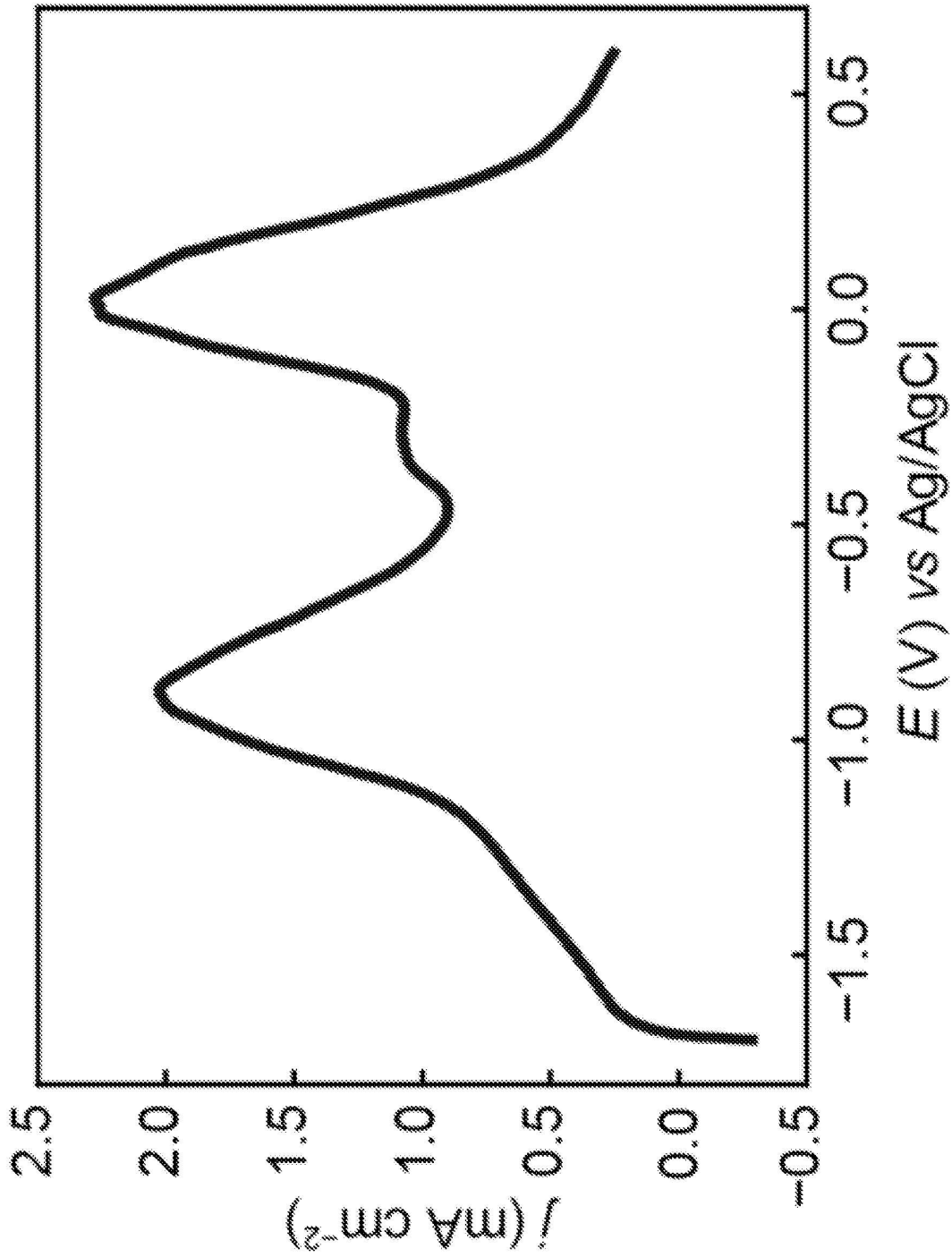

Fig. 3

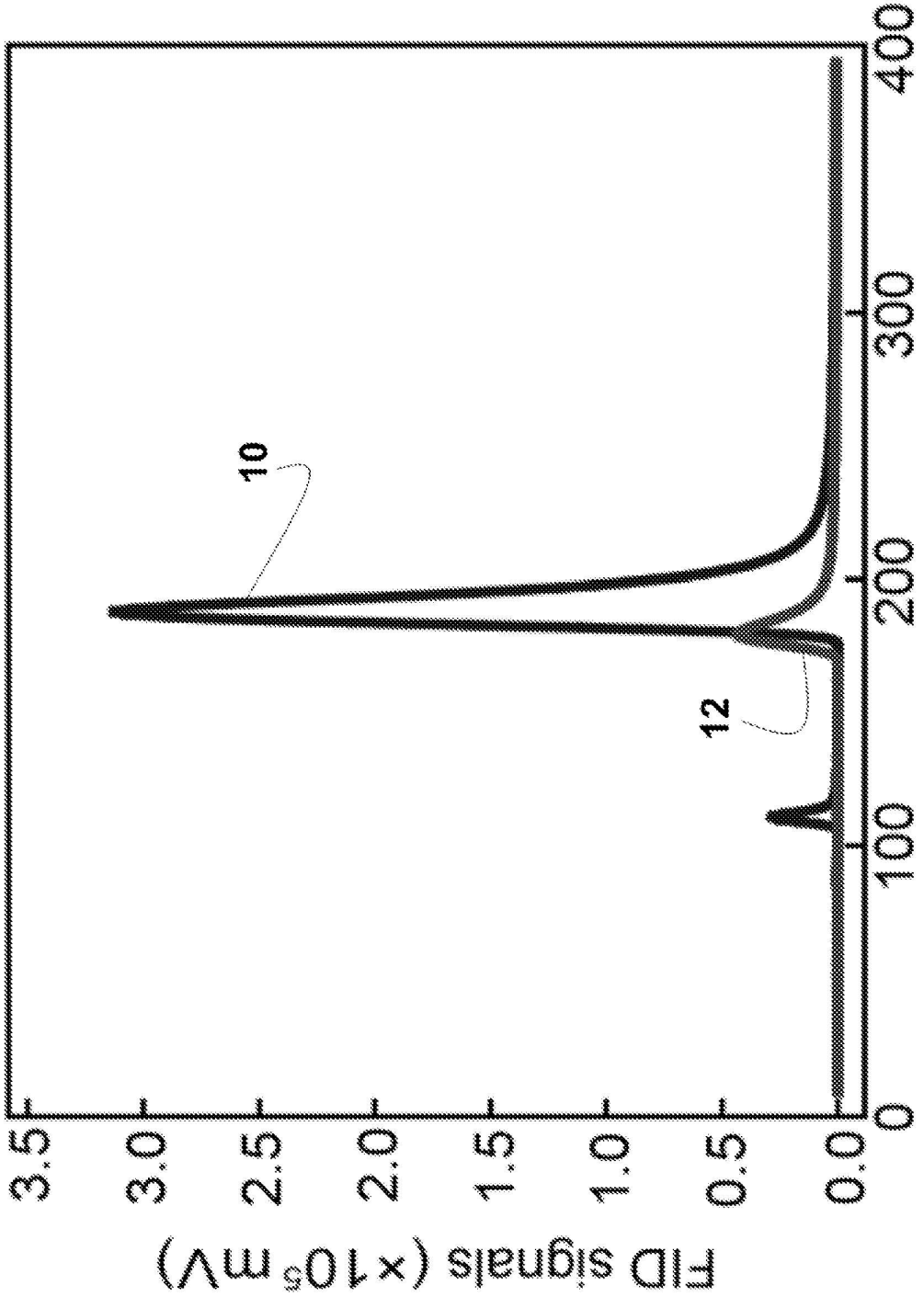
FID signals (×10⁵ mV)
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
0
100
200
300
400
Time (s)
10
12

Fig. 4

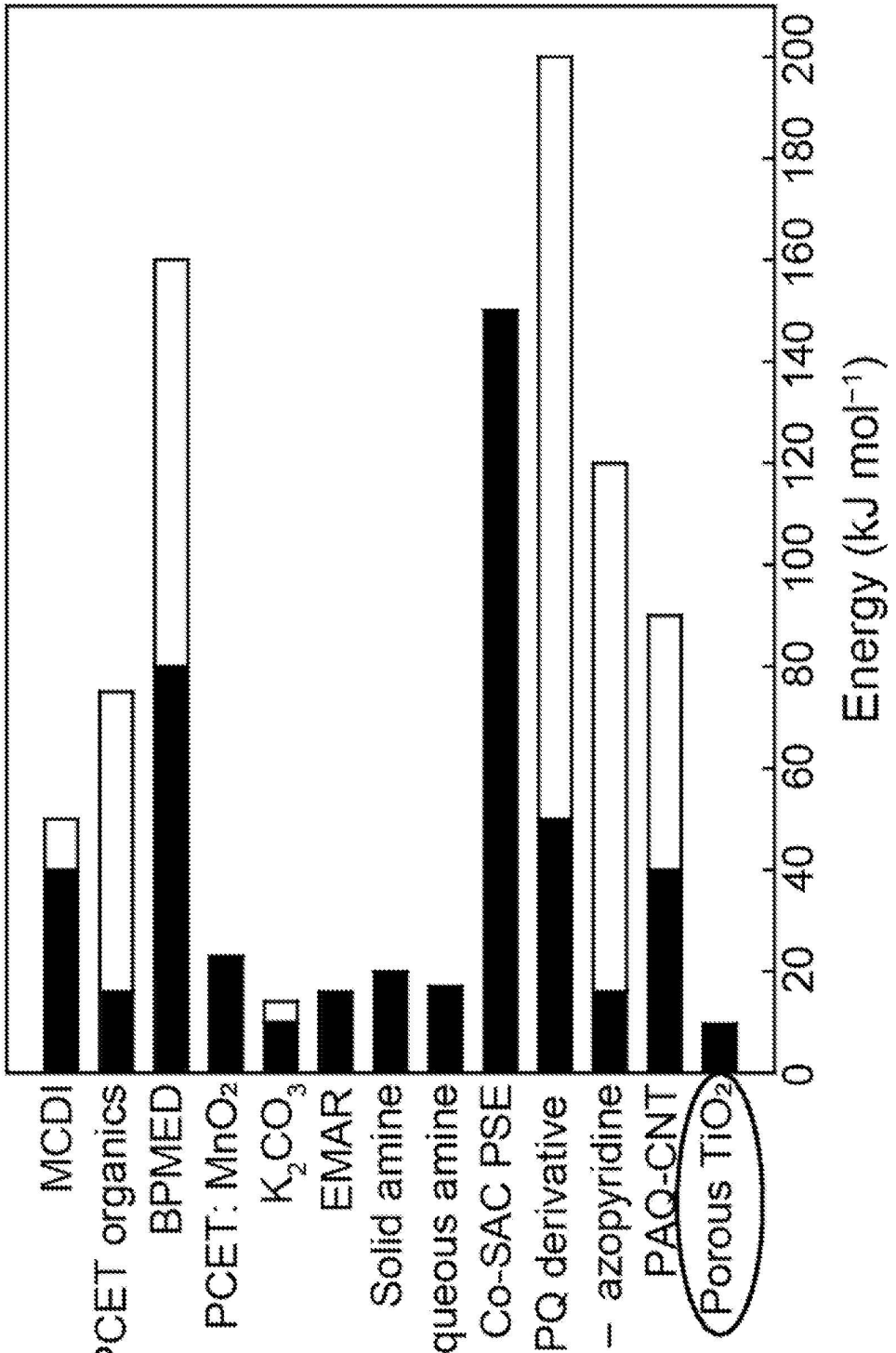
MCDI
PCET organics
BPMED
PCET: MnO_2
K_2CO_3
EMAR
Solid amine
Aqueous amine
Co-SAC PSE
GM NPQ derivative
4,4' – azopyridine
PAQ-CNT
Porous TiO_2
0
20
40
60
80
100
120
140
160
180
200
Energy (kJ mol^{-1})

Fig. 5

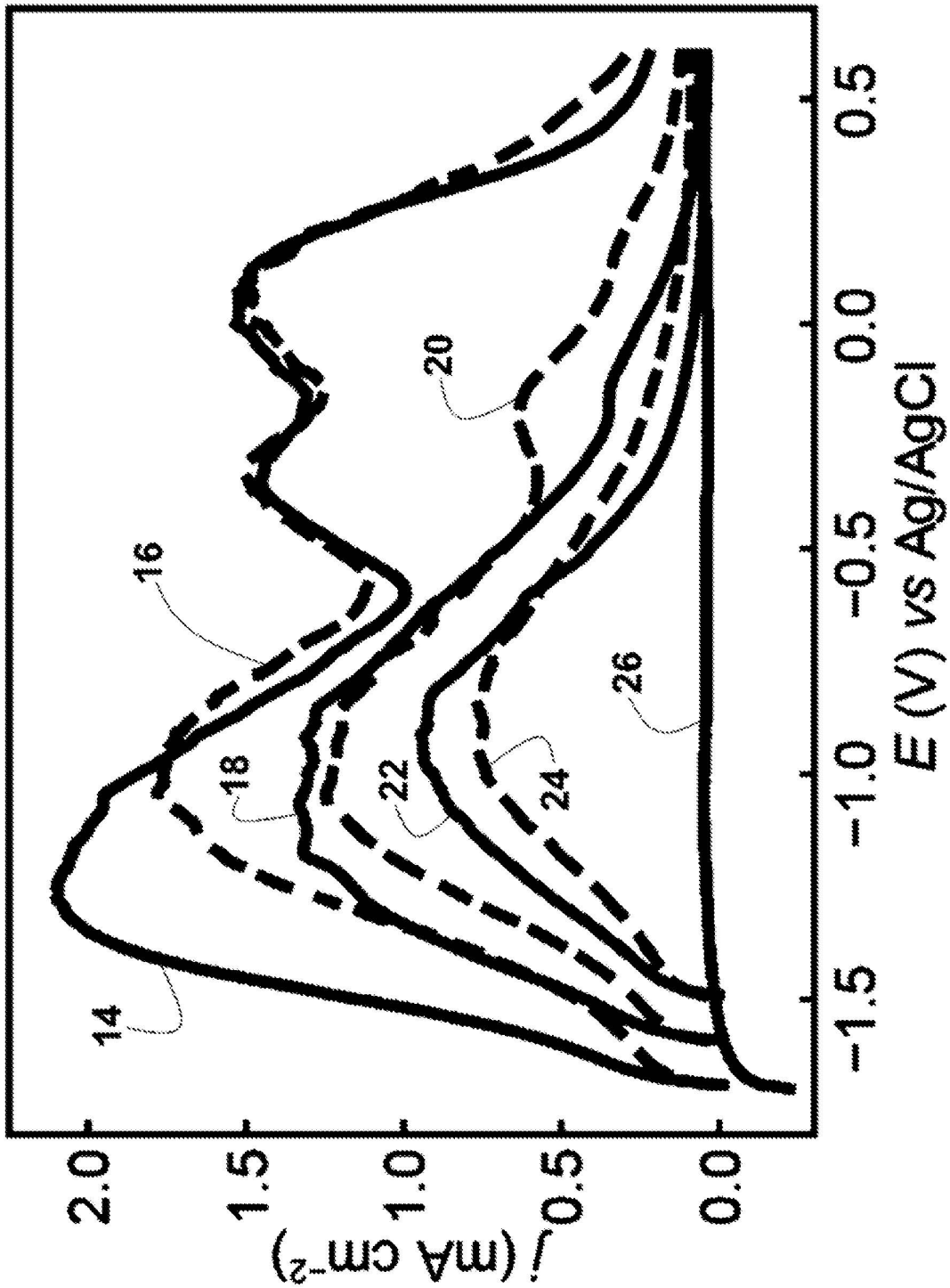
2.0
1.5
1.0
0.5
0.0
j (mA cm⁻²)
−1.5
−1.0
−0.5
0.0
0.5
E (V) vs Ag/AgCl
14
16
18
20
22
24
26

Fig. 6

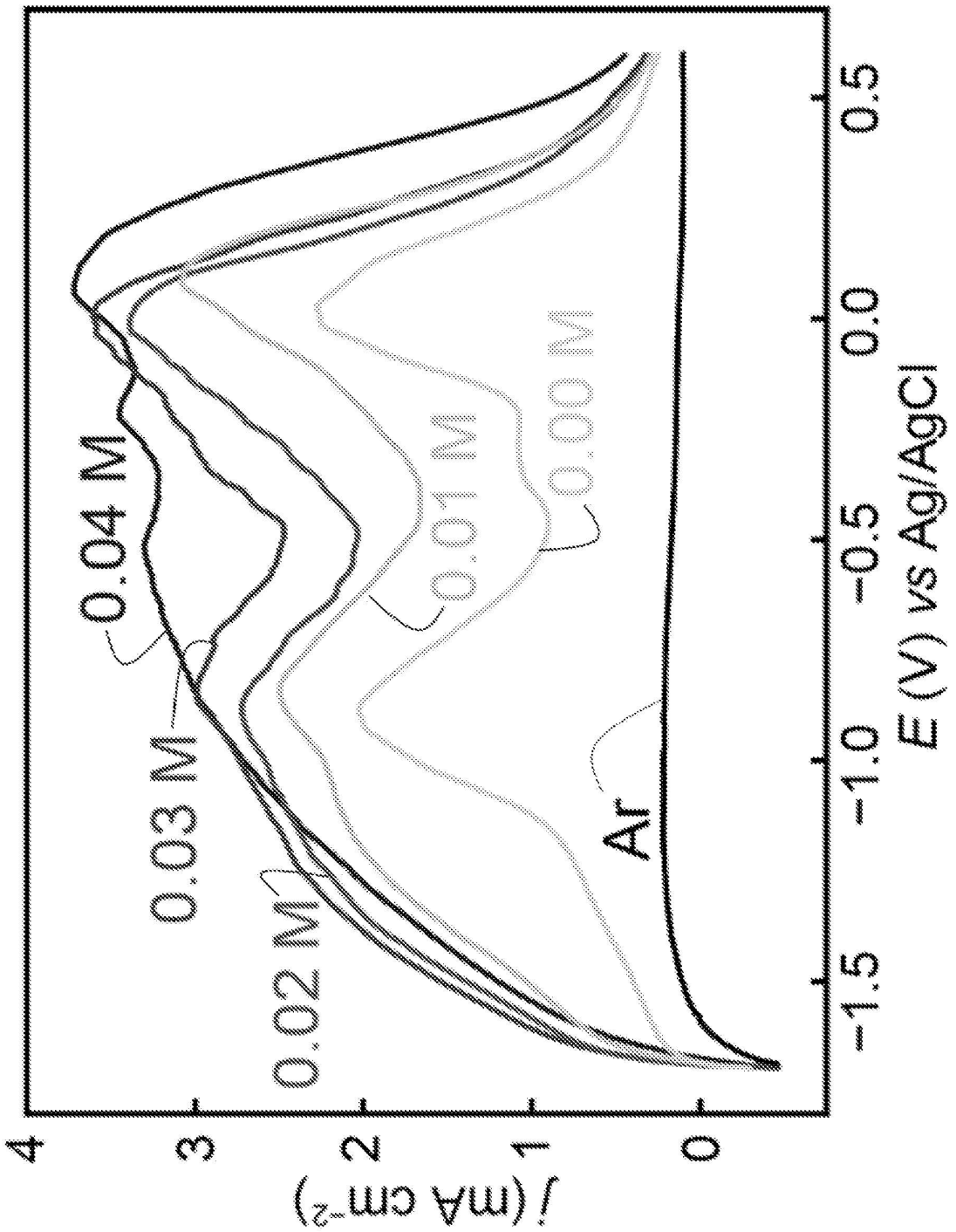
0.04 M
0.03 M
0.02 M
0.01 M
0.00 M
Ar
4
3
2
1
0
j (mA cm⁻²)
−1.5
−1.0
−0.5
0.0
0.5
E (V) vs Ag/AgCl

Fig. 7

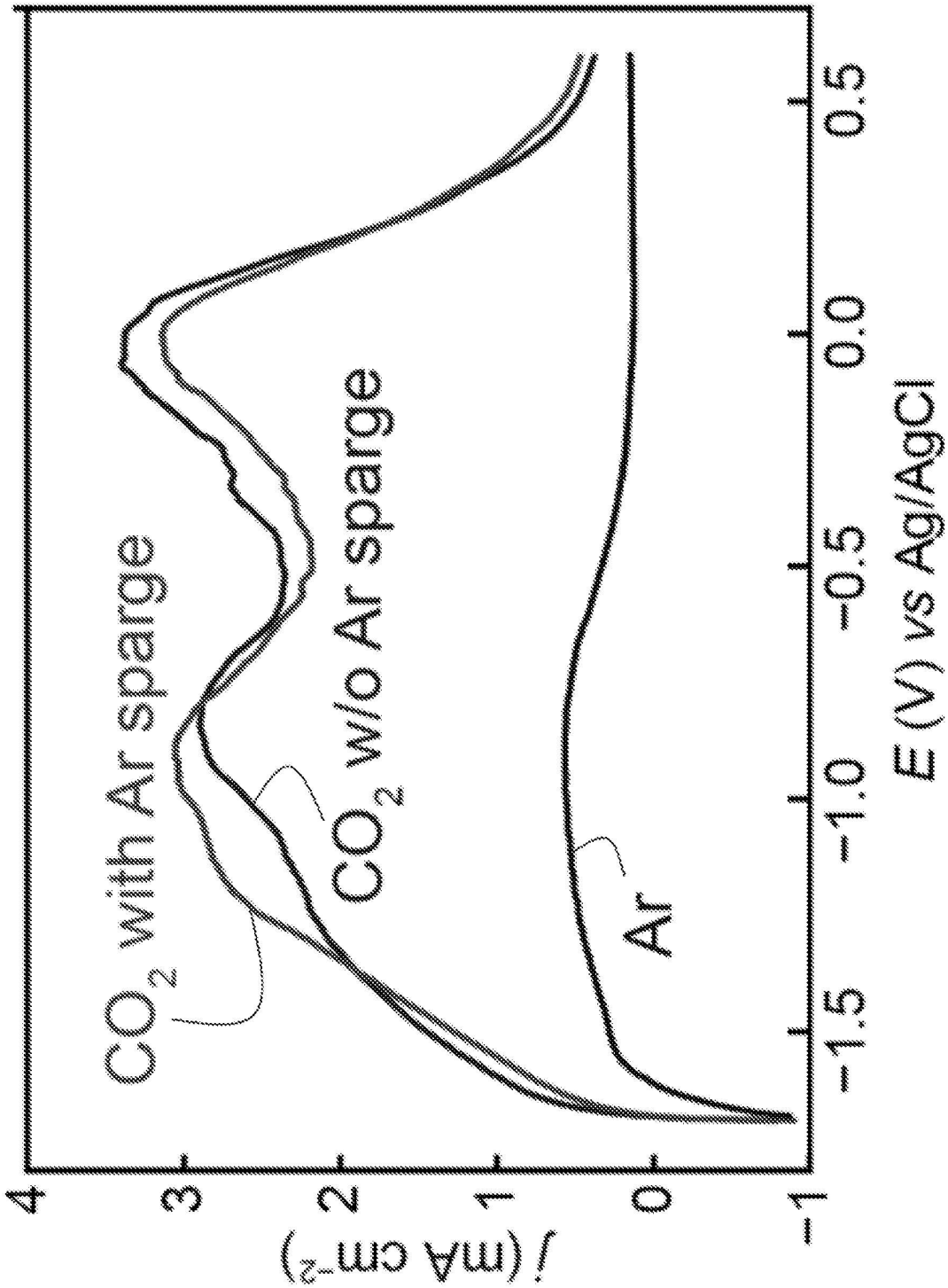
CO2 with Ar sparge
CO2 w/o Ar sparge
Ar
j (mA cm−2)
E (V) vs Ag/AgCl
4
3
2
1
0
−1
−1.5
−1.0
−0.5
0.0
0.5

Fig. 8

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2024/059551

A. CLASSIFICATION OF SUBJECT MATTER

IPC: ***B01D 53/14*** (2025.01); ***C25B 9/23*** (2025.01); *C25B 9/17* (2025.01)

CPC: ***B01D 53/1456; B01D 53/1475; C25B 9/23;*** *C25B 9/17*

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	US 2016/0293985 A1 (ExxonMobil Research and Engineering Company) 06 October 2016 (06.10.2016) entire document	1-3
A	WO 2023/094487 A1 (Vito NV) 01 June 2023 (01.06.2023) entire document	1-3
Y	Liu et al. Nanoporous Tin Oxides for Efficient Electrochemical CO2 Reduction to Formate. 10 November 2021. Retrieved from Internet URL: < https://www.sciencedirect.com/science/article/pii/S2666952821000728?ref=pdf_download&fr=RR-2&rr=90c4db97cb3e1238 > Pg. 139 Col 1 Para 3; Pg. 139 Col 2 Para 3; Pg. 144 Col 1 Para 2; Pg. 144 Col 1 Para 3	1-3
Y	Tufa et al. Towards Highly Efficient Electrochemical CO2 reduction: Cell designs, Membranes and Electrocatalysts. 01 November 2020. Retrieved from Internet URL: < https://www.sciencedirect.com/science/article/abs/pii/S0306261920310692 > Pg. 9 Para 1; Pg. 19 Para 4	1-3

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"D" document cited by the applicant in the international application
"E" earlier application or patent but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"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	Date of mailing of the international search report
31 March 2025 (31.03.2025)	**08 April 2025 (08.04.2025)**

Name and mailing address of the ISA/US	Authorized officer
COMMISSIONER FOR PATENTS **MAIL STOP PCT, ATTN: ISA/US** **P.O. Box 1450** **Alexandria, VA 22313-1450** **UNITED STATES OF AMERICA**	**KARI RODRIQUEZ**
Facsimile No. **571-273-8300**	Telephone No. **PCT Help Desk: 571-272-4300**

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2024/059551

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
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:

3. ☑ Claims Nos.: **4-11 and 15-17**
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

This application contains the following inventions or groups of inventions which are not so linked as to form a single general inventive concept under PCT Rule 13.1.

Group I: Claims 1-3 directed toward a method of adsorbing CO2 in a gaseous input, the method comprising: contacting the gaseous input with a non-aqueous solution comprising a dissolved electrolyte and having disposed therein a working electrode comprising a porous inorganic oxide, and a counter electrode; and applying a negative voltage across the electrodes wherein at least a portion of the CO2 in the gaseous input is adsorbed to the working electrode.

Group II: Claims 12-14 directed toward a system configured to adsorb and desorb CO2, the system comprising: a working electrode comprising a porous inorganic oxide; a counter electrode; and a non-aqueous solution comprising a dissolved electrolyte.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2024/059551

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.

3. ☐ 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.:

4. ☑ 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.: **1-3**

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.