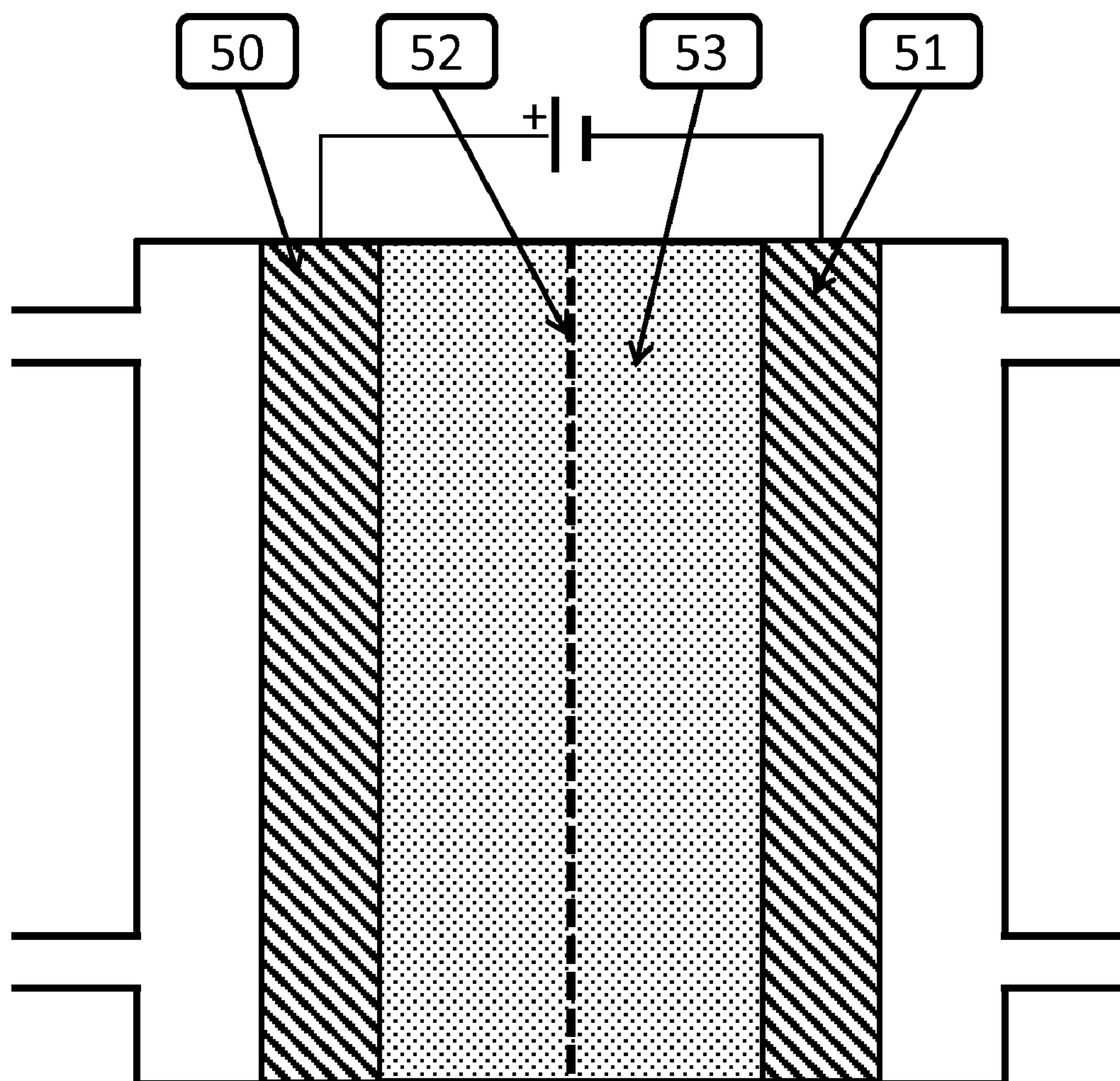


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IL (US)(73) Assignee: **Dioxide Materials Inc**, Champaign,
IL (US)(21) Appl. No.: **12/830,338**(22) Filed: **Jul. 4, 2010****Related U.S. Application Data**(60) Provisional application No. 61/317,955, filed on Mar.
26, 2010.(51) **Int. Cl.****C07C 51/15** (2006.01)**B01J 31/02** (2006.01)(52) **U.S. Cl.** **562/550; 502/167**(57) **ABSTRACT**

Catalysts comprised of at least one catalytically active element and at least one helper catalyst are disclosed. The catalysts may be used to increase the rate, the selectivity or lower the overpotential of chemical reactions. These catalysts may be useful for a variety of chemical reactions including in particular the electrochemical conversion of carbon dioxide to formic acid.



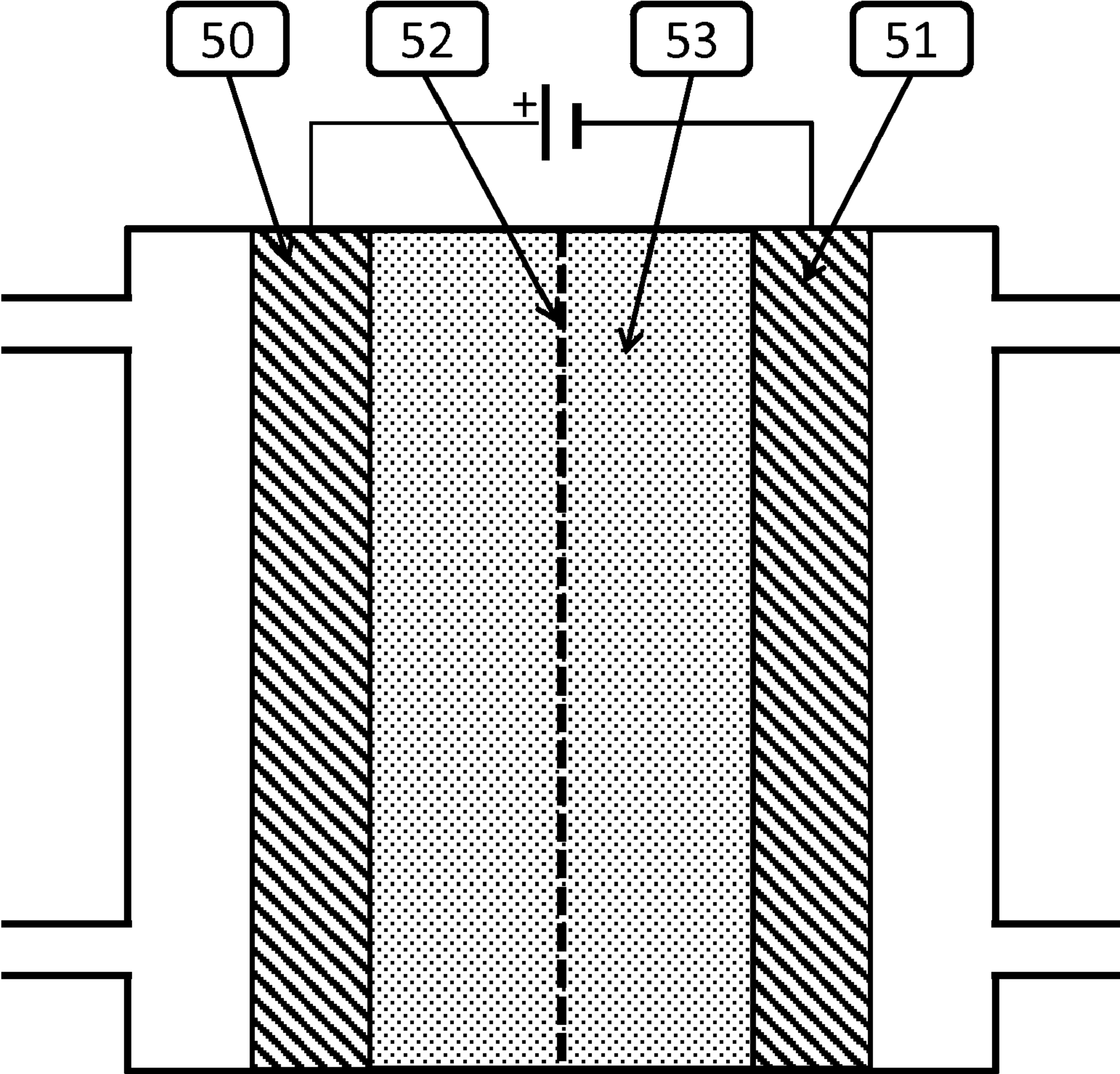


Fig. 1

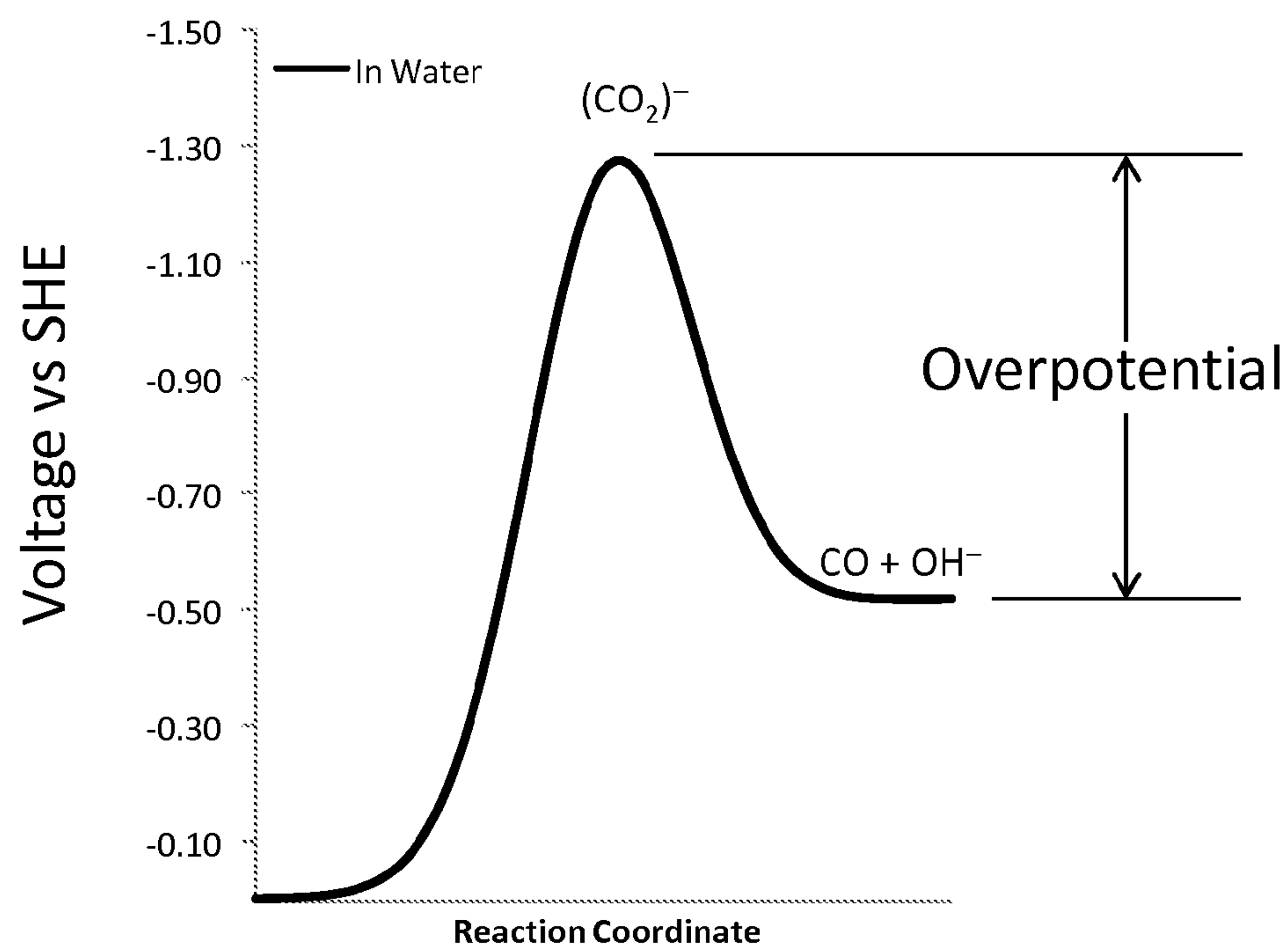


Fig. 2

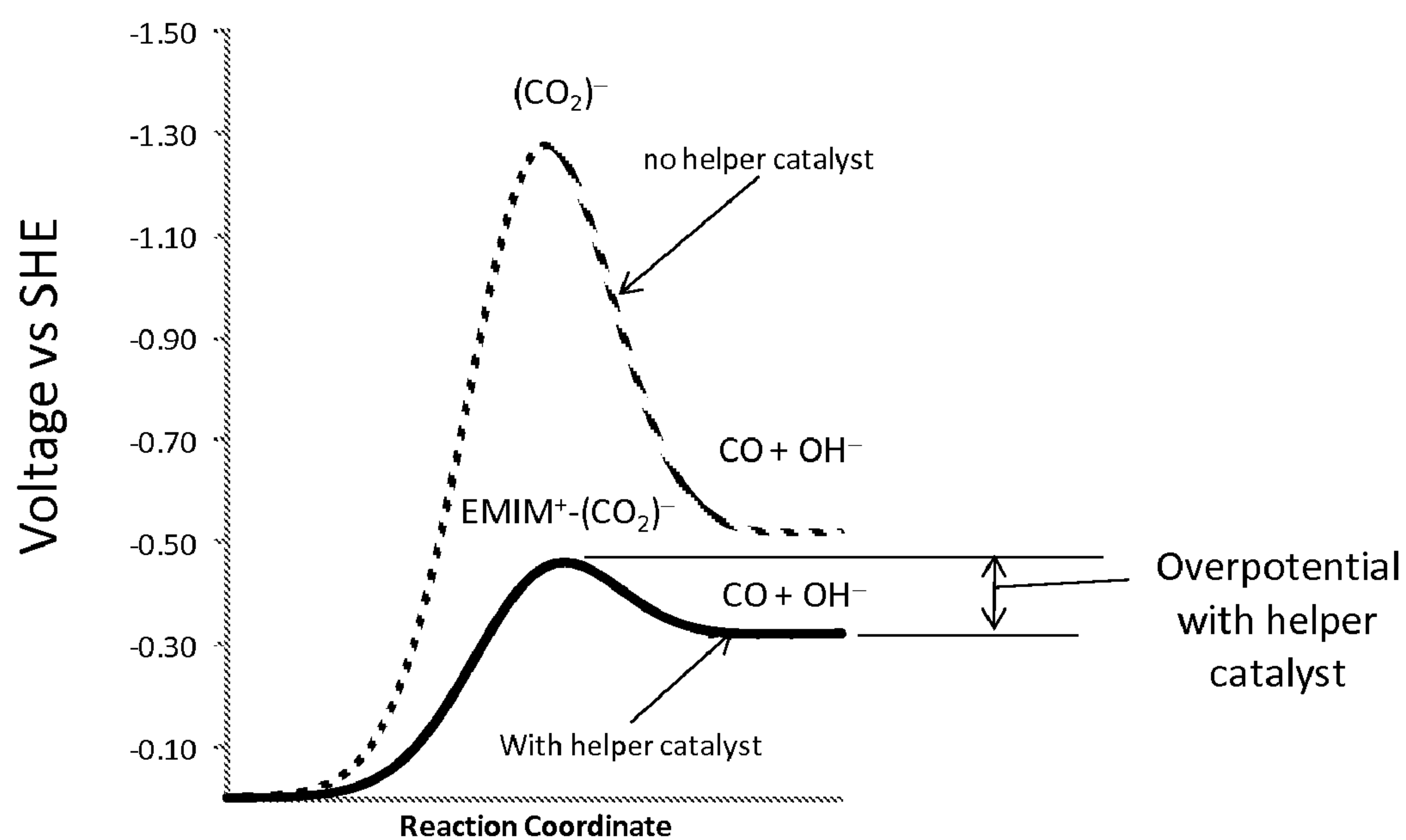


Fig. 3

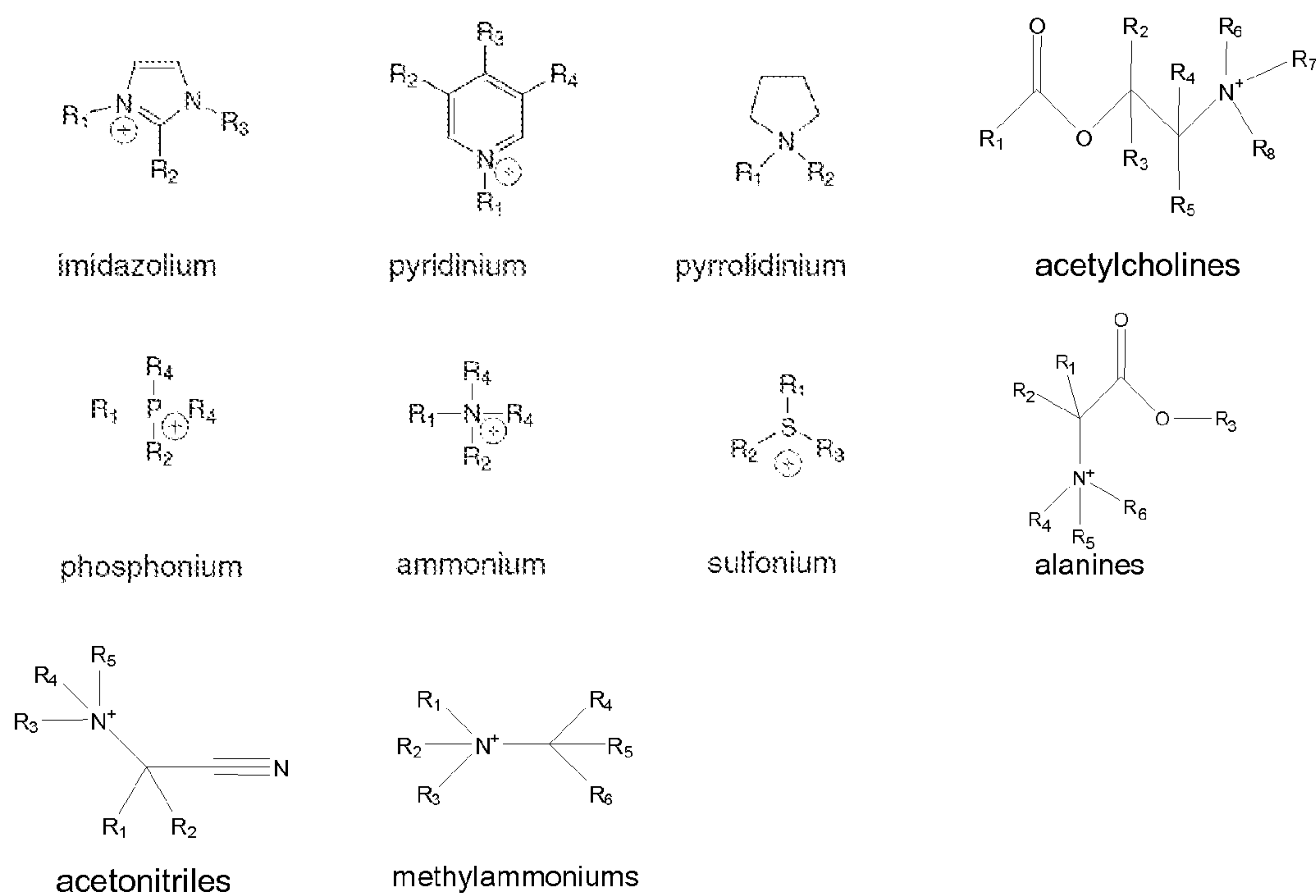
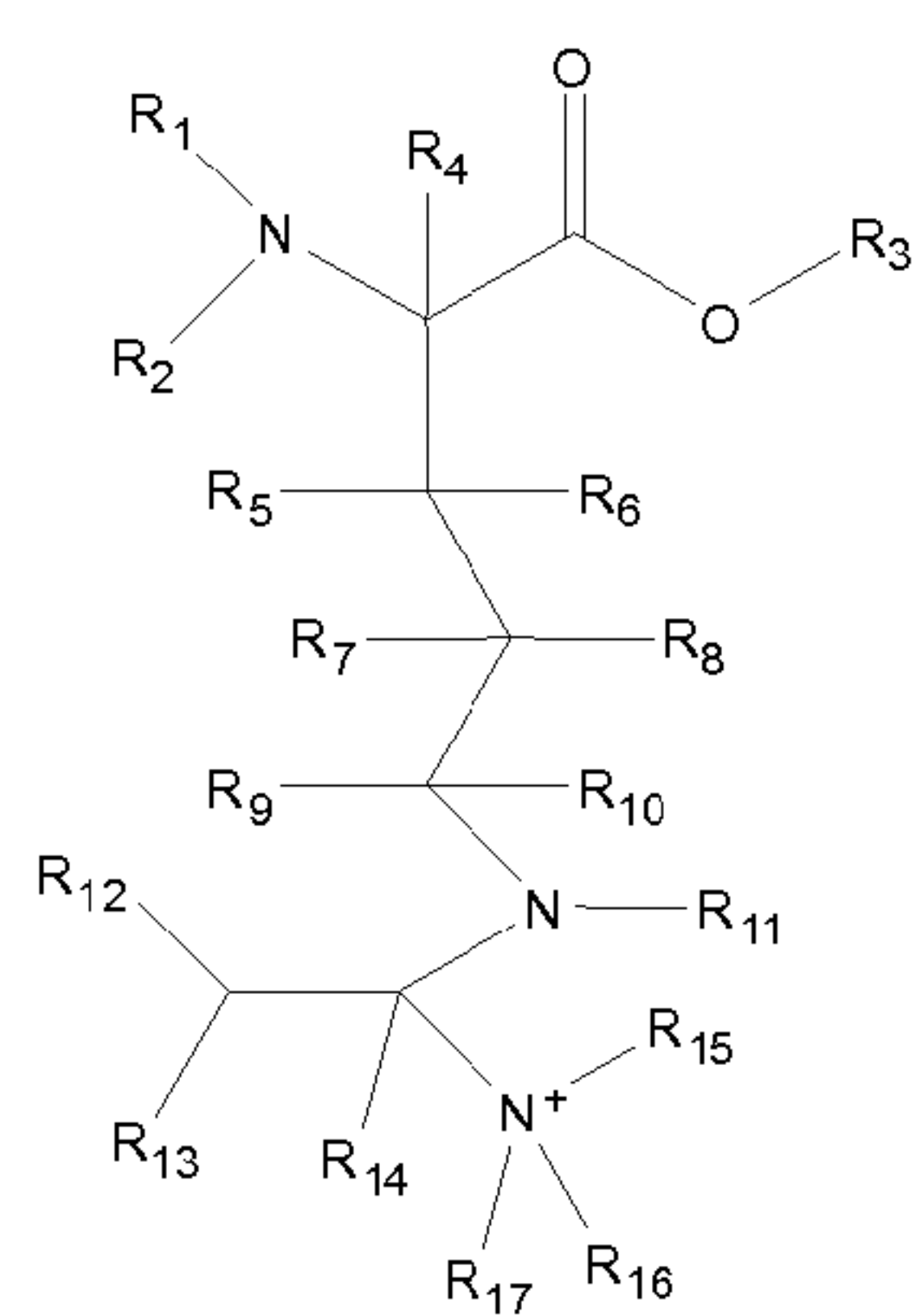
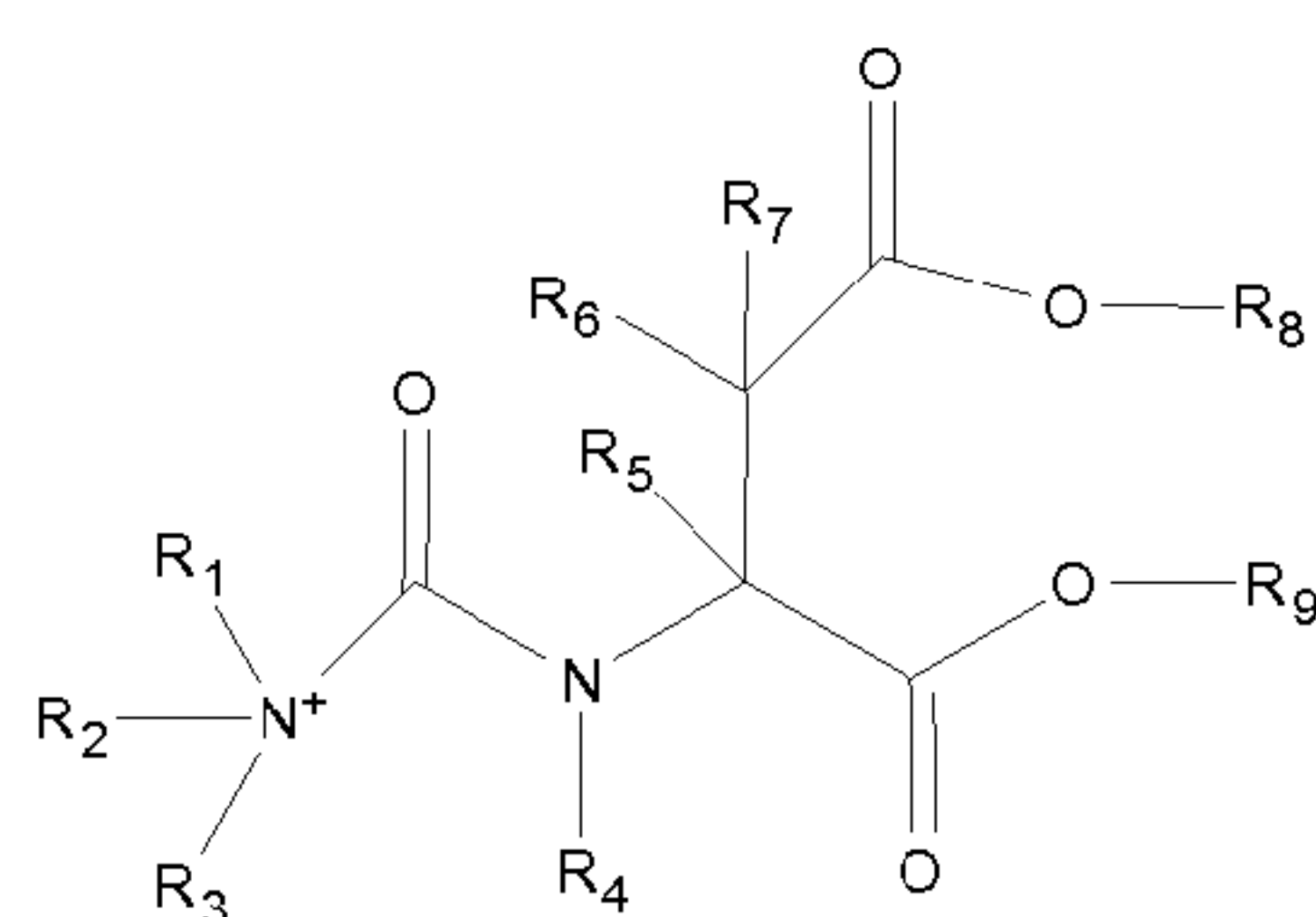


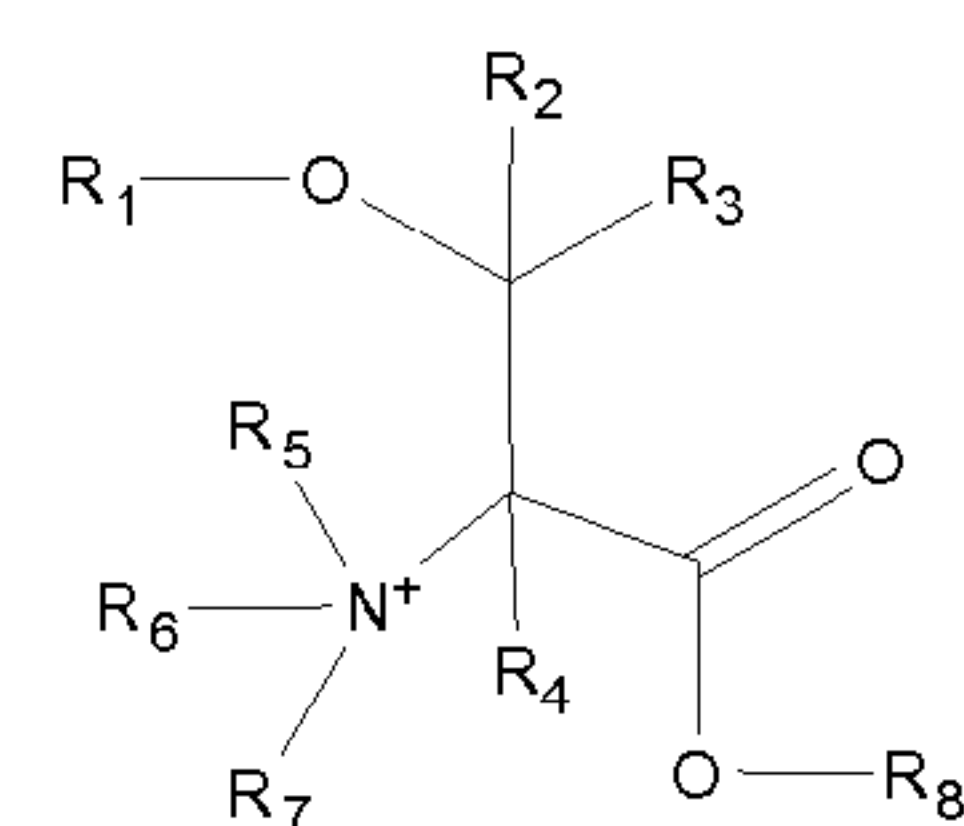
Fig. 4A



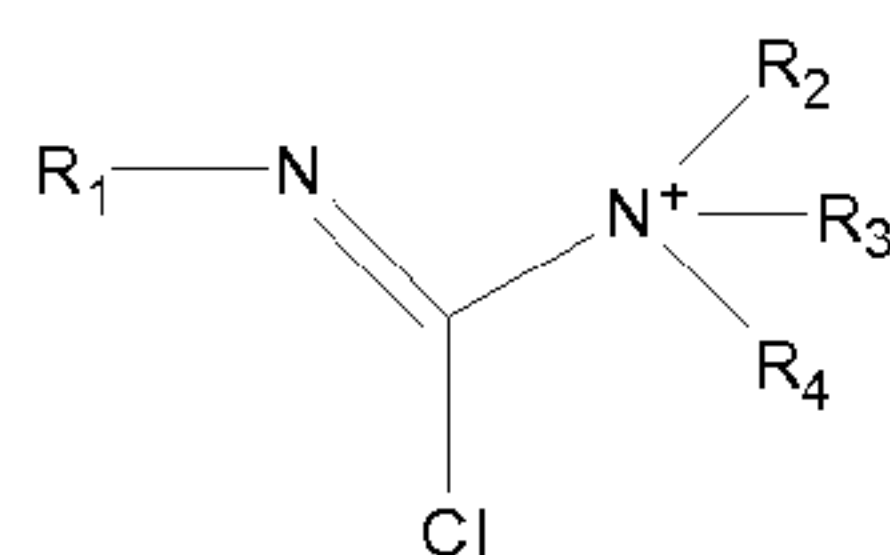
arginines



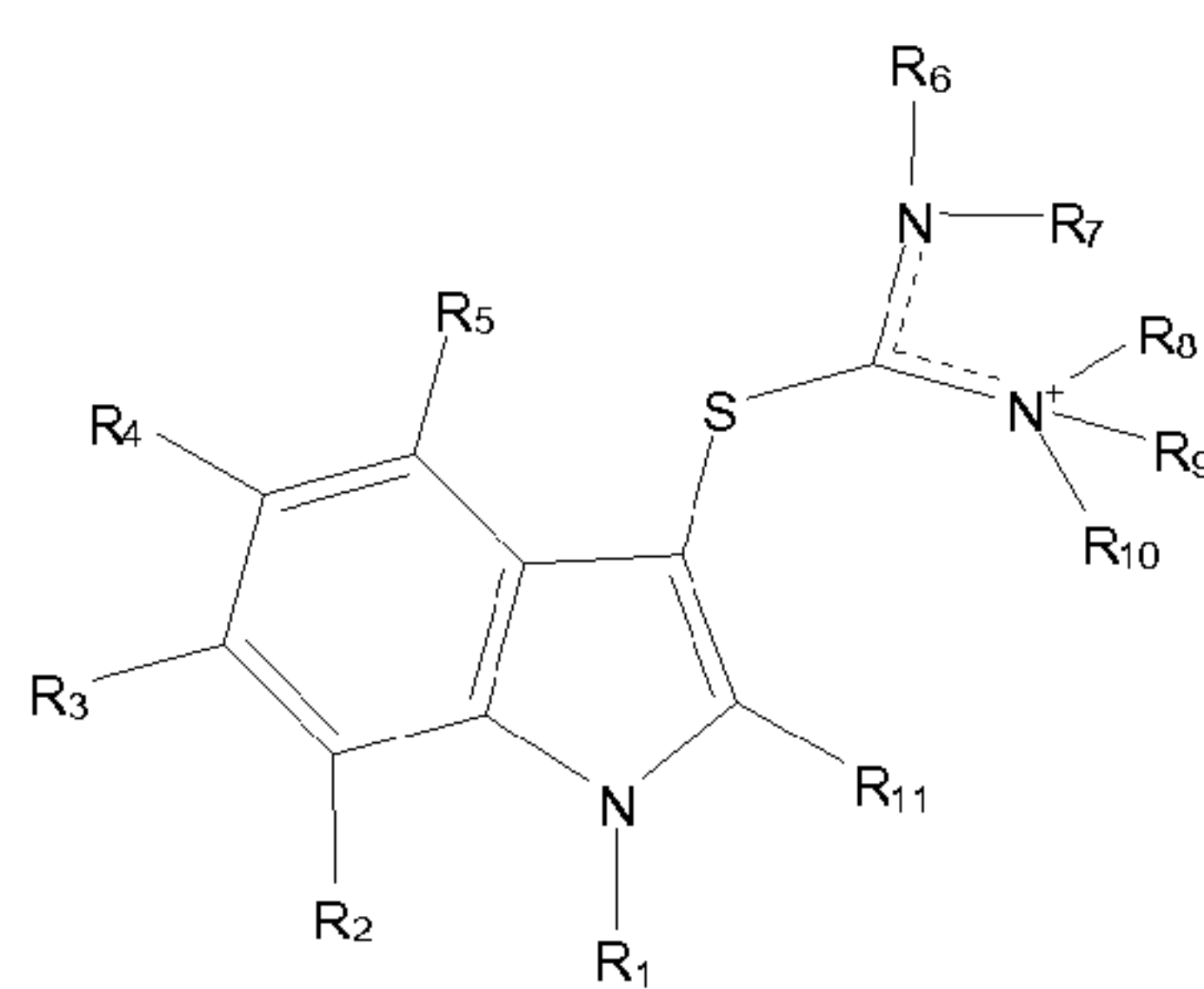
aspartic acids



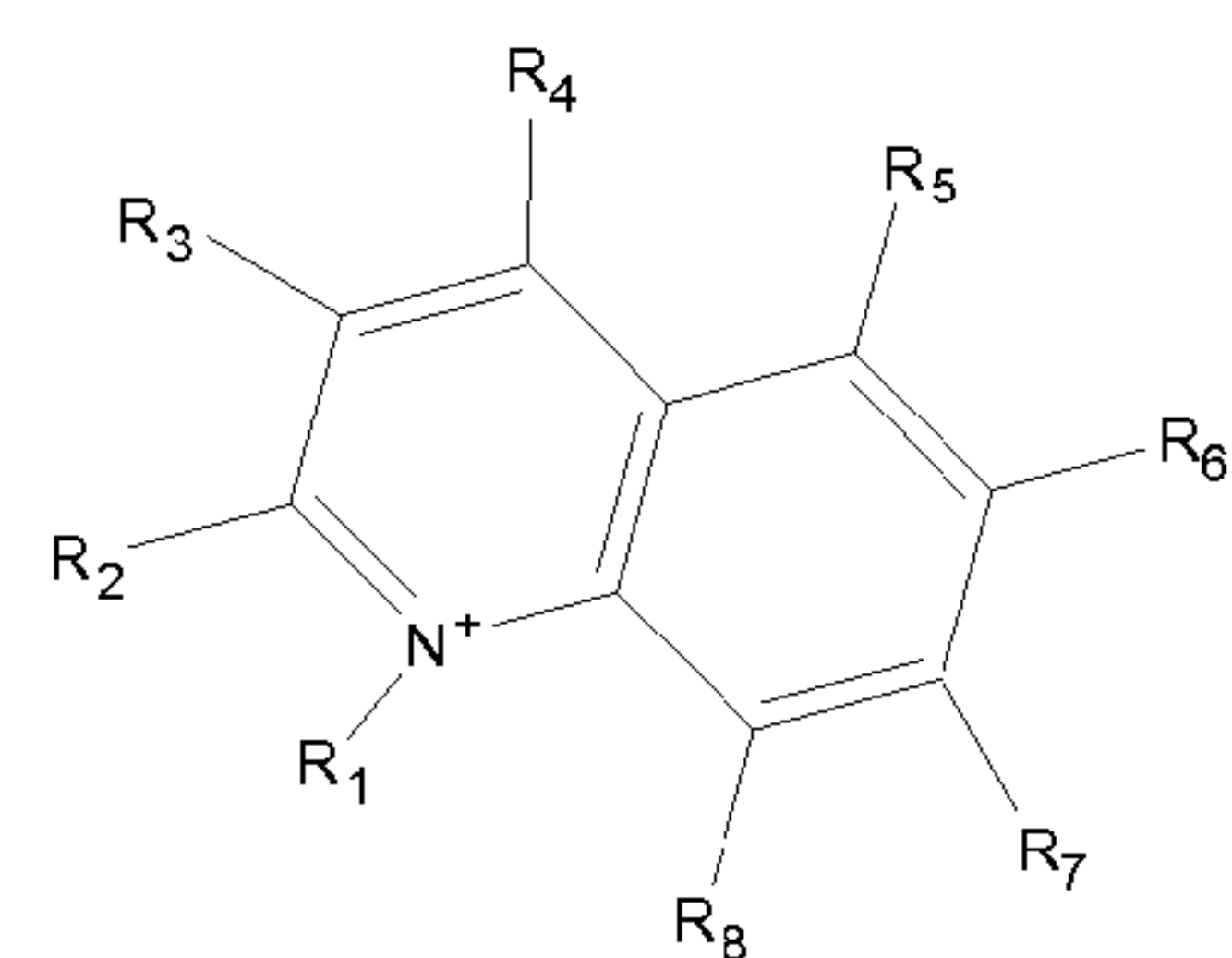
threonines



chlorofomamidiniums

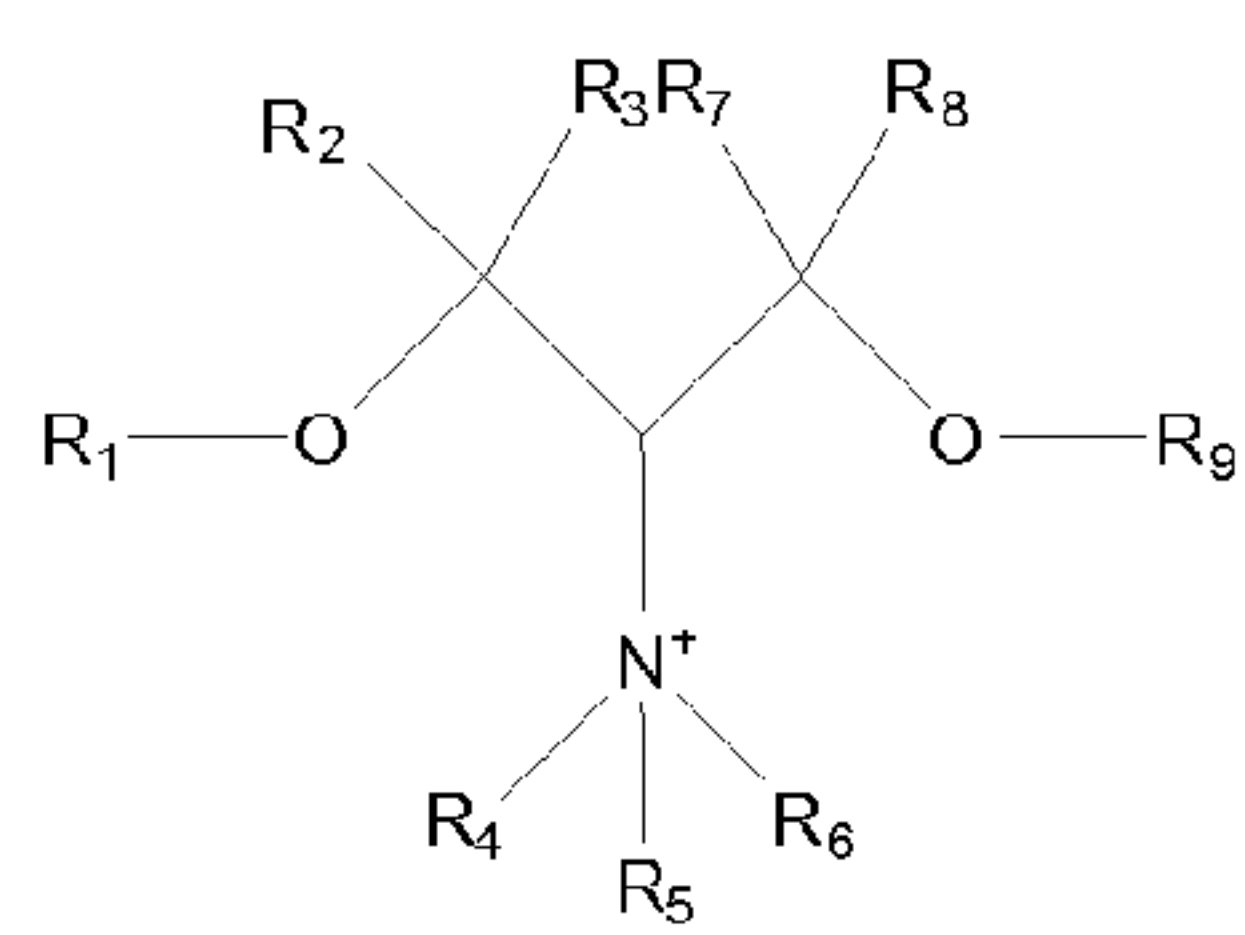


thiuroniums

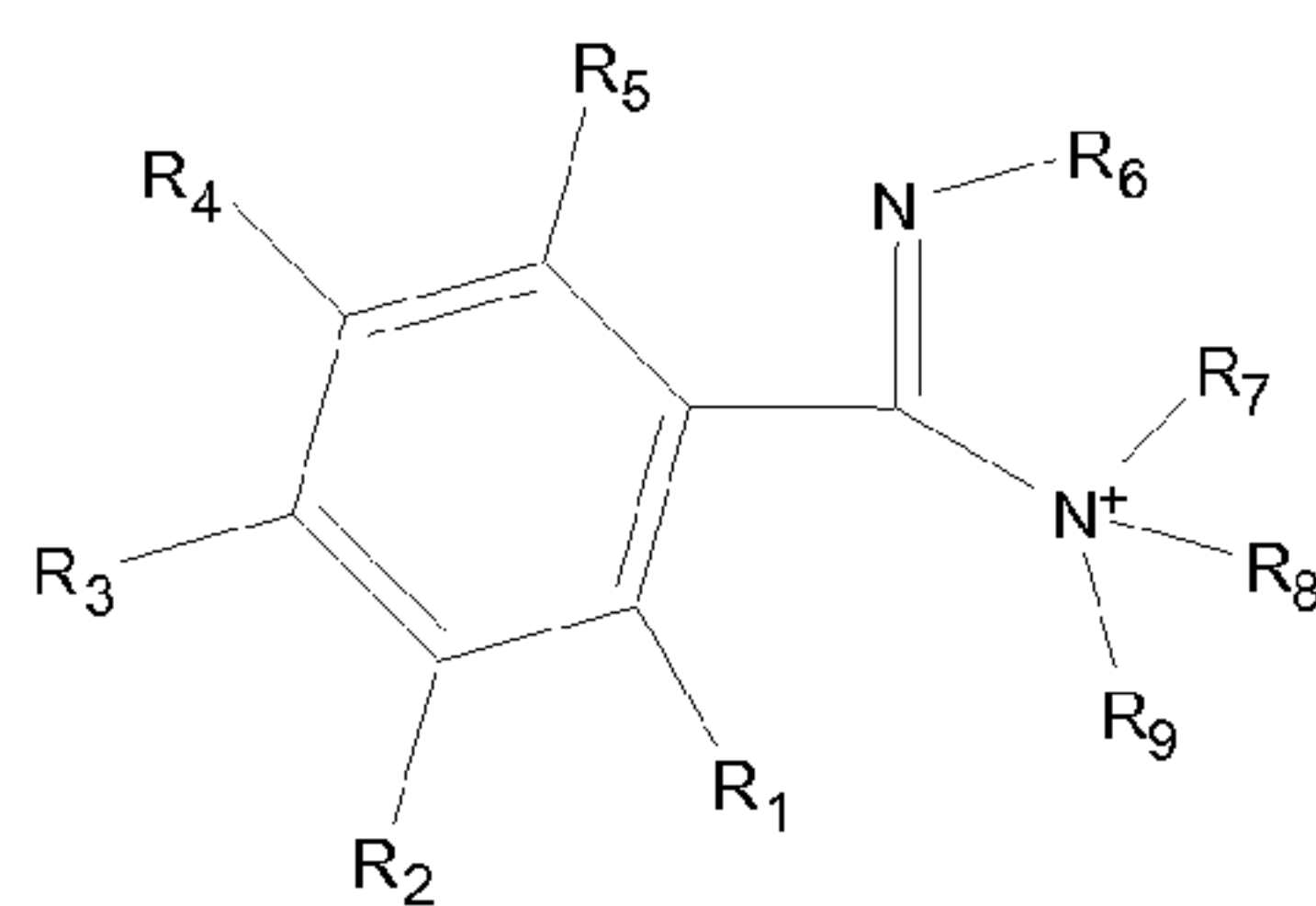


propulisoquinoliniums

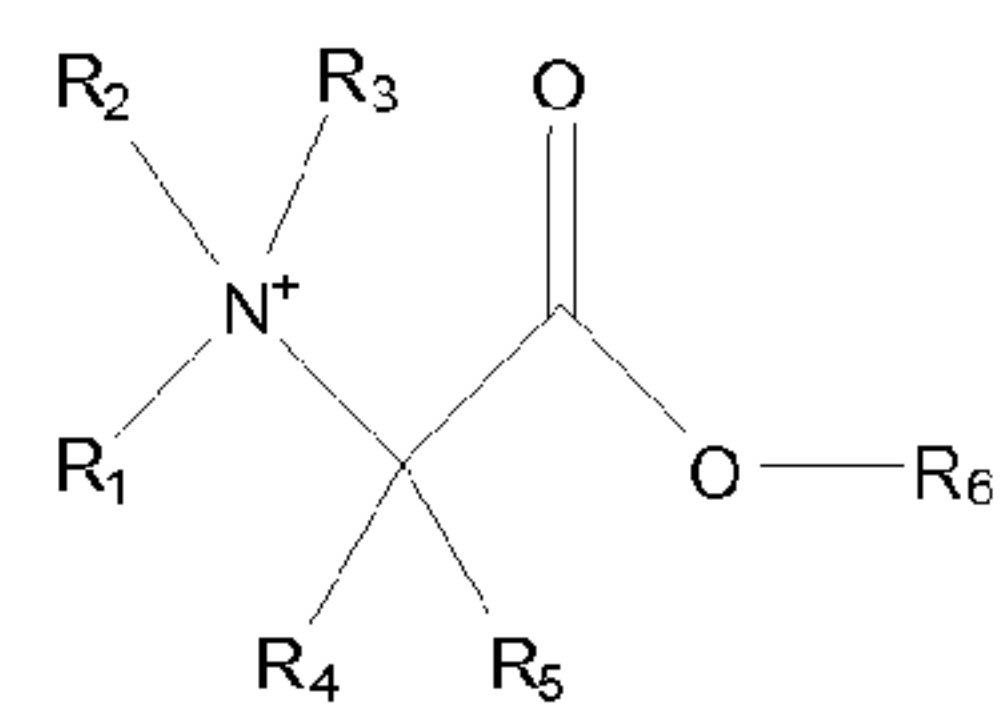
Fig. 4B



serinols

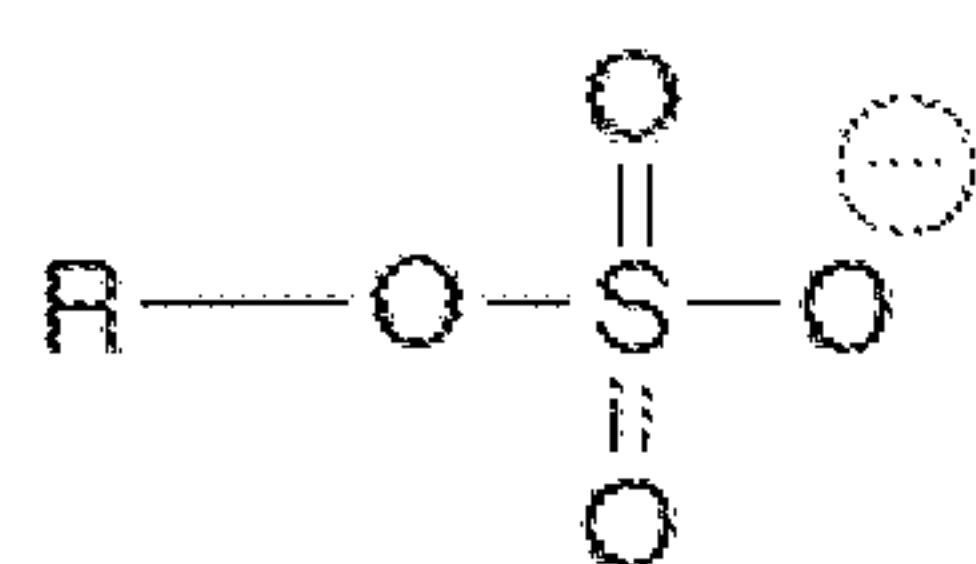


benzamidines

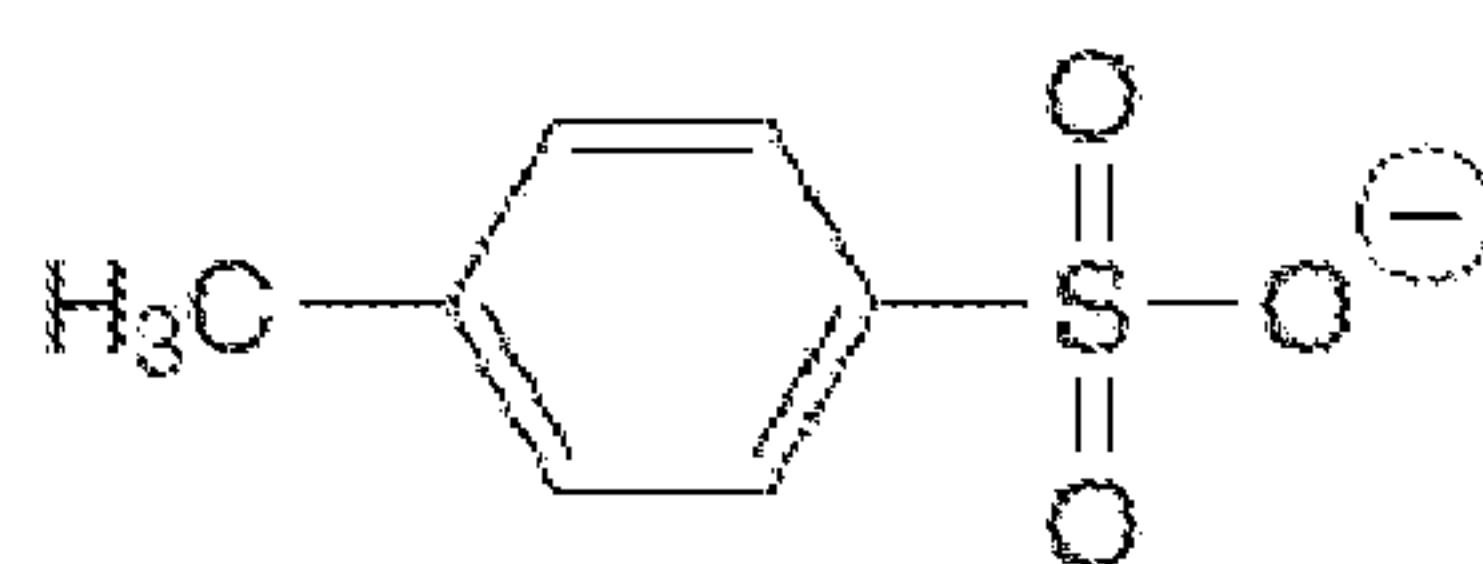


sarcosines

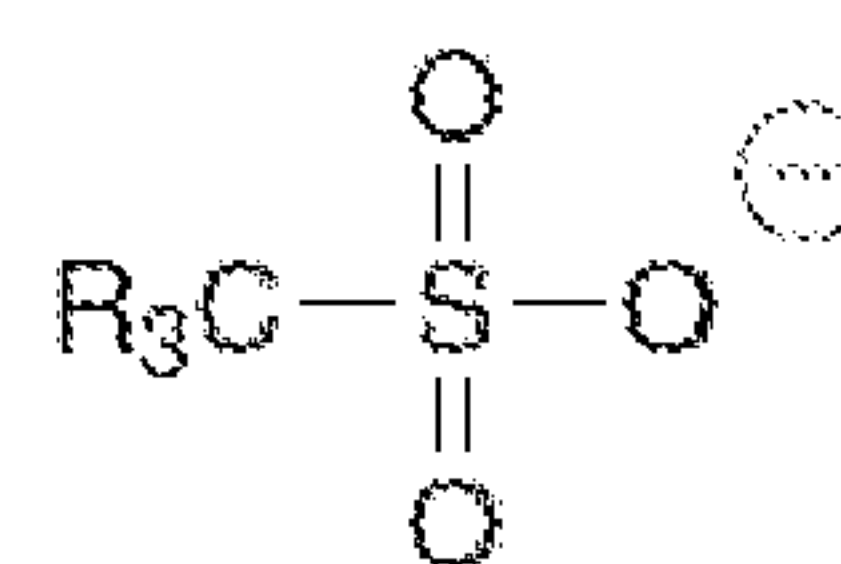
Fig. 4C



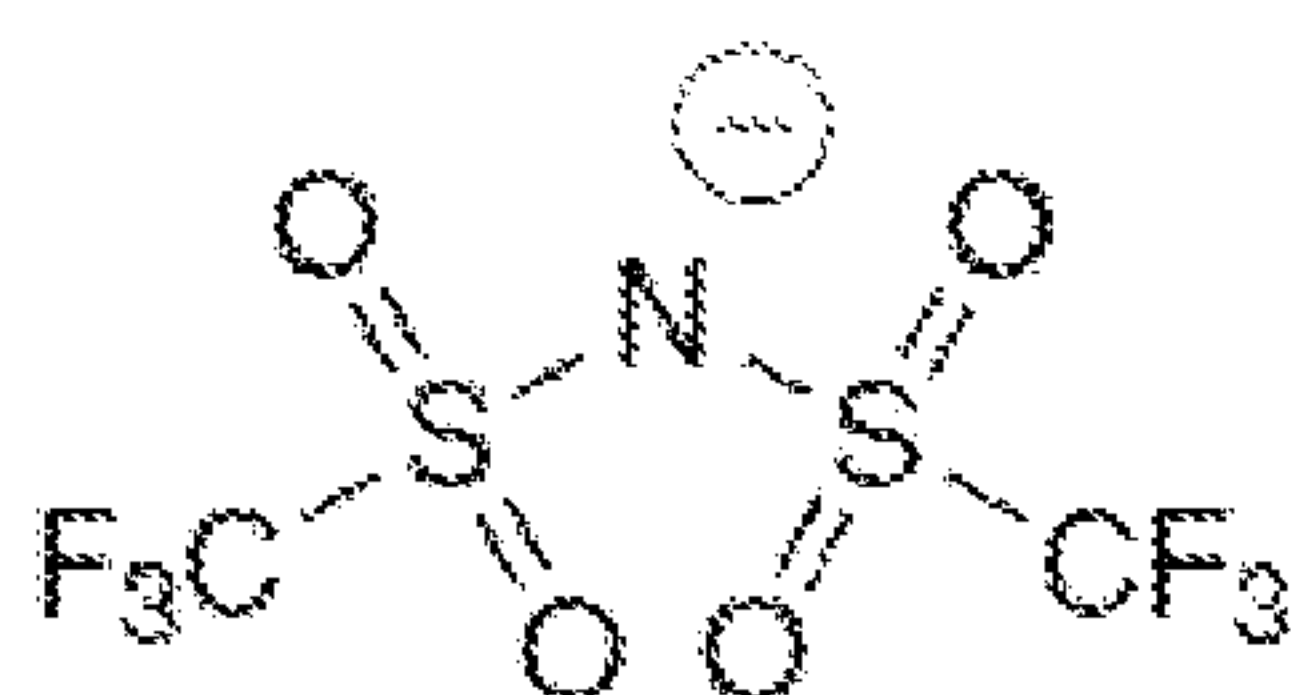
alkylsulfate



tosylate



methanesulfonate



bis(trifluoromethyl-
sulfonyl)imide



hexafluoro-
phosphate



tetrafluoro-
borate

Fig. 5A

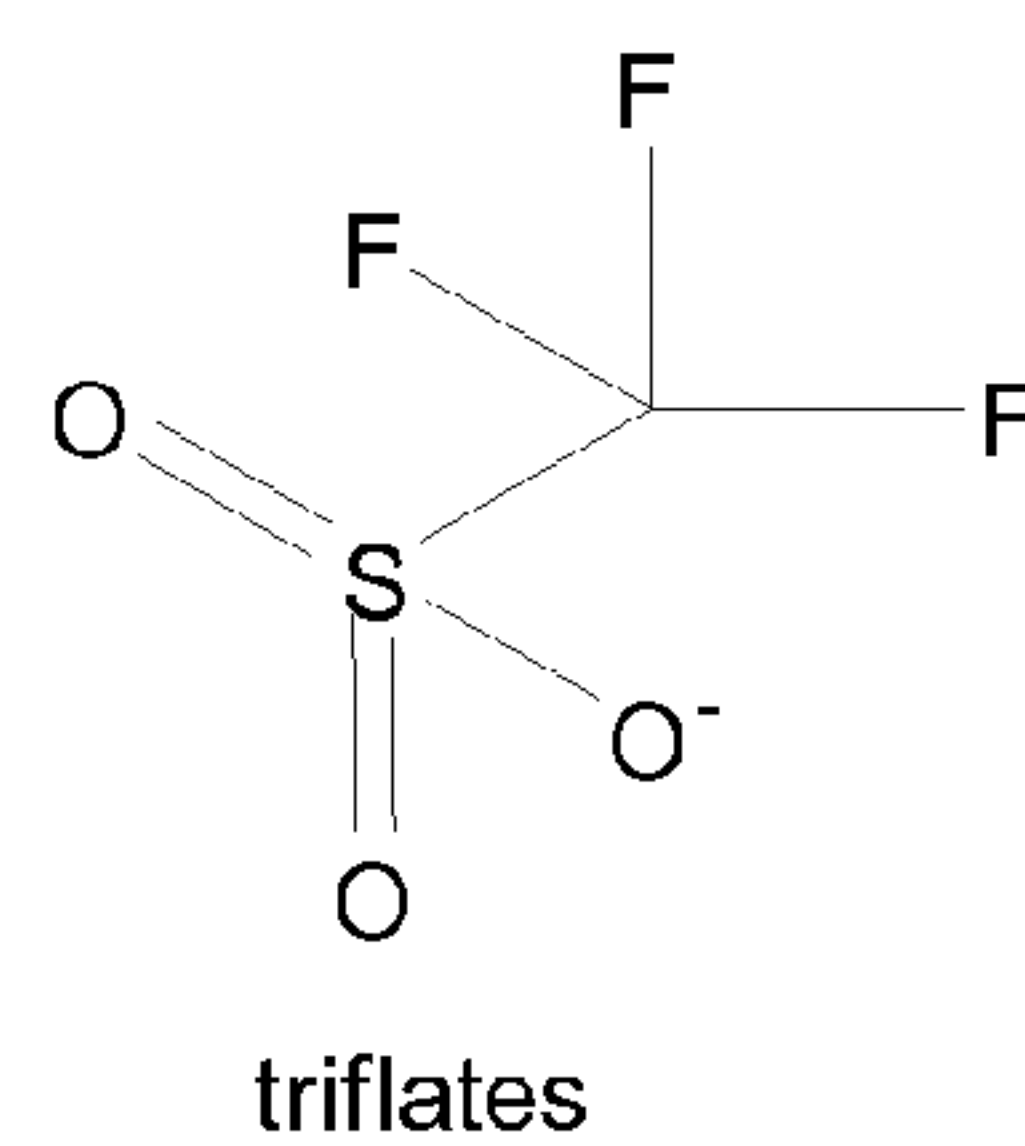
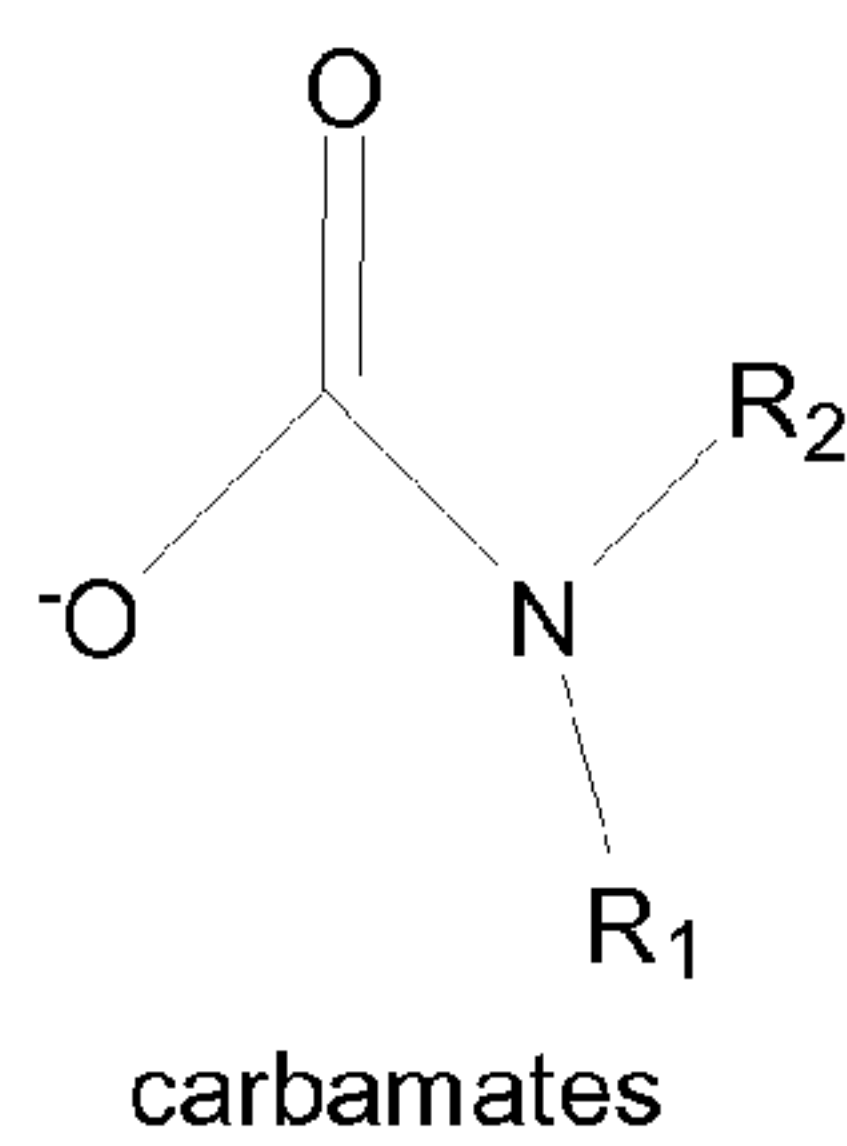
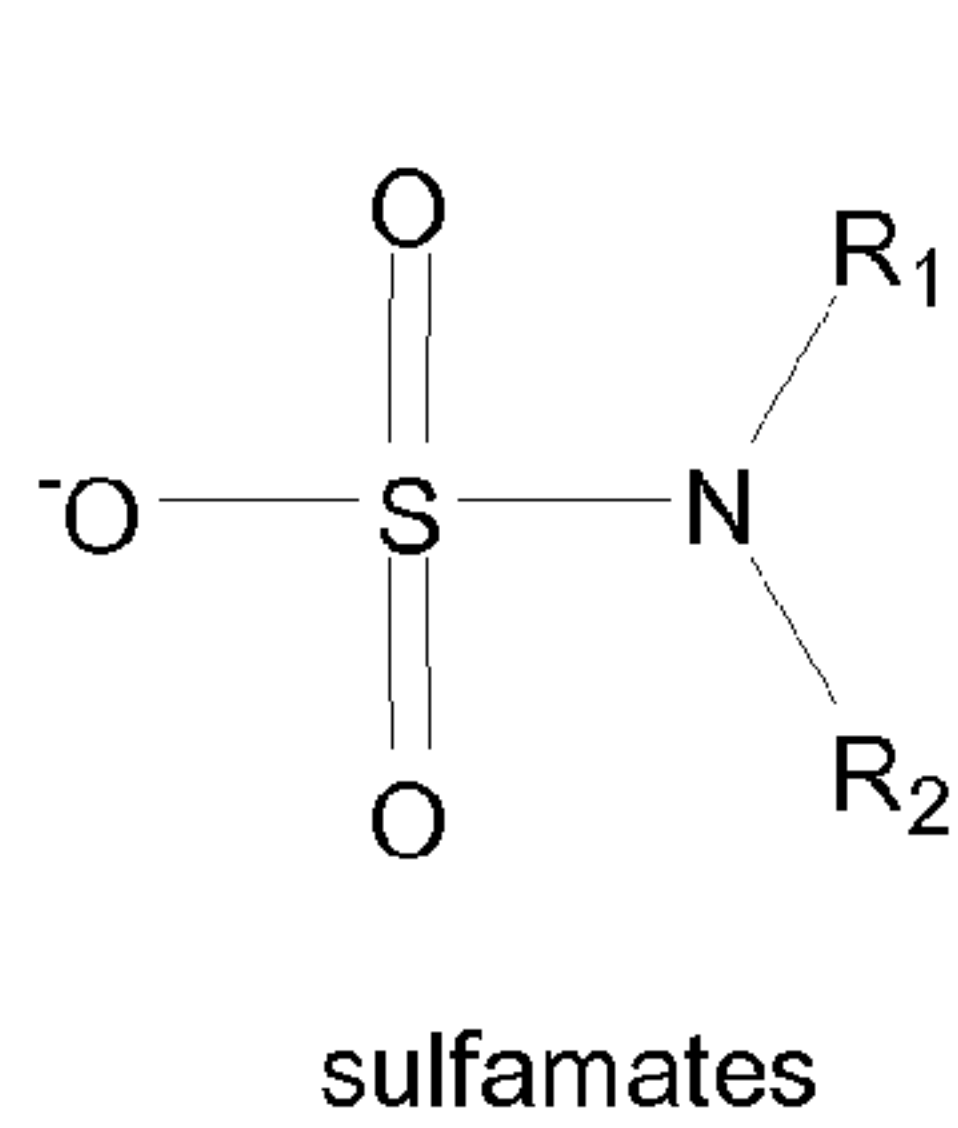
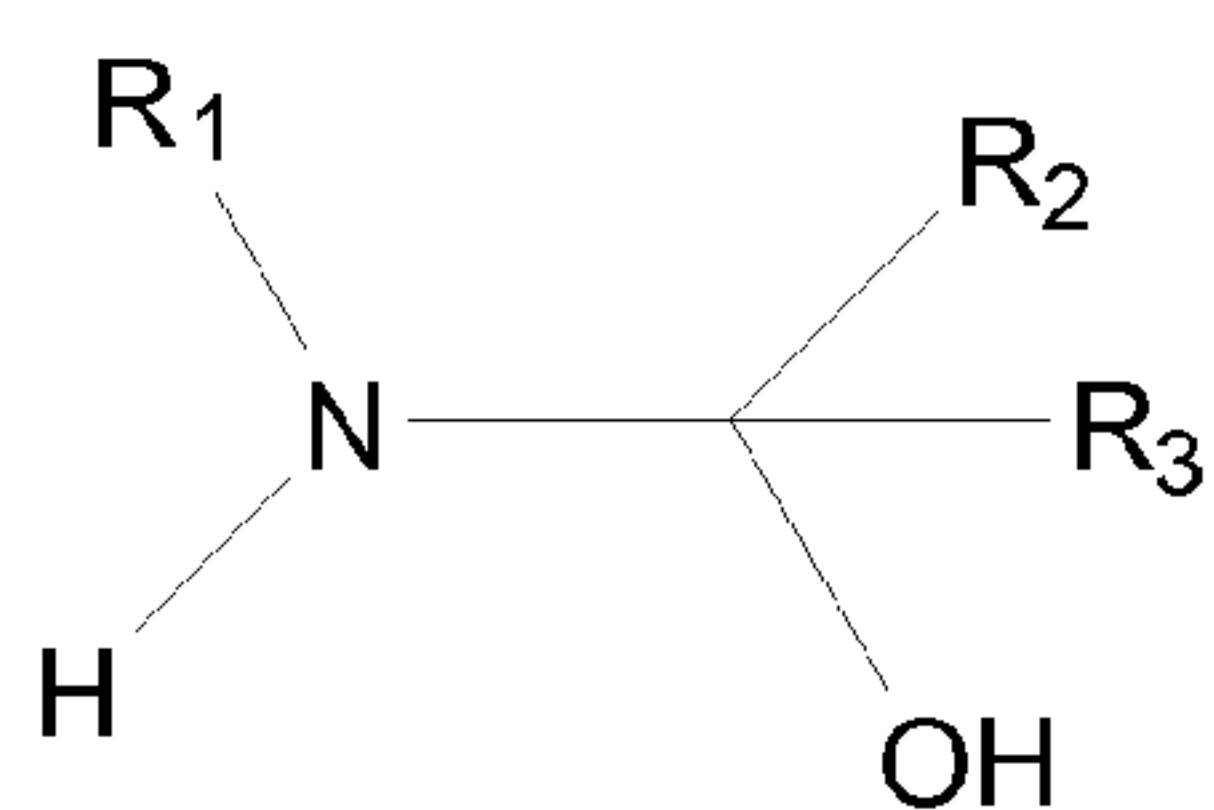
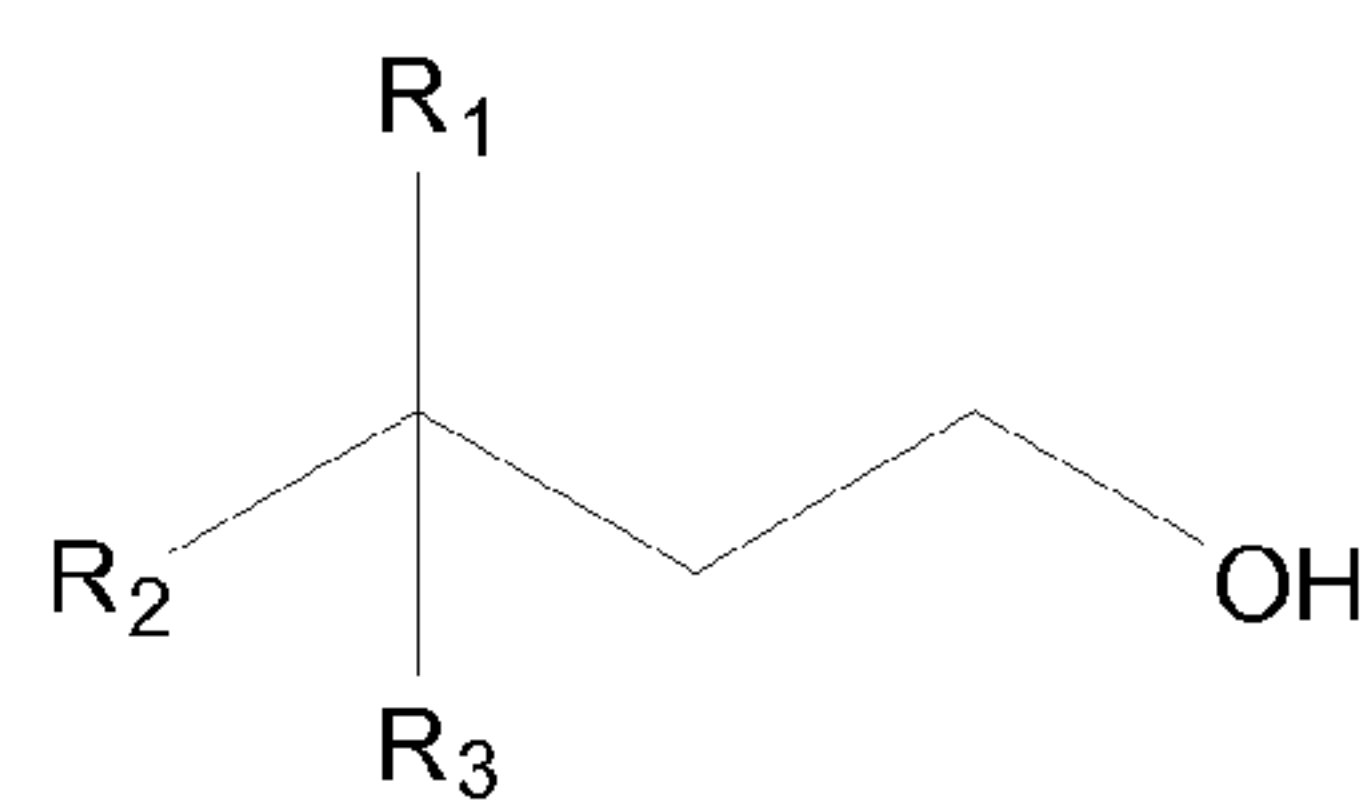


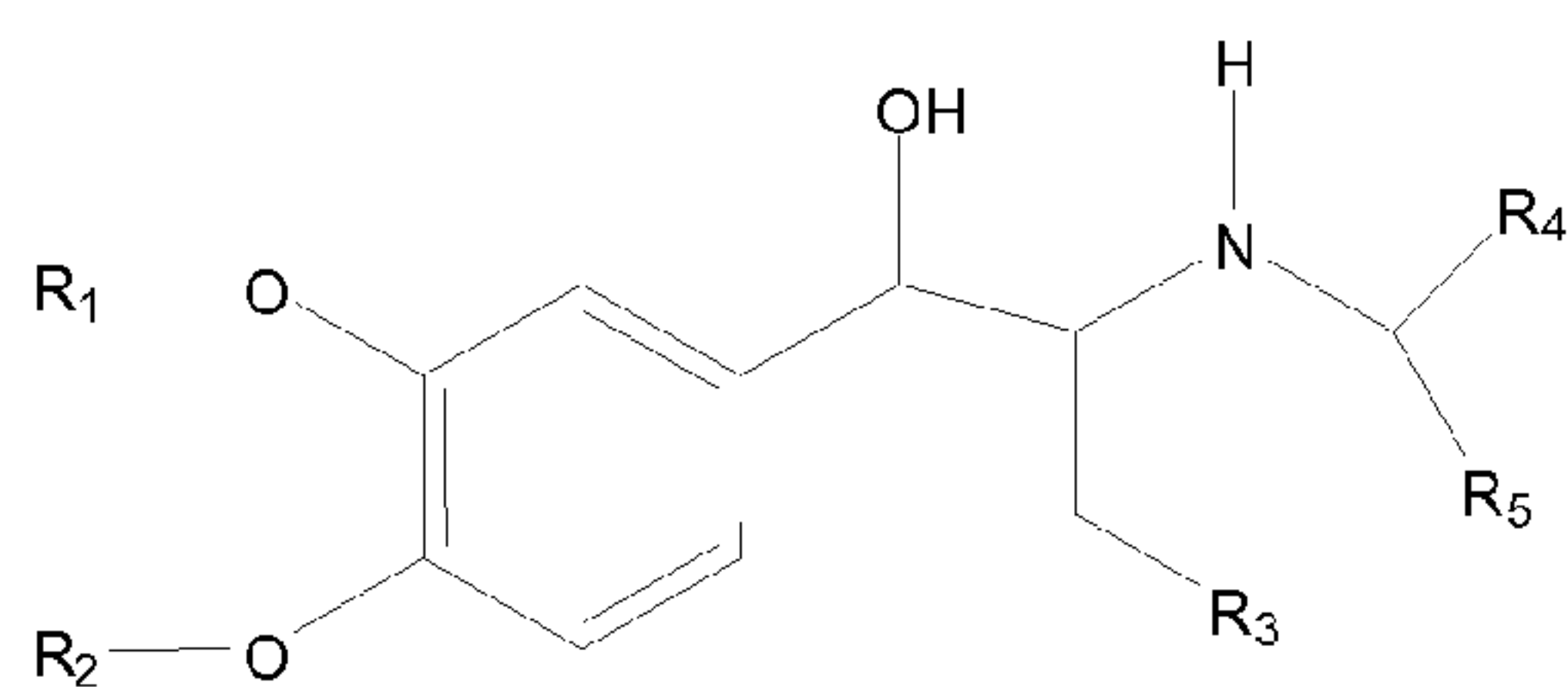
Fig. 5B



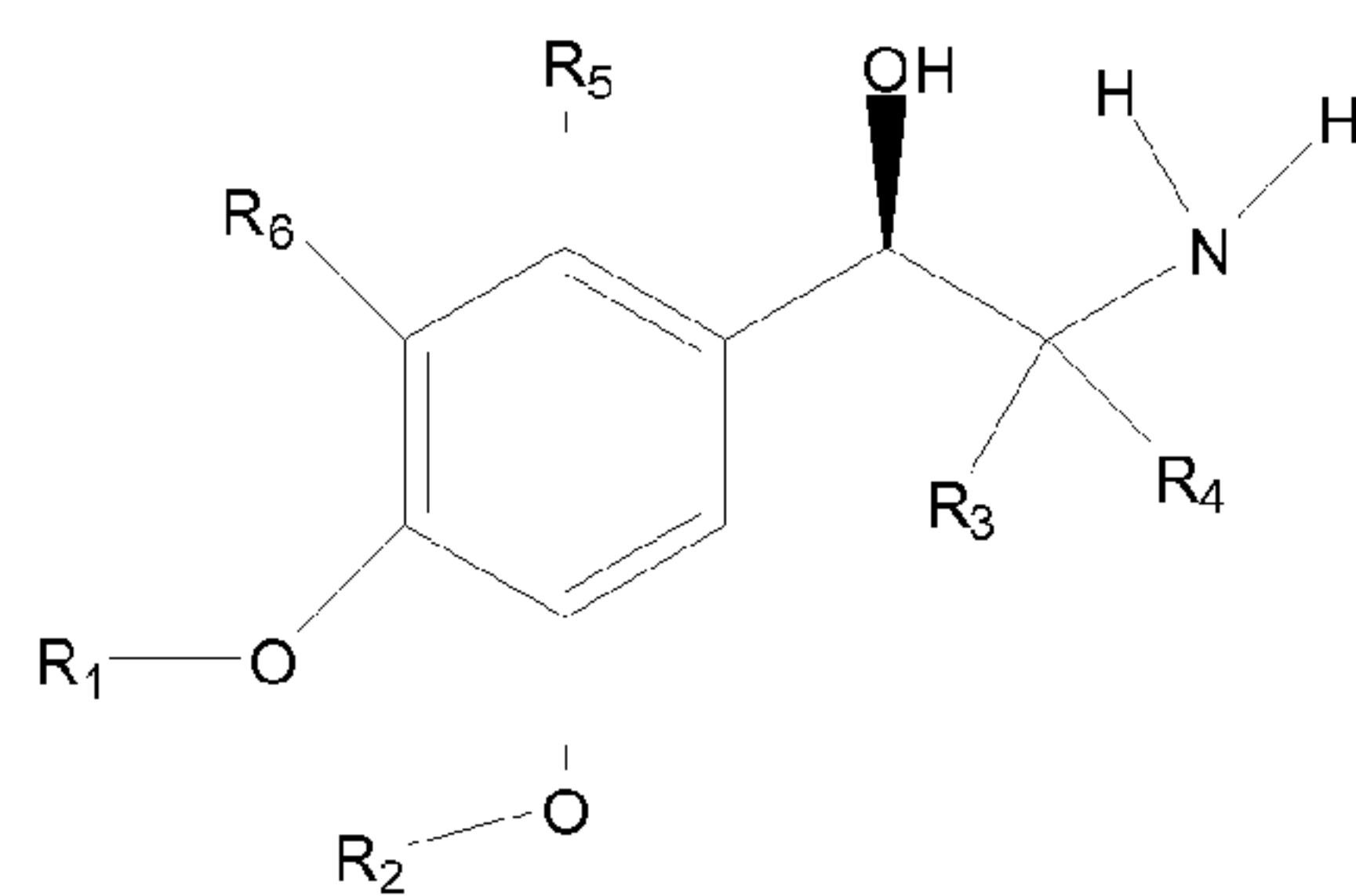
2' amino alcohols
($R_1 = H$, 1' amino alcohols)



cholines



isoetarines



norepinephrines

Fig. 6

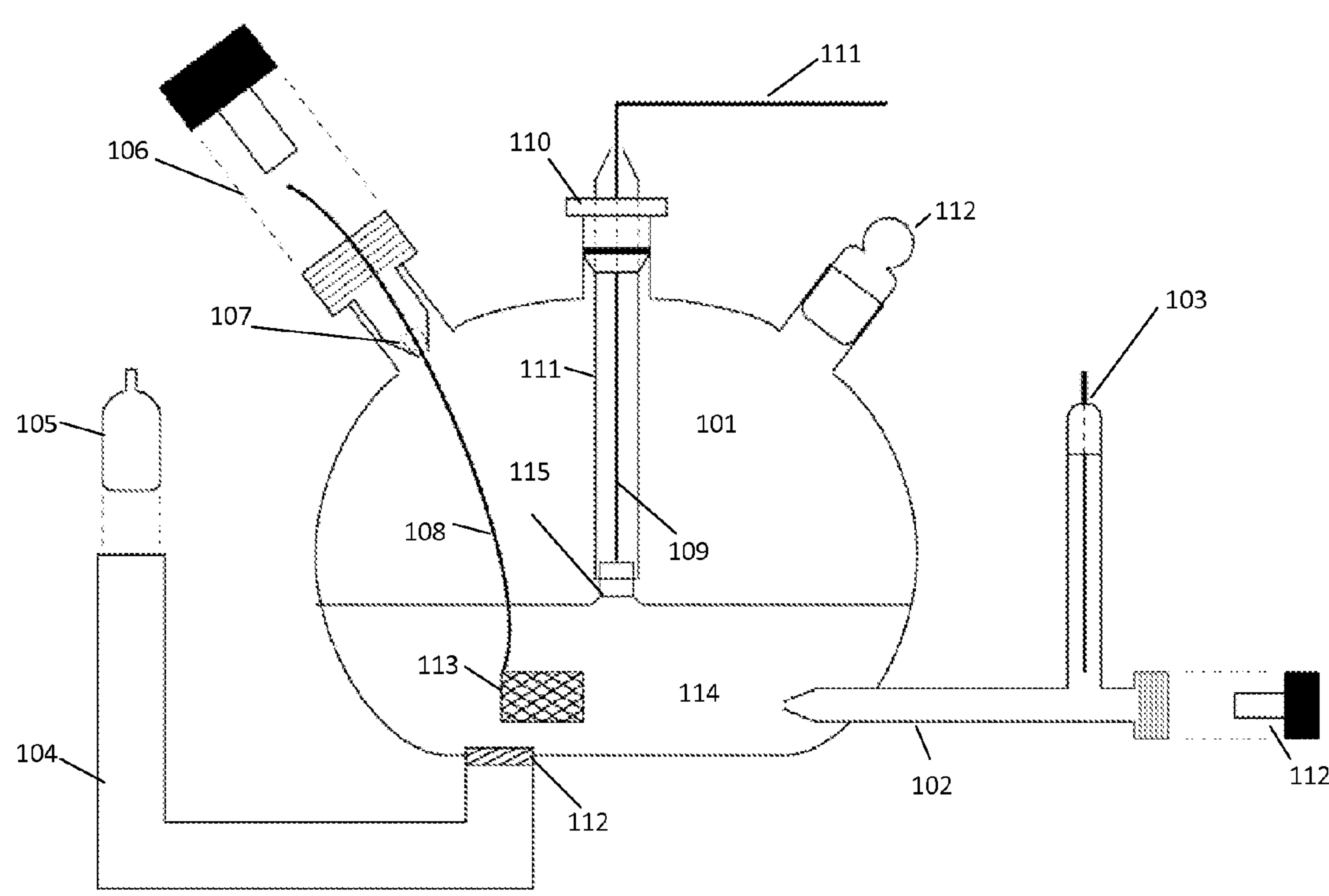


Fig. 7

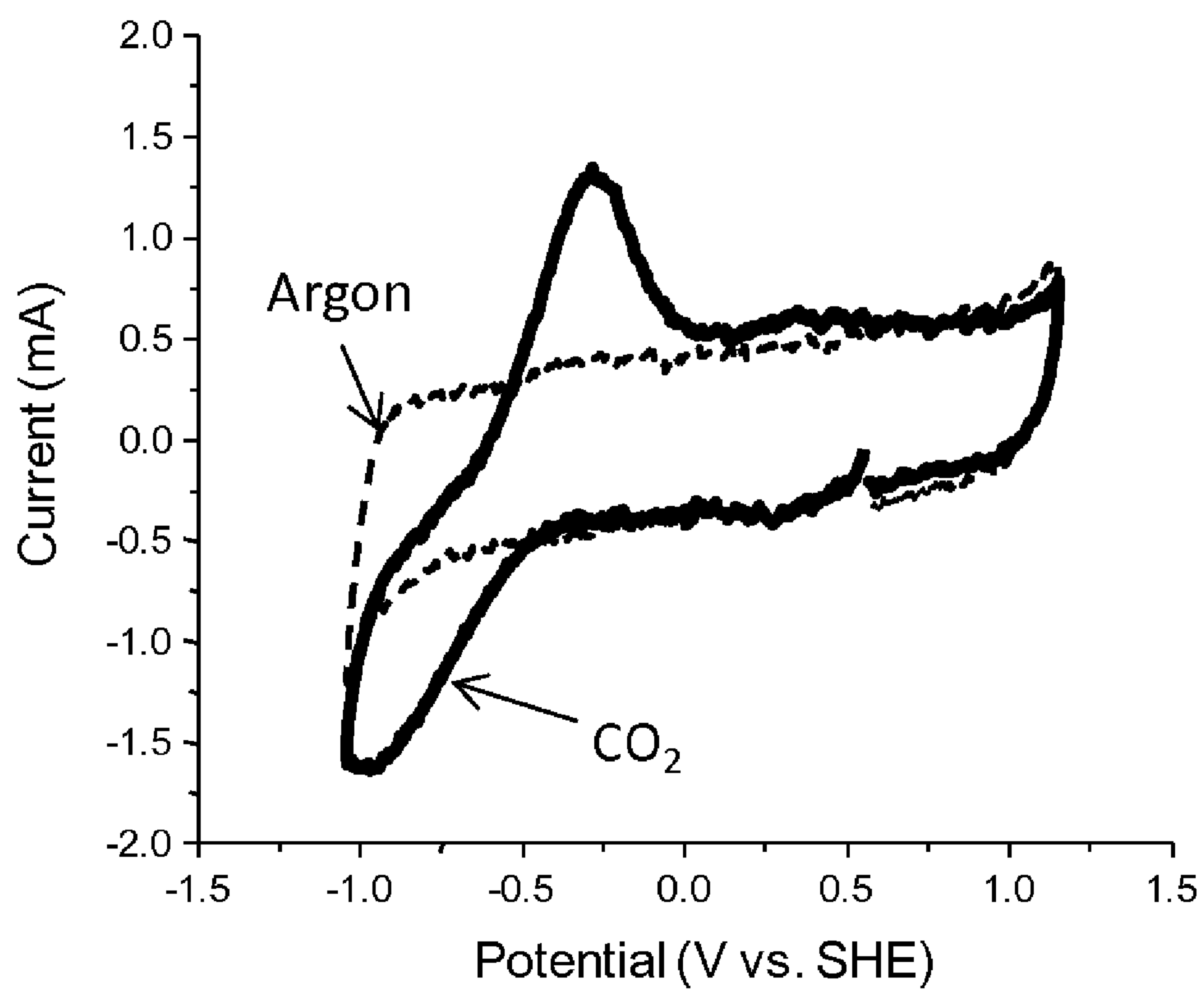


Fig. 8

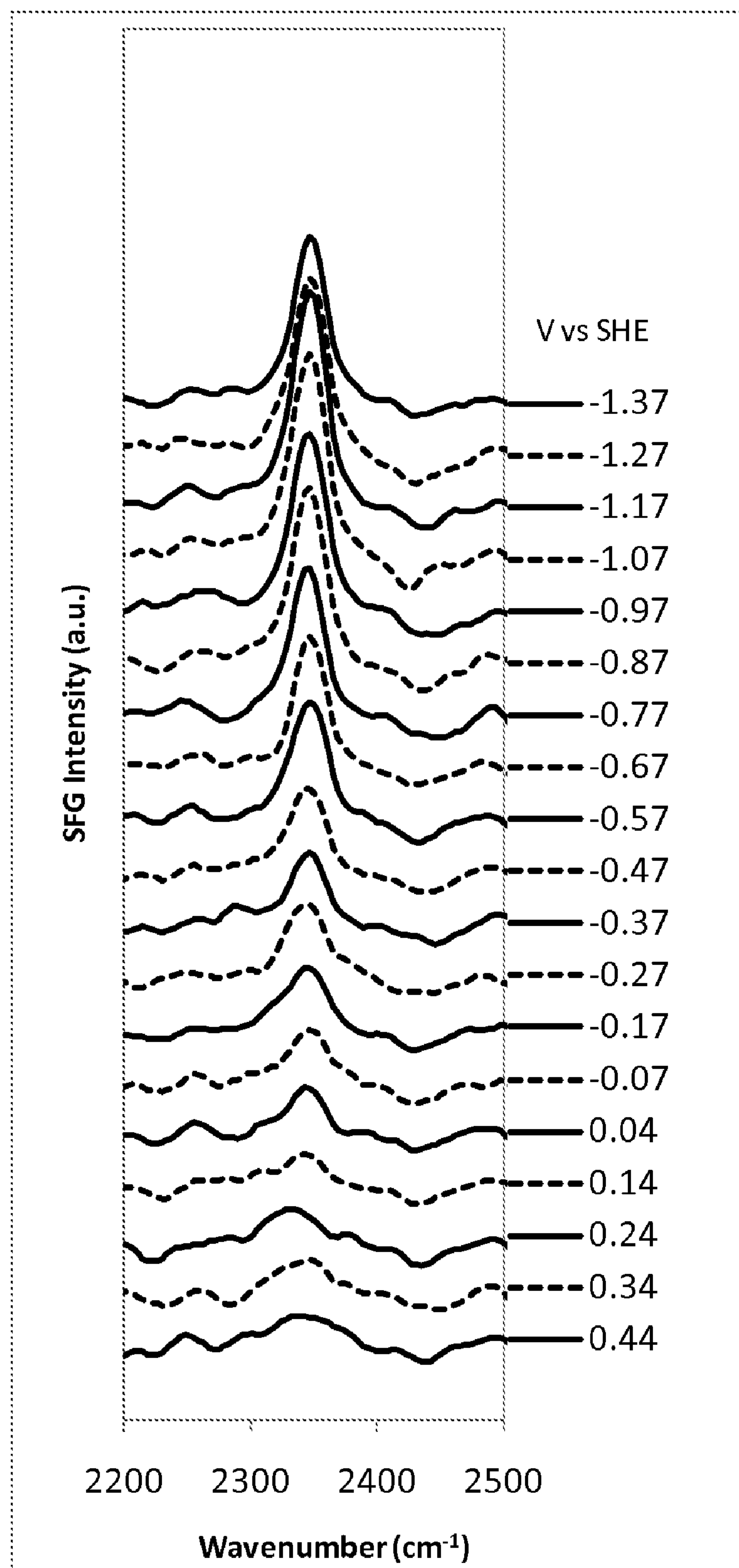


Fig. 9

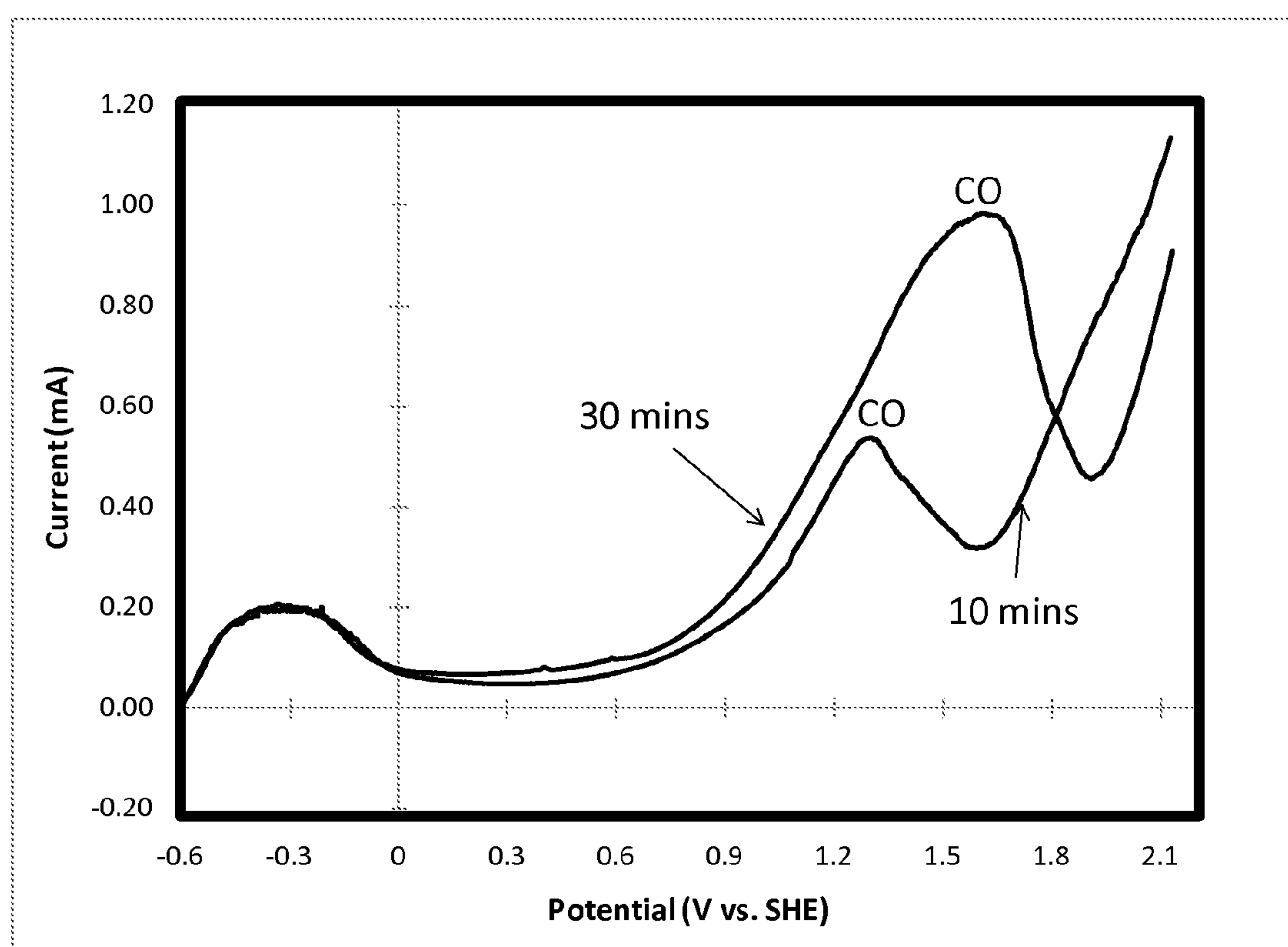


Fig. 10

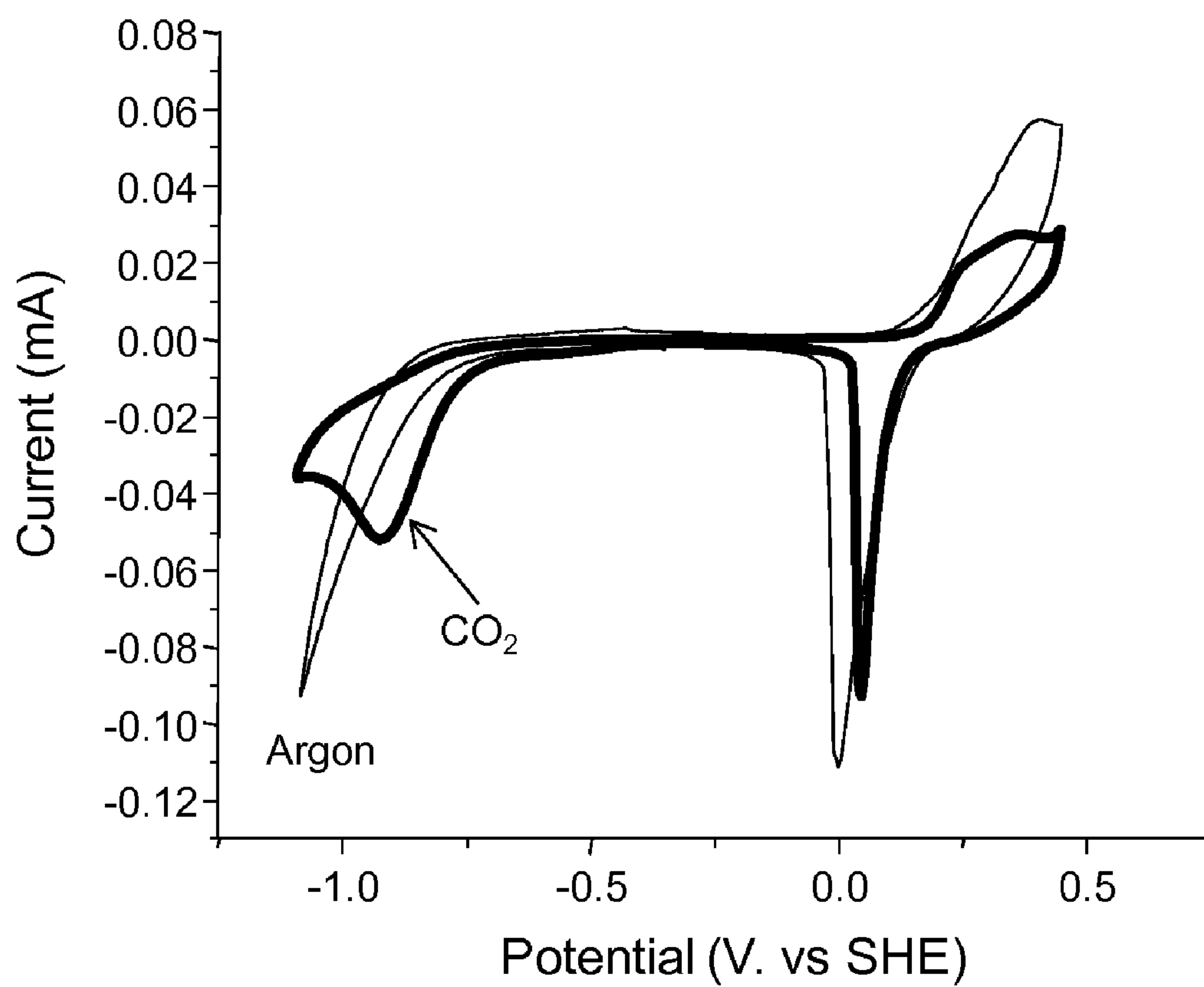


Fig. 11

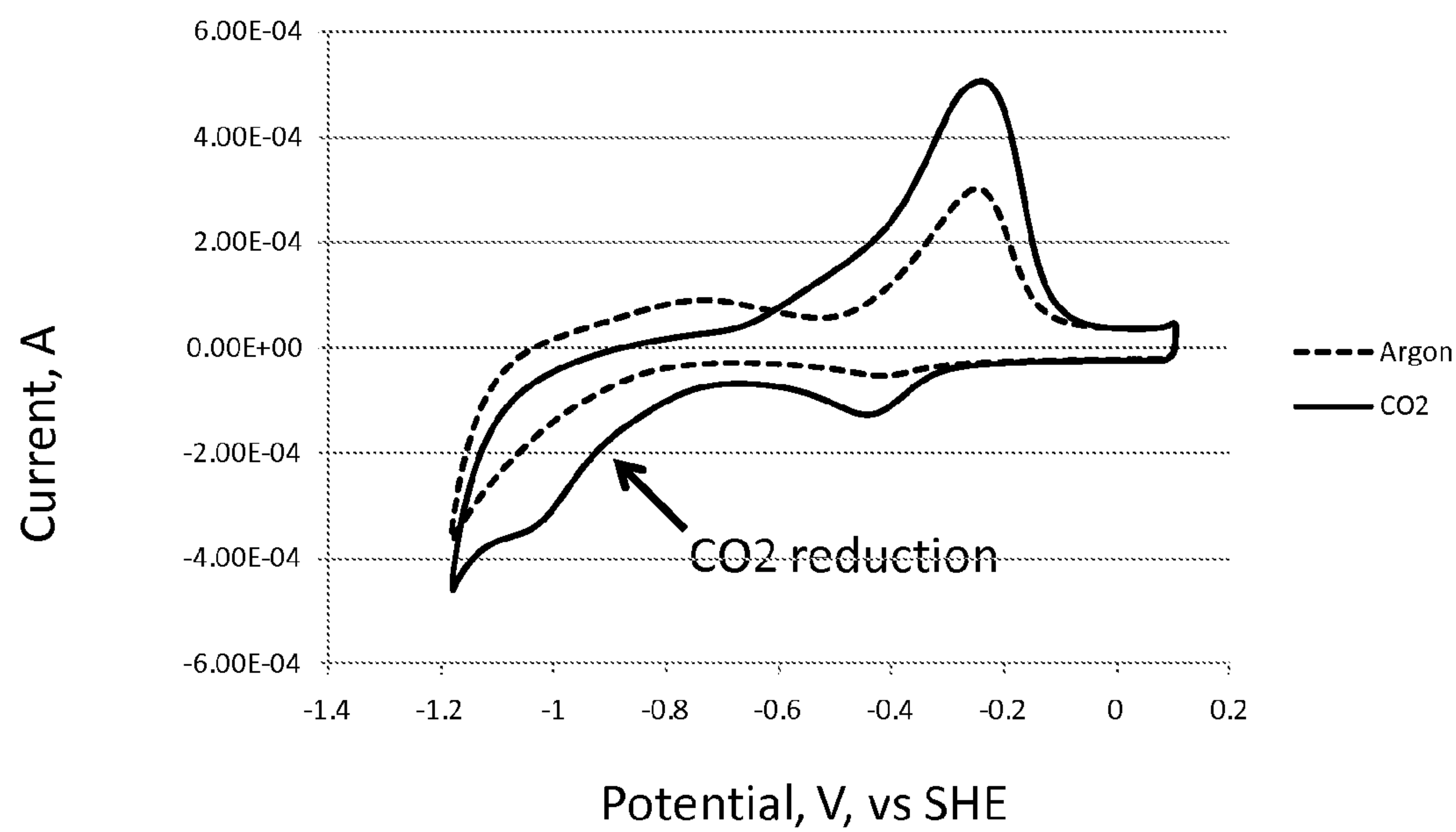


Fig. 12

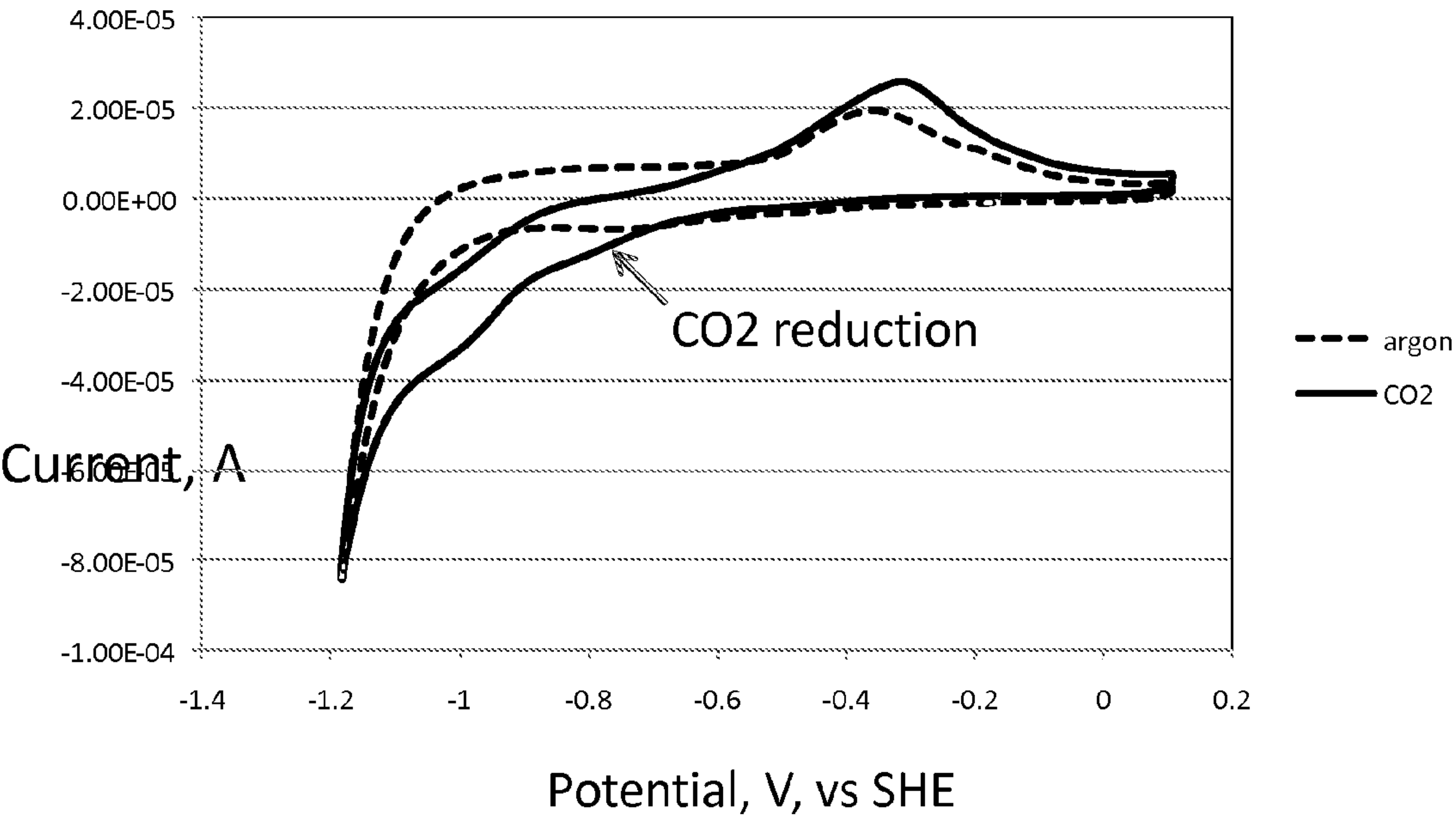


Fig. 13

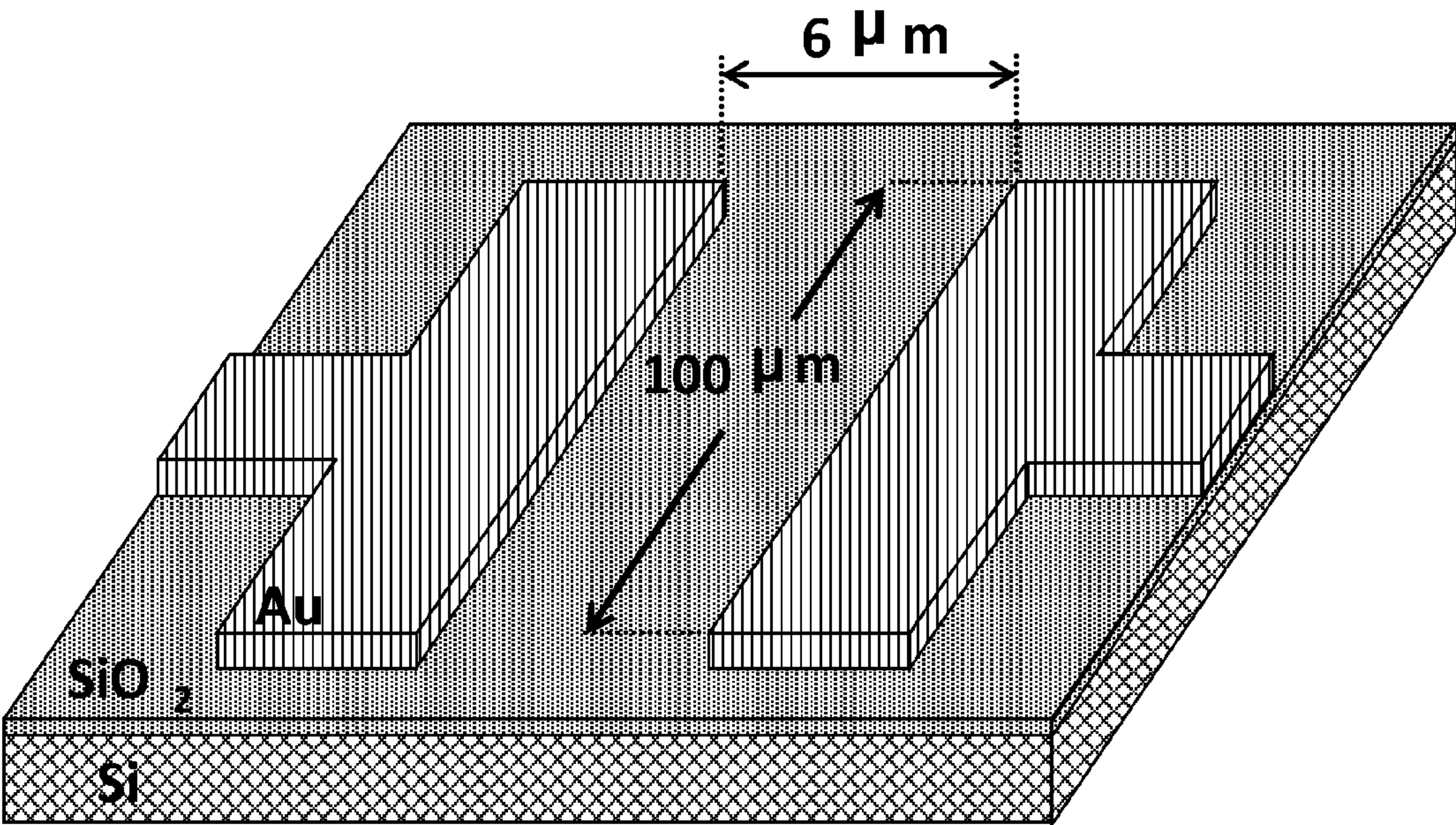


Fig. 14

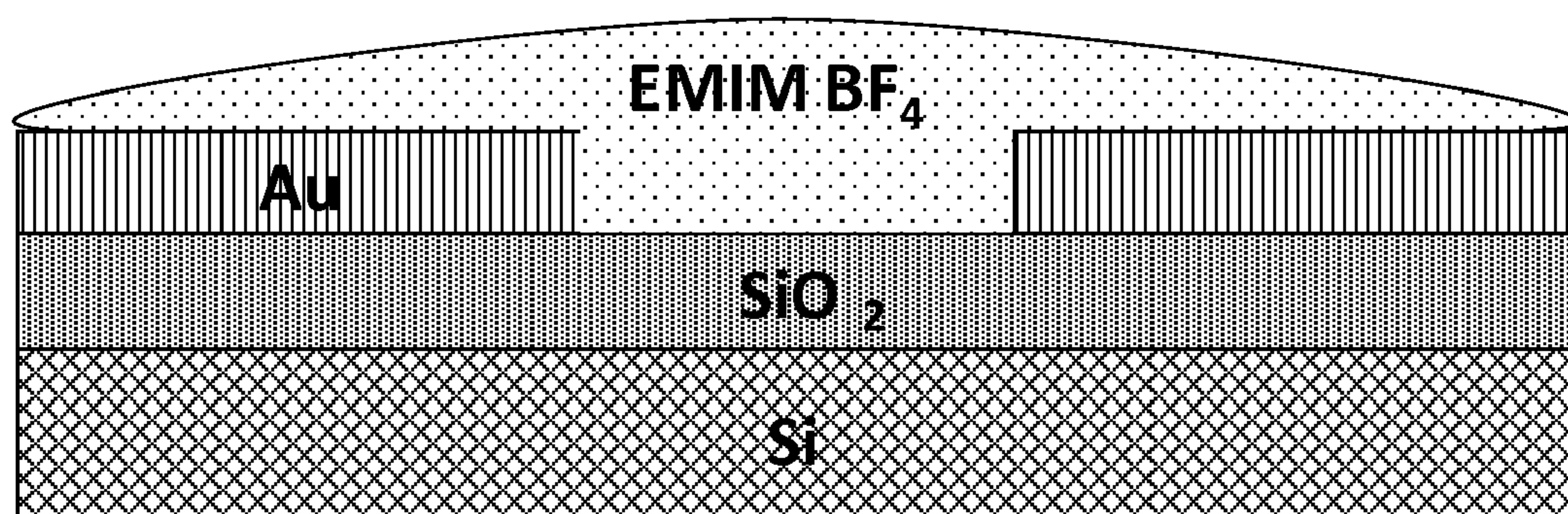


Fig. 15

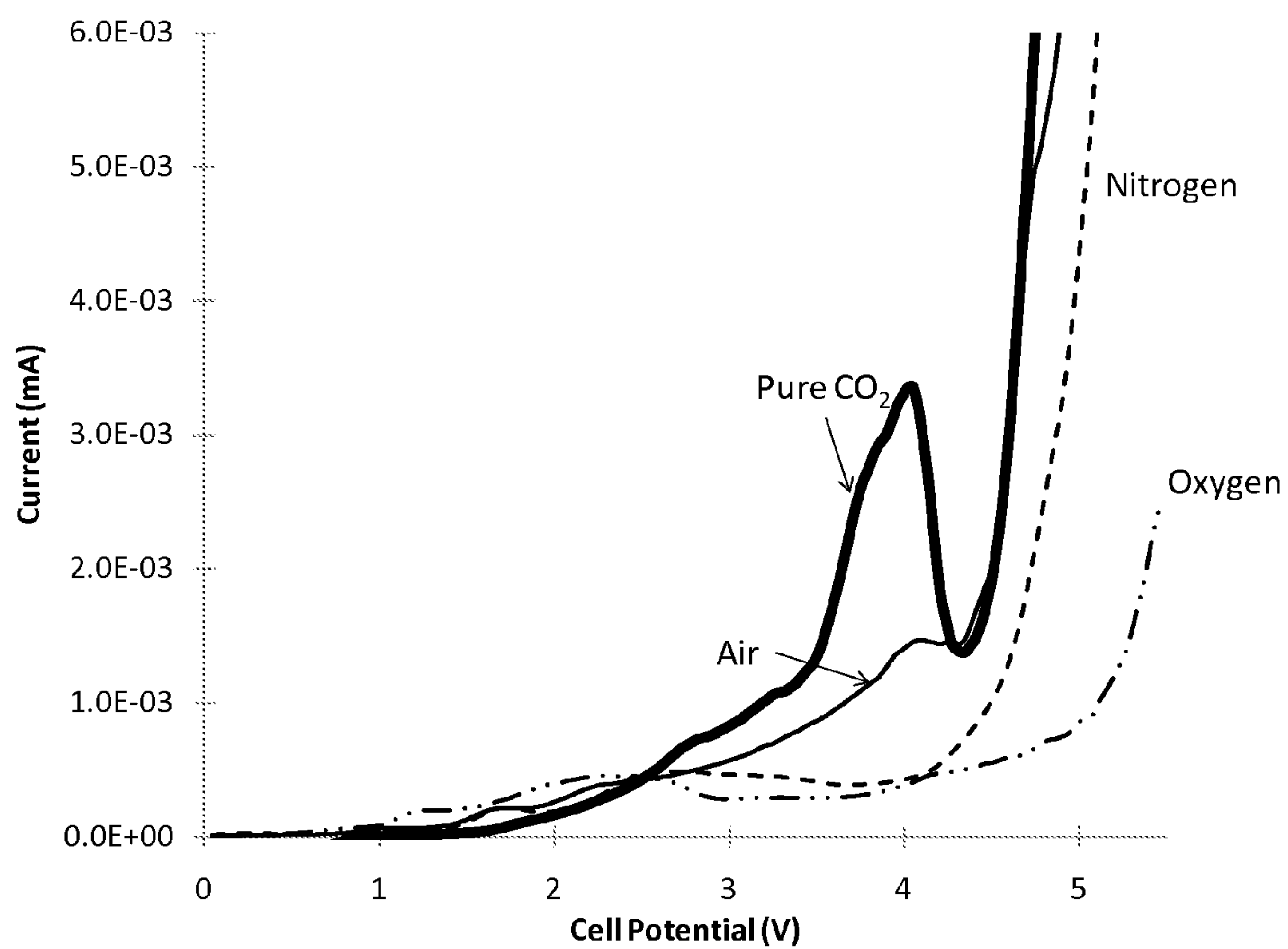


Fig. 16

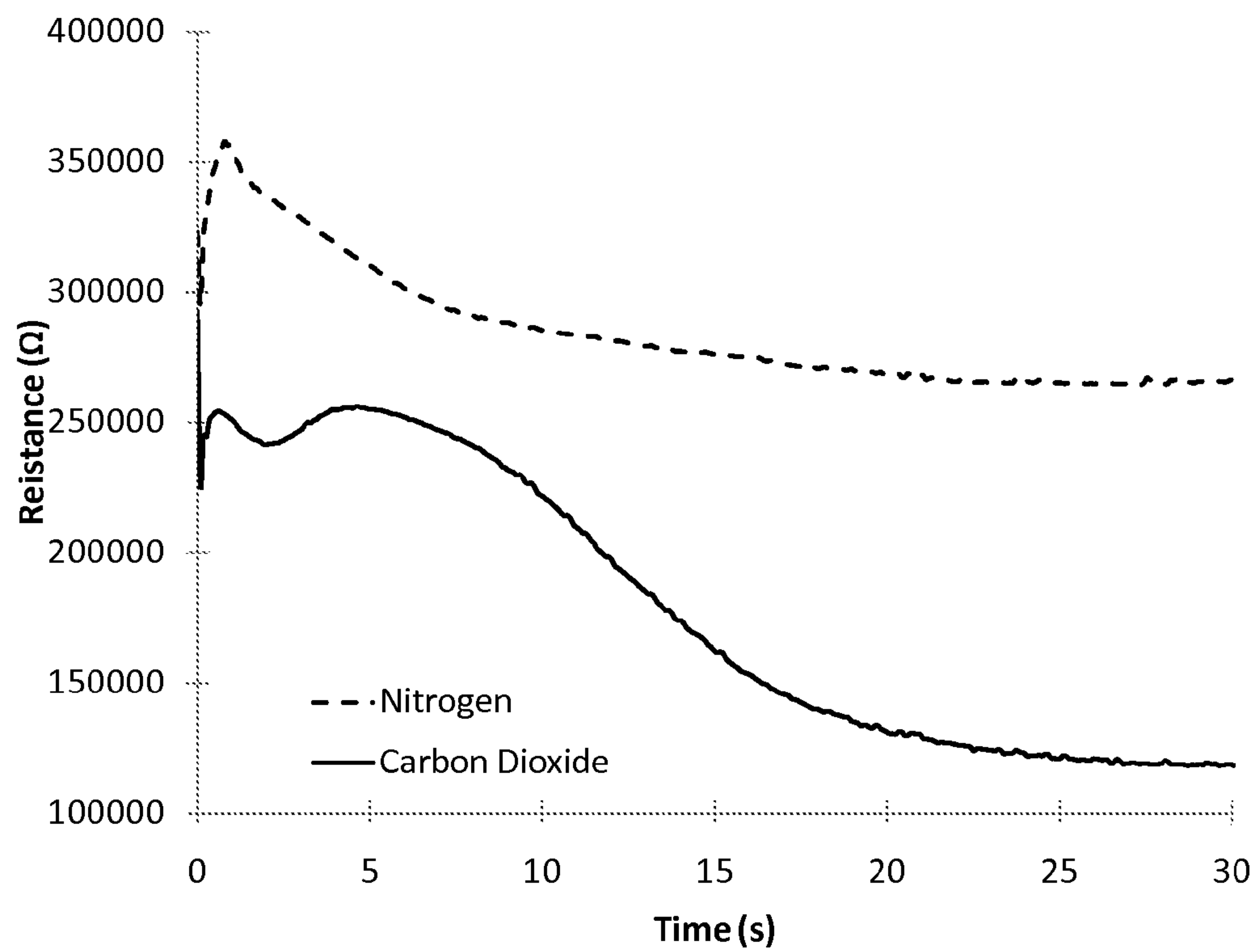


Fig. 17

NOVEL CATALYST MIXTURES

CROSS-REFERENCES TO RELATED APPLICATIONS

[0001] This application claims priority to and the benefit under 35 U.S.C. §119(e) to provisional application 61/317,955, filed Mar. 26, 2010, the disclosure of which is expressly incorporated herein by reference in its entirety.

FIELD OF THE INVENTION

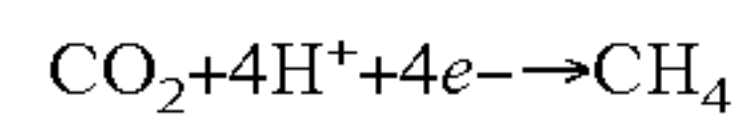
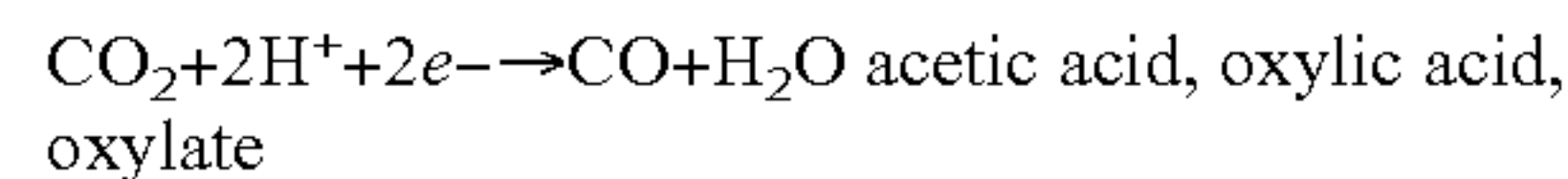
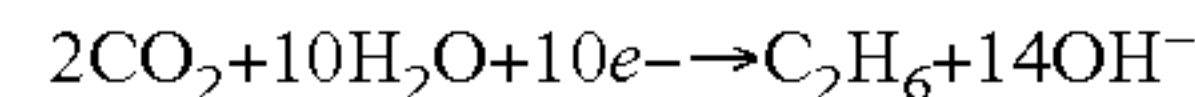
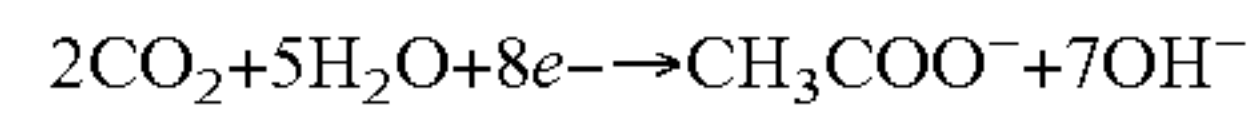
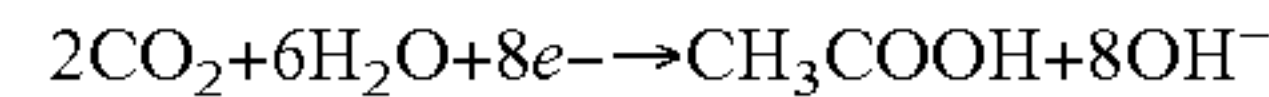
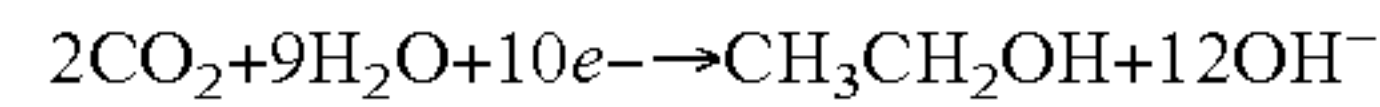
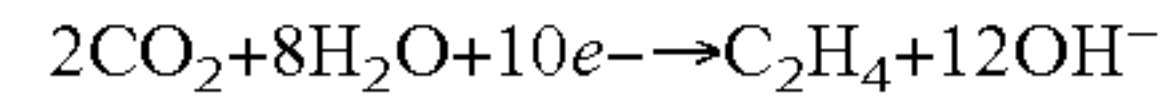
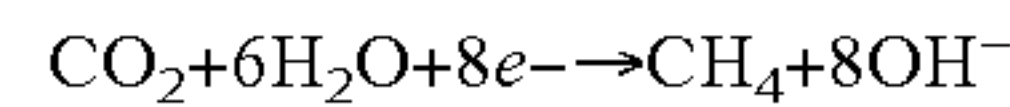
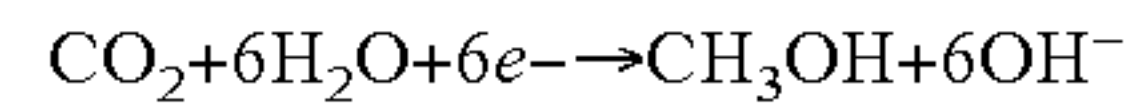
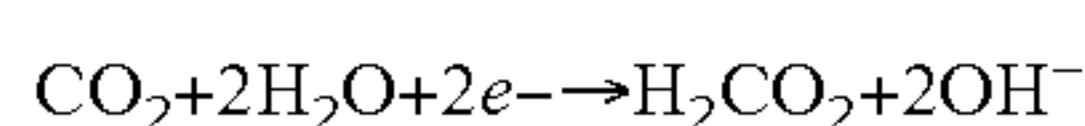
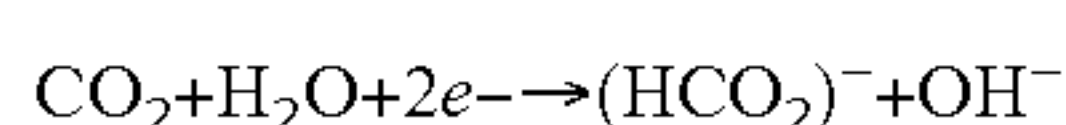
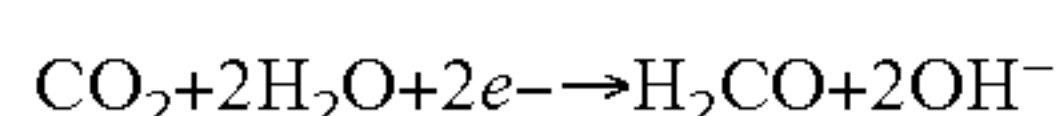
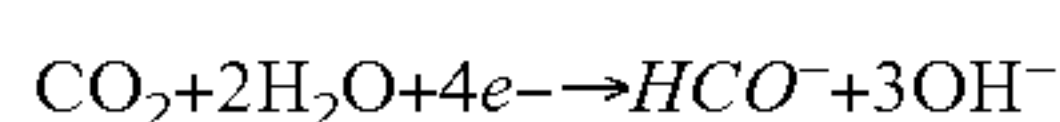
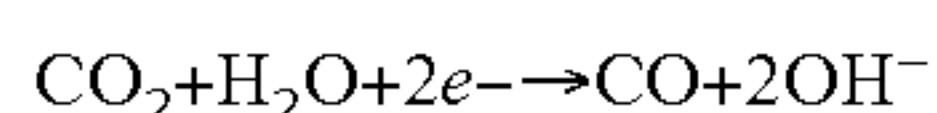
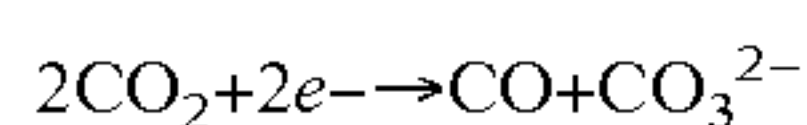
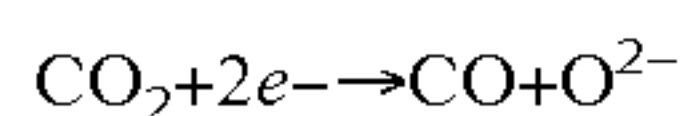
[0002] The field of the invention is catalysis and catalysts. The catalysts of this invention are applicable, for example, to the electrochemical conversion of carbon dioxide into formic acid.

BACKGROUND

[0003] There is a present need to decrease carbon dioxide (CO₂) emissions from industrial facilities. Over the years, a number of electrochemical processes have been suggested for the conversion of CO₂ into useful products. Processes for CO₂ conversion and the catalysts for them are discussed in U.S. Pat. Nos. 3,959,094 4,240,882 4,523,981 4,545,872, 4,595,465 4,608,132 4,608,133 4,609,441 4,609,440, 4,620,906, 4,668,349, 4,673,473, 4,711,708, 4,756,807, 4,756,807, 4,818,353 5,064,733 5,284,563 5,382,332 5,709,789, 5,928,806, 5,952,540 6,024,855 6,660,680 6,987,134 (the '134 patent), 7,157,404, 7,378,561, 7,479,570, patent application 20080223727 (The '727 application) and papers reviewed by Hori (Modern Aspects of Electrochemistry, 42, 89-189, 2008) ("The Hori Review"), Gattrell, et al. (Journal of Electroanalytical Chemistry, 594, 1-19, 2006) ("The Gattrell Review"), DuBois (Encyclopedia of Electrochemistry, 7a, 202-225, 2006) ("The DuBois Review"), and the papers Li, et al. (Journal of Applied Electrochemistry, 36, 1105-1115, 2006, Li, et al. (Journal of Applied Electrochemistry, 37, 1107-1117, 2007, and Oloman, et al. (ChemSusChem, 1, 385-391, 2008) ("The Li and Oloman Papers")

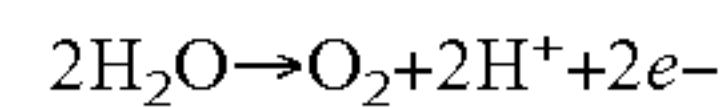
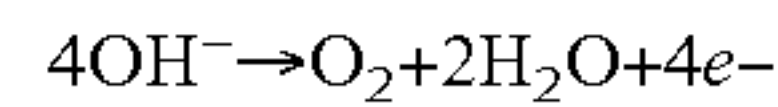
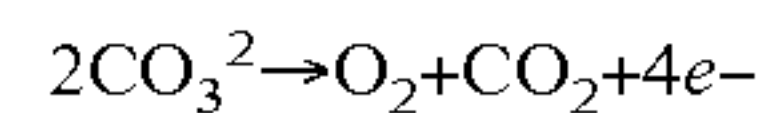
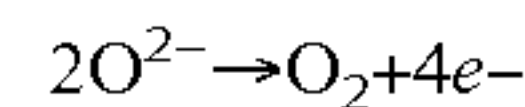
[0004] Generally an electrochemical cell contains an anode (50), a cathode (51) and an electrolyte (53) as indicated in FIG. 1. Catalysts are placed on the anode, and or cathode and or in the electrolyte to promote desired chemical reactions. During operation, reactants or a solution containing reactants is fed into the cell. Then a voltage is applied between the anode and the cathode, to promote an electrochemical reaction.

[0005] When an electrochemical cell is used as a CO₂ conversion system, a reactant comprising CO₂, carbonate or bicarbonate is fed into the cell. A voltage is applied to the cell and the CO₂ reacts to form new chemical compounds. Examples of cathode reactions in The Hori Review include



where e⁻ is an electron. The examples given above are merely illustrative and are not meant to be an exhaustive list of all possible cathode reactions.

[0006] Examples of reactions on the anode mentioned in The Hori Review include



The examples given above are merely illustrative and are not meant to be an exhaustive list of all possible anode reactions.

[0007] In the previous literature, catalysts comprising one or more of V, Cr, Mn, Fe, Co, Ni, Cu, Sn, Zr, Nb, Mo, Ru, Rh, Pd, Ag, Cd, Hf, Ta, W, Re, Ir, Pt, Au, Hg, Al, Si, C, In, Sn, Ti, Pb, Bi, Sb, Te, U, Sm, Tb, La, Ce, and Nd have all shown activity for CO₂ conversion. Reviews include Ma, et al. (Catalysis Today, 148, 221-231, 2009) Hori (Modern Aspects of Electrochemistry, 42, 89-189, 2008), Gattrell, et al. (Journal of Electroanalytical Chemistry, 594, 1-19, 2006), DuBois (Encyclopedia of Electrochemistry, 7a, 202-225, 2006) and references therein.

[0008] The results in The Hori Review show that the conversion of CO₂ is only mildly affected by solvent unless the solvent also acts as a reactant. Water can act like a reactant, so reactions in water are different than reactions in non-aqueous solutions. But the reactions are the same in most non-aqueous solvents, and importantly, the overpotentials are almost the same in water and in the non-aqueous solvents.

[0009] Zhang, et al. (ChemSusChem, 2, 234-238, 2009) and Chu, et al. (ChemSusChem, 1, 205-209, 2008) report CO₂ conversion catalyzed by an ionic liquid. Zhao, et al. (The Journal of Supercritical Fluids, 32, 287-291, 2004) and Yan et al. (Electrochimica Acta 54 (2009) 2912-2915) report the use of an ionic liquid as a solvent and electrolyte, but not a co-catalyst, for CO₂ electroconversion. Each of these papers are incorporated by reference. The catalysts have been in the form of either bulk materials, supported particles, collections of particles, small metal ions or organometallics. Still according to Bell Basic Research Needs, Catalysis For Energy, US Department Of Energy Report PNNL-17214, 2008), ("The Bell Report") "The major obstacle preventing efficient conversion of carbon dioxide into energy-bearing products is the lack of catalyst" with sufficient activity at low overpotentials and high electron conversion efficiencies.

[0010] The overpotential is associated with lost energy of the process and so one needs the overpotential to be as low as possible. Yet, according to The Bell Report “*Electron conversion efficiencies of greater than 50 percent can be obtained, but at the expense of very high overpotentials*” This limitation needs to be overcome before practical processes can be obtained.

[0011] The '134 patent also considers the use of salt (NaCl) as a secondary “catalyst” for CO₂ reduction in the gas phase but salt does not lower the overpotential for the reaction.

[0012] A second disadvantage of many of the catalysts is that they also have low electron conversion efficiency. Electron conversion efficiencies over 50% are needed for practical catalyst systems.

[0013] The examples above consider applications for CO₂ conversion but the invention overcomes limitations for other systems. For example some commercial CO₂ use an electrochemical reaction to detect the presence of CO₂. At present, these sensors require over 1-5 watts of power, which is too high for portable sensing applications.

[0014] Finally, the invention considers new methods to form formic acid. Other methods are discussed in U.S. Pat. Nos. 7,618,725, 7,612,233, 7,420,088, 7,351,860, 7,323,593, 7,253,316, 7,241,365, 7,138,545, 6,992,212, 6,963,909, 6,955,743, 6,906,222, 6,867,329, 6,849,764, 6,841,700, 6,713,649, 6,429,333, 5,879,915, 5,869,739, 5,763,662, 5,639,910, 5,334,759, 5,206,433, 4,879,070, 4,299,891. These processes do not use CO₂ as a reactant.

BRIEF SUMMARY OF THE INVENTION

[0015] The invention provides a novel catalyst mixture that can overcome one or more of the limitations of low rates, high overpotentials and low electron conversion efficiencies (i.e. selectivities) for catalytic reactions and high powers for sensors. The catalyst mixture includes at least one Catalytically Active Element, and at least one Helper Catalyst. When the Catalytically Active Element and the Helper Catalyst are combined the rate and/or selectivity of a chemical reaction can be enhanced over the rate seen in the absence of the Helper Catalyst. For example, the overpotential for electrochemical conversion of carbon-dioxide can be substantially reduced and the current efficiency (i.e. selectivity) for CO₂ conversion can be substantially increased.

[0016] The invention is not limited to catalysts for CO₂ conversion. In particular, catalysts that include Catalytically Active Elements and Helper Catalysts might enhance the rate of a wide variety of chemical reactions. Reaction types include: homogeneously catalyzed reactions, heterogeneously catalyzed reactions, chemical reactions in chemical plants, chemical reactions in power plants, chemical reactions in pollution control equipment and devices, chemical reactions in fuel cells, chemical reactions in sensors. The invention includes all of these examples. The invention also includes processes using these catalysts.

BRIEF DESCRIPTION OF THE DRAWINGS

[0017] FIG. 1 is a diagram of a typical electrochemical cell.

[0018] FIG. 2 is a schematic of how the potential of the system moves as it proceeds along the reaction coordinate in the absence of the ionic liquid if the system goes through a (CO₂)⁻ intermediate. The reaction coordinate indicates the fraction of the reaction that has completed. A high potential for (CO₂)⁻ formation can create a high overpotential for the reaction.

[0019] FIG. 3 illustrates how the potential could change when a helper catalyst is used. In this case the reaction could

go through a CO₂-EMIM complex rather than a (CO₂)⁻ substantially lowering the overpotential for the reaction.

[0020] FIGS. 4A, 4B and 4C illustrate some of the cations that may be used to form a complex with (CO₂)⁻

[0021] FIGS. 5A and 5B illustrates some of the anions that may stabilize the (CO₂)⁻ anion.

[0022] FIG. 6 illustrates some of the neutral molecules that may be used to form a complex with (CO₂)⁻

[0023] FIG. 7 shows a schematic of a cell used for the experiments in Examples 1, 2, 3, 4 and 5.

[0024] FIG. 8 shows comparison of the cyclic voltametry for a blank scan where the catalyst was synthesized as in Example 1 where i) the EMIM-BF₄ was sparged with argon and ii) a scan where the EMIM-BF₄ was sparged with CO₂.

Notice the large negative peak associated with CO₂ formation [0025] FIG. 9 shows a series of Broad Band Sum Frequency Generation (BB-SFG) taken sequentially as the potential in the cell was scanned from +0. to -1.2 with respect to SHE.

[0026] FIG. 10 shows a CO stripping experiment done by holding the potential at -0.6 V for 10 or 30 minutes and then measuring the size of the CO stripping peak between 1.2 and 1.5 V with respect to RHE.

[0027] FIG. 11 shows a comparison of the cyclic voltametry for a blank scan where the catalyst was synthesized as in Example 3 where i) the water-choline iodide mixture was sparged with argon and ii) a scan where the water-choline iodide mixture was sparged with CO₂.

[0028] FIG. 12 shows a comparison of the cyclic voltametry for a blank scan where the catalyst was synthesized as in Example 4 where i) the water-choline chloride mixture was sparged with argon and ii) a scan where the water-choline chloride mixture was sparged with CO₂.

[0029] FIG. 13 shows a comparison of the cyclic voltametry for a blank scan where the catalyst was synthesized as in Example 5 where i) the water-choline chloride mixture was sparged with argon and ii) a scan where the water-choline chloride mixture was sparged with CO₂.

[0030] FIG. 14 shows a schematic of the sensor.

[0031] FIG. 15 shows a schematic of where EMBF₄ is placed on the sensor.

[0032] FIG. 16 shows the current measured when the voltage on the sensor was exposed to various gases, the applied voltage on the sensor was swept from 0 to 5 volts at 0.1 V/sec.

[0033] FIG. 17 shows the resistance of the sensor, in nitrogen and in carbon dioxide. The resistance was determined by measuring the voltage needed to maintain a current of 1 microamp. Time is the time from when the current was applied.

DETAILED DESCRIPTION OF THE INVENTION

[0034] It is understood that the invention is not limited to the particular methodology, protocols, and reagents, etc., described herein, as these may vary as the skilled artisan will recognize. It is also to be understood that the terminology used herein is used for the purpose of describing particular embodiments only, and is not intended to limit the scope of the invention. It also is to be noted that as used herein and in the appended claims, the singular forms “a,” “an,” and “the” include the plural reference unless the context clearly dictates otherwise. Thus, for example, a reference to “a linker” is a reference to one or more linkers and equivalents thereof known to those skilled in the art.

[0035] Unless defined otherwise, all technical and scientific terms used herein have the same meanings as commonly understood by one of ordinary skill in the art to which the invention pertains. The embodiments of the invention and the various features and advantageous details thereof are

explained more fully with reference to the non-limiting embodiments and/or illustrated in the accompanying drawings and detailed in the following description. It should be noted that the features illustrated in the drawings are not necessarily drawn to scale, and features of one embodiment may be employed with other embodiments as the skilled artisan would recognize, even if not explicitly stated herein.

[0036] Any numerical values recited herein include all values from the lower value to the upper value in increments of one unit provided that there is a separation of at least two units between any lower value and any higher value. As an example, if it is stated that the concentration of a component or value of a process variable such as, for example, size, angle size, pressure, time and the like, is, for example, from 1 to 90, specifically from 20 to 80, more specifically from 30 to 70, it is intended that values such as 15 to 85, 22 to 68, 43 to 51, 30 to 32 etc., are expressly enumerated in this specification. For values which are less than one, one unit is considered to be 0.0001, 0.001, 0.01 or 0.1 as appropriate. These are only examples of what is specifically intended and all possible combinations of numerical values between the lowest value and the similar manner.

[0037] Moreover, provided immediately below is a "Definition" section, where certain terms related to the invention are defined specifically. Particular methods, devices, and materials are described, although any methods and materials similar or equivalent to those described herein can be used in the practice or testing of the invention. All references referred to herein are incorporated by reference herein in their entirety.

DEFINITIONS

[0038] The term "electrochemical conversion of CO₂" as used here refers to any electrochemical process, where carbon dioxide, carbonate, or bicarbonate is converted into another chemical substance in any step of the process.

[0039] The term "CV" as used here refers to a cyclic voltamogram or cyclic voltammetry.

[0040] The term "Overpotential" as used here refers to the potential (voltage) difference between a reaction's thermodynamically determined reduction or oxidation potential and the potential at which the event is experimentally observed.

[0041] The term "Cathode Overpotential" as used here refers to the overpotential on the cathode of an electrochemical cell.

[0042] The term "Anode Overpotential" as used here refers to the overpotential on the anode of an electrochemical cell.

[0043] The term "Electron Conversion Efficiency" refers to selectivity of an electrochemical reaction. More precisely, it is defined as the fraction of the current that is supplied to the cell that goes to the production of a desired product.

[0044] The term "Catalytically Active Element" as used here refers to any chemical element that can serve as a catalyst for the electrochemical conversion of CO₂.

[0045] The term "Helper Catalyst" refers to any organic molecule or mixture of organic molecules that does at least one of the following:

[0046] 1) Speeds up an electrochemical reaction

[0047] 2) Lowers the overpotential of the reaction

[0048] without being substantially consumed in the process.

[0049] The term "Active Element, Helper Catalyst Mixture" refers to any mixture that includes one or more Catalytically Active Element and at least one Helper Catalyst

[0050] The term "Ionic Liquid" refers to salts or ionic compounds that form stable liquids at temperatures below 200° C.

[0051] The term "Deep Eutectic Solvent" refers to an ionic solvent that includes of a mixture which forms a eutectic with a melting point lower than that of the individual components.

Specifics

[0052] The invention relates generally to Active Element, Helper Catalyst Mixtures where the mixture does at least one of the following:

[0053] Speeds up a chemical reaction

[0054] Lowers the overpotential of the reaction

[0055] without being substantially consumed in the process.

[0056] For example such mixtures can lower the overpotential for CO₂ conversion to a value less than the overpotentials seen when the same Catalytically Active Element is used without the Helper Catalyst.

[0057] According to The Hori Review, Gattrell, et al. (Journal of Electroanalytical Chemistry, 594, 1-19, 2006), DuBois (Encyclopedia of Electrochemistry, 7a, 202-225, 2006) and references therein, catalysts include one or more of V, Cr, Mn, Fe, Co, Ni, Cu, Sn, Zr, Nb, Mo, Ru, Rh, Pd, Ag, Cd, Hf, Ta, W, Re, Ir, Pt, Au, Hg, Al, Si, In, Sn, Tl, Pb, Bi, Sb, Te, U, Sm, Tb, La, Ce, and Nd all show activity for CO₂ conversion. Products include one or more of CO, OH⁻, HCO⁻, H₂CO, (HCO₂)⁻, H₂CO₂, CH₃OH, CH₄, C₂H₄, CH₃CH₂OH, CH₃COO⁻, CH₃COOH, C₂H₆, CH₄, O₂, H₂(COOH)₂, (COO⁻)₂. Therefore, V, Cr, Mn, Fe, Co, Ni, Cu, Sn, Zr, Nb, Mo, Ru, Rh, Pd, Ag, Cd, Hf, Ta, W, Re, Ir, Pt, Au, Hg, Al, Si, In, Sn, Tl, Pb, Bi, Sb, Te, U, Sm, Tb, La, Ce, and Nd are each examples of Catalytically Active Elements but the invention is not limited to this list of chemical elements. Possible products of the reaction are include one or more of CO, OH⁻, HCO⁻, H₂CO, (HCO₂)⁻, H₂CO₂, CH₃OH, CH₄, C₂H₄, CH₃CH₂OH, CH₃COO⁻, CH₃COOH, C₂H₆, CH₄, O₂, H₂(COOH)₂, (COO⁻)₂, but the invention is not limited to this list of products.

[0058] The Hori Review also notes that Pb, Hg, Tl, In, Cd, Bi, Zr, Cr, Sn and W are best for formic acid production. Furuya, et al. (Journal of Electroanalytical Chemistry, 431, 39-41, 1997) notes that Pd/Ru is also active.

[0059] The Hori Review notes that there has been over 30 years of work on the electrochemical conversion of CO₂ into saleable products, but still, according to page 69 of The Bell Report "*Electron conversion efficiencies of greater than 50 percent can be obtained, but at the expense of very high overpotentials*" This limitation needs to be overcome before practical processes can be obtained.

[0060] FIGS. 2 and 3 illustrate one possible mechanism by which a Helper Catalyst can enhance the rate of CO₂ conversion. According to Chandrasekaran, et al. (Surface Science, 185, 495-514, 1987) the high overpotentials for CO₂ conversion occur because the first step in the electroreduction of CO₂ is the formation of a (CO₂)⁻ intermediate. It takes energy to form the intermediate as illustrated in FIG. 2. This results in a high overpotential for the reaction.

[0061] FIG. 3 illustrates what might happen if a solution containing 1-ethyl-3-methylimidazolium (EMIM⁺) cations is added to the mixture. EMIM⁺ might be able to form a complex with the (CO₂)⁻ intermediate. In that case, the reaction could proceed via the EMIM⁺-(CO₂)⁻ complex instead of going through a bare (CO₂)⁻ intermediate as illustrated in FIG. 3. If the energy to form the EMIM⁺-(CO₂)⁻ complex is

less than the energy to form the $(\text{CO}_2)^-$ intermediate, the overpotential to for CO_2 conversion could be substantially reduced. Therefore any substance including EMIM⁺ cations could act as a Helper Catalyst for CO_2 conversion.

[0062] Those trained in the state of art should recognize that in most cases, solvents only have small effects on the progress of catalytic reactions. The interaction between a solvent and an adsorbate is usually much weaker than the interaction with a Catalytically Active Element, so the solvent only makes a small perturbation to the chemistry occurring on metal surfaces. The diagram in FIG. 3 postulates that such an effect could be large.

[0063] Of course a Helper catalyst, alone, will be insufficient to convert CO_2 . Instead, one still needs a Catalytically Active Element that can catalyze reactions of $(\text{CO}_2)^-$ in order to get high rates of CO_2 conversion. Catalysts include at least one of the following Catalytically Active Elements have been previously reported to be active for electrochemical conversion of CO_2

[0064] V, Cr, Mn, Fe, Co, Ni, Cu, Sn, Zr, Nb, Mo, Ru, Rh, Pd, Ag, Cd, Hf, Ta, W, Re, Ir, Pt, Au, Hg, Al, Si, In, Sn, Tl, Pb, Bi, Sb, Te, U, Sm, Tb, La, Ce, and Nd.

Many of these catalysts also show activity for a number of other reactions. All of these elements are specifically included as Catalytically Active Elements for the purposes of the invention. This list of elements is meant for illustrative purposes only, and is not meant to limit the scope of the invention.

[0065] Further, those skilled in the art should realize that the diagram in FIG. 3 could be drawn for any molecule that could form a complex with $(\text{CO}_2)^-$. Previous literature indicates that solutions including one or more of: ionic liquids, deep eutectic solvents, amines, and phosphines, including specifically imidazoniums, pyridiniums, pyrrolidiniums, phosphoniums, ammoniums sulfoniums, prolinates, methioninates, form complexes with CO_2 . Consequently, they may serve as Helper Catalysts. Also Davis Jr, et al. (In ACS Symposium Series 856: Ionic Liquids as Green Solvents Progress and Prospects, 100-107, 2003) list a number of other salts that show ionic properties. Specific examples include compounds including one or more of Acetocholines, alanines, aminoacetonitriles, methylammoniums, arginines, aspartic acids, threonines, chloroformamidiniums, thiouroniums, quinoliniums, pyrrolidinols, serinols, benzamidines, sulfamates, acetates, carbamates, triflates, and cyanides. These salts may act as helper catalysts. These examples are meant for illustrative purposes only, and are not meant to limit the scope of the invention.

[0066] Of course, not every substance that forms a complex with $(\text{CO}_2)^-$ will act as a helper catalyst. Masel (Chemical Kinetics and Catalysis, Wiley 2001, p717-720), notes that when an intermediate binds to a catalyst, the reactivity of the intermediate decreases. If the intermediate bonds too strongly to the catalyst, the intermediate will become unreactive, so the substance will not be effective. This provides a key limitation on substances that act as helper catalysts. The helper catalyst cannot form too strong of a bond with the $(\text{CO}_2)^-$ that the $(\text{CO}_2)^-$ is unreactive toward the Catalytically Active Element.

[0067] More specifically, one wishes the substance to form a complex with the $(\text{CO}_2)^-$ so is that the complex is stable (i.e. has a negative free energy of formation) at potentials less negative than -1 V with respect to SHE. However the complex should not be so stable, that the free energy of the

reaction between the complex and the Catalytically Active Element is more positive than about 3 kcal/mol.

[0068] For example Zhao, et al. (The Journal of Supercritical Fluids, 32, 287-291, 2004) examined CO_2 conversion over copper in 1-n-butyl-3-methylimidazolium hexafluorophosphate (BMIM-PF6) but FIG. 3 in Zhao et al shows that the BMIM-PF6 did NOT lower the overpotential for the reaction (i.e. the BMIM-PF6 did not act as a Helper Catalyst)/ This may be because the BMIM-PF6 formed such a strong bond to the $(\text{CO}_2)^-$ that the CO_2 was unreactive with the copper. Similarly Yuan et al Electrochimica Acta 54 (2009) 2912-2915 examined the reaction between methanol and CO_2 in 1-butyl-3-methylimidazolium bromide (BMIM-Br). The BMIM-Br did not act as a helper catalyst. This may be because the complex was too weak or that the bromine poisoned the reaction.

[0069] Solutions consisting of one or more of the cations in FIG. 4, the anions in FIG. 5, the neutral species in FIG. 6, where R1, R2 and R3 include H, OH or any ligand containing at least on carbon atom are believed to form complexes with CO_2 or $(\text{CO}_2)^-$. Specific examples include: imidazoniums, pyridiniums, pyrrolidiniums, phosphoniums, ammoniums and sulfoniums, prolinates, methioninates. All of these examples might be able to be used as Helper Catalysts for CO_2 conversion and are specifically included in the invention. These examples are meant for illustrative purposes only, and are not meant to limit the scope of the invention.

[0070] Further the Helper Catalyst could be in any one of the following forms i) a solvent for the reaction, ii) an electrolyte, iii) an additive to any component of the system, or iv) something that is bound to at least one of the catalysts in a system. These examples are meant for illustrative purposes only, and are not meant to limit the scope of the invention.

[0071] Those trained in the state of the art should recognize that one might only need a tiny amount of the Helper Catalyst to have a significant effect. Catalytic reactions often occur on distinct active sites. The active site concentration can be very low so in principle a small amount of Helper Catalyst can have a significant effect on the rate. One can obtain an estimate of how little of the helper catalyst would be needed to change the reaction from Pease et al, JACS 47, 1235 (1925)'s study of the effect of carbon monoxide (CO) on the rate of ethylene hydrogenation on copper. This paper is incorporated into this disclosure by reference. Pease et al found that 0.05 cc's (62 micrograms) of carbon monoxide (CO) was sufficient to almost completely poison a 100 gram catalyst towards ethylene hydrogenation. This corresponds to a poison concentration of 0.0000062% by weight of CO in the catalyst. Those trained in the state of the art know that if 0.0000062% by weight of the poison in a Catalytically Active element-poison mixture could effectively suppresses a reaction, then as little as 0.0000062% by weight of Helper Catalyst in an Active Element, Helper Catalyst Mixture could enhance a reaction. This provides a lower limit to the Helper Catalyst concentration in an Active Element, Helper Catalyst Mixture.

[0072] The upper limit is illustrated in Example 1 below where the Active Element, Helper Catalyst Mixture has approximately 99.999% by weight of Helper Catalyst, and the helper catalyst can be an order of magnitude more concentrated. Thus the range of Helper Catalyst concentrations for the invention here may be 0.0000062% to 99.9999%

[0073] FIG. 3 only considered the electrochemical conversion of CO_2 , but the method is general. There are many

examples where energy is needed to create a key intermediate in a reaction sequence. Examples include: homogeneously catalyzed reactions, heterogeneously catalyzed reactions, chemical reactions in chemical plants, chemical reactions in power plants, chemical reactions in pollution control equipment and devices, chemical reactions in safety equipment, chemical reactions in fuel cells, and chemical reactions in sensors. Theoretically, if one could find a Helper Catalyst that forms a complex with a key intermediate the rate of the reaction should increase. All of these examples are within the scope of the invention.

[0074] Specific examples of specific processes that may benefit with Helper Catalysts, include the electrochemical process to produce products including one or more of Cl_2 , Br_2 , I_2 , NaOH , KOH , NaClO , NaClO_3 , KClO_3 , CF_3COOH .

[0075] Further, the Helper Catalyst, could enhance the rate of a reaction even if it does not form a complex with a key intermediate. Examples of possible mechanisms of action include the Helper Catalyst i) lowering the energy to form a key intermediate by any means ii) donating or accepting electrons or atoms or ligands, iii) weakening bonds or otherwise making them easier to break, iv) stabilizing excited states, v) stabilizing transition states, vi) holding the reactants in close proximity or in the right configuration to react vii) block side reactions. Each of these mechanisms are described on pages 707 to 742 of Masel, Chemical Kinetics and Catalysis, Wiley, NY 2001. All of these modes of action are within the scope of the invention.

[0076] Also, the invention is not limited to just the catalyst. Instead it includes any process or device that uses an Active Element, Helper Catalyst Mixture as a catalyst. Fuel cells are sensors are specifically included in the invention.

[0077] Without further elaboration, it is believed that one skilled in the art using the preceding description can utilize the invention to the fullest extent. The following examples are illustrative only, and not limiting of the disclosure in any way whatsoever. These are merely illustrative and are not meant to be an exhaustive list of all possible embodiments, applications or modifications of the invention.

Specific Example 1

Using a Active Element, Helper Catalyst Mixture including of Platinum and 1-ethyl-3-Methylimidazolium Tetrafluoroborate (EMIM-BF_4) to Lowering the Overpotential for Electrochemical Conversion of CO_2 and Raising the Selectivity (Current Efficiency) of the Reaction

[0078] The experiments used the glass three electrode cell shown in FIG. 7. The cell consisted of a Three neck flask (101), to hold the anode (108), and the cathode (109). A silver/0.01 molar silver ion reference electrode (103) in acetonitrile was connected to the cell through a Luggin Capillary (102). The reference electrode (103) was fitted with a vycor frit to prevent any of the reference electrode solution from contaminating the ionic liquid in the capillary. The reference electrode was calibrated against the Fc/Fc^+ redox couple. A conversion factor of +535 was used convert our potential axis to reference the Standard Hydrogen Electrode (SHE). A 25×25 mm Platinum gauze (size 52) (113) was connected to the anode while a 0.33 cm^2 polycrystalline gold plug (115) was connected to the cathode.

[0079] Prior to the experiments all glass parts were put through a 1% Nochromix bath (2 hrs), followed by a 50/50 v/v

Nitric Acid/Water bath (12 hrs), followed by rinsing with Millipore water. In addition the gold plug (115) and platinum gauze (113) were mechanically polished using procedures known to workers trained in the art. They were then cleaned in a sulfuric acid bath for 12 hours.

[0080] During the experiment a catalyst ink comprising a Catalytically Active Element, platinum was first prepared as follows: First 0.0056 grams of Johnson-Matthey Hispec 1000 platinum black purchased from Alfa-Aesar was mixed with 1 grams of milipore water and sonicating for 10 minutes to produce a solution containing a 5.6 mg/ml suspension of platinum black in Millipore water. A 25 μl drop of the ink was placed on the gold plug and allowed to dry under a heat lamp for 20 min, and subsequently allowed to dry in air for an additional hour. This yielded a catalyst with 0.00014 grams of Catalytically Active Element, a platinum, on a gold plug. The gold plug was mounted into the three neck flask (101). Next a Helper Catalyst, EMIM-BF_4 (EMD chemicals) was to be heated to 120° C. under a -23 inch Hg vacuum for 12 hours to remove residual water and oxygen. The concentration of water in the ionic liquid after this procedure was found to be ca. 90 mM by conducting a Karl-Fischer titration. (i.e. the ionic liquid contained 99.9999% of helper catalyst) 13 grams of the EMIM-BF_4 was added to the vessel, creating an Active Element, Helper Catalyst Mixture that contained about 99.9999% of the Helper Catalyst. The geometry was such that the gold plug formed a meniscus with the EMIM-BF_4 . Next ultra-high-purity (UHP) Argon was fed through the sparging tube (104) and glass frit (112) for 2 hours at 200 sccm to further remove any moisture picked up by contact with the air.

[0081] Next the cathode was connected to the working electrode connection in a SI 1287 Solatron electrical interface, the anode was connected to the counter electrode connection and the reference electrode was connected to the reference electrode connection on the Solartron. Then the potential on the cathode was swept from -1.5 V versus a standard hydrogen electrode (SHE) to 1V vs. SHE and then back to -1.5 volts versus SHE thirty times at a scan rate of 50 mV/s. The current produced during the last scan is labeled as the "blank" scan in FIG. 8.

[0082] Next carbon dioxide was bubbled through the sparging tube at 200 sccm for 30 minutes and the same scanning technique was used. That produced the CO_2 scan in FIG. 8. Notice the peak starting at -0.2 volts with respect to SHE, and reaching a maximum at -0.4 V with respect to SHE. That peak is associated with CO_2 conversion.

[0083] We have also used broad-band sum frequency generation (BB-SFG) to look for products of the reaction. We only detect our desired produce carbon monoxide in the voltage range shown (i.e. the selectivity is about 100%) Oxylic acid is detected at higher potentials.

[0084] Tables 1 compares these results to results from the previous literature. The table shows the actual cathode potential. More negative cathode potentials correspond to higher overpotentials. More precisely the overpotential is the difference between the thermodynamic potential for the reaction (about -0.2 V with respect to SHE) and the actual cathode potential. The values of the cathode overpotential are also given in the table. Notice that the addition of the Helper Catalyst has reduced the cathode overpotential (i.e. lost work) on platinum by a factor of 4.5 and improved the selectivity to nearly 100%.

TABLE 1

A comparison of the data in example 1 to results in the previous literature.				
Reference	Catalytically active element	Cathode potential versus SHE	Cathode overpotential	Selectivity to carbon containing products
Data Here	Platinum + EMIM-BF ₄	-0.4 V	0.2 V	~100%
The Hori Review table 3	Platinum + water	-1.07 V	0.87 V	0.1%
The Li and Oloman Papers and the '727 application	Tin	-2.5 to -3.2 V	2.3 to 3 V	40-70%

TABLE 2

The cathode potentials where CO ₂ conversion starts on a number of Catalytically Active Elements as reported in The Hori Review.					
Metal	Cathode potential (SHE)	Metal	Cathode potential (SHE)	Metal	Cathode potential (SHE)
Pb	-1.63	Hg	-1.51	Tl	-1.60
In	-1.55	Sn	-1.48	Cd	-1.63
Bi	-1.56	Au	-1.14	Ag	-1.37
Zn	-1.54	Pd	-1.20	Ga	-1.24
Cu	-1.44	Ni	-1.48	Fe	-0.91
Pt	-1.07	Ti	-1.60		

[0085] Table 2 indicates the cathode potential needed to convert CO₂. Notice that all of the values are more negative than -0.9 V. By comparison, FIG. 8 shows that CO₂ conversion starts at -0.2 V with respect to RHE, when the Active Element, Helper Catalyst Mixture is used as a catalyst. More negative cathode potentials correspond to higher overpotentials. This is further confirmation Active Element, Helper Catalyst Mixtures are advantageous for CO₂ conversion.

[0086] FIG. 9 shows a series of BB-SFG spectra taken during the reaction. Notice the peak at 2350 cm⁻¹. This peak corresponds to the formation of a stable complex between the Helper Catalyst and (CO₂)⁻. It is significant that the peak starts at -0.1 with respect to SHE. According to The Hori Review, (CO₂)⁻ is thermodynamically unstable unless the potential is more negative than -1.2 V with respect to SHE on platinum. Yet FIG. 9 shows that the complex between EMIM-BF₄ and (CO₂)⁻ is stable at -0.1 V with respect to SHE.

[0087] Those trained in the art should recognize that this result is very significant. According to The Hori Review, The Dubois Review and references therein, the formation of

(CO₂)⁻ is the rate determining step in CO₂ conversion to CO, OH⁻, HCO⁻, H₂CO, (HCO₂)⁻, H₂CO₃, CH₃OH, CH₄, C₂H₄, CH₃CH₂OH, CH₃COO⁻, CH₃COOH, C₂H₆, CH₄, O₂, H₂, (COOH)₂, (COO⁻)₂ on V, Cr, Mn, Fe, Co, Ni, Cu, Sn, Zr, Nb, Mo, Ru, Rh, Pd, Ag, Cd, Hf, Ta, W, Re, Ir, Pt, Au, Hg, Al, Si, In, Sn, Tl, Pb, Bi, Sb, Te, U, Sm, Tb, La, Ce, and Nd. The (CO₂)⁻ is thermodynamically unstable at low potentials, which leads to a high overpotential for the reaction as indicated in FIG. 2. The data in FIG. 9 shows that one can form the EMIM-BF₄-(CO₂) complex at low potentials. The complex is thermodynamically stable. Thus, the reaction can follow a low energy pathway for CO₂ conversion to CO, OH⁻, HCO⁻, H₂CO, (HCO₂)⁻, H₂CO₃, CH₃OH, CH₄, C₂H₄, CH₃CH₂OH, CH₃COO⁻, CH₃COOH, C₂H₆, CH₄, O₂, H₂, (COOH)₂, (COO⁻)₂ on V, Cr, Mn, Fe, Co, Ni, Cu, Sn, Zr, Nb, Mo, Ru, Rh, Pd, Ag, Cd, Hf, Ta, W, Re, Ir, Pt, Au, Hg, Al, Si, In, Sn, Tl, Pb, Bi, Sb, Te, U, Sm, Tb, La, Ce, and Nd as indicated in FIG. 3.

[0088] Those trained in the state of the art also recognize that this effect is very unusual. In most cases, the interaction between a solvent and an adsorbate is weak, so the solvent only makes a small perturbation to the chemistry occurring on metal surfaces. Here the effect is large.

[0089] In order to understand the economic consequences of this result, we calculated the cost of the electricity needed to create 100,000 metric tons per year of formic acid via two processes, i) the process described in The Li and Oloman Papers and the '727 application, and ii) a similar process using the catalyst in this example. In both cases we assumed that the anode would run at +1.4 V with respect to SHE and that electricity would cost \$0.06/kW-hr and we scaled the current to be reasonable. The results of the calculations are given in Table 2. Notice that the calculations predict that the electricity cost will go down by almost a factor of 5 if the new catalysts are used. These results demonstrate the possible impact of the new catalysts disclosed here.

TABLE 3

A comparison of the projected costs using the catalyst in the The Li and Oloman papers and the '727 application, and ii) a similar process using the catalyst in this example.					
Catalyst	Cathode potential, V (SHE)	Anode Potential, V (SHE)	Net Potential V	Selectivity	Yearly Electricity cost
The Li and Oloman Papers and the '727 application	-3.2	1.2	4.4	0.6	\$65,000,000

TABLE 3-continued

A comparison of the projected costs using the catalyst in the The Li and Oloman papers and the '727 application, and ii) a similar process using the catalyst in this example.					
Catalyst	Cathode potential, V (SHE)	Anode Potential, V (SHE)	Net Potential V	Selectivity	Yearly Electricity cost
Active Element, Helper Catalyst Mixture	-0.4	1.2	1.6	1	\$14,000,000

Specific Example 2

The Effect of Dilution on the Electrochemical Conversion of CO₂

[0090] This example shows that water additions speed the formation of CO. The experiment used the Cell and procedures in Example 1, with the following exception: a solution containing 98.55% EMIM-BF₄ and 0.45% water was substituted for the 99.9999% EMIM-BF₄ used in Example 1, the potential was held for 10 or 30 minutes at -0.6V with respect to RHE, and then the potential was ramped positively at 50 mV/sec. FIG. 10 shows the result. Notice the peak at between 1.2 and 1.5 eV. This is the peak associated with CO formation and is much larger than in example 1. Thus the addition of water has accelerated the formation of CO presumably by acting as a reactant.

Specific Example 3

Using a Active Element, Helper Catalyst Mixture that include Palladium and choline Iodide to Lowering the Overpotential for Electrochemical Conversion of CO₂ in Water

[0091] The next example is to demonstrate that the invention can be practiced using Palladium as an active element and Choline Iodide as a Helper Catalyst.

[0092] The experiment used the cell and procedures in Example 1, with the following exceptions: ii) A 10.3% by weight of a Helper Catalyst, choline iodide in water solution was substituted for the 1-ethyl-3-methylimidazolium tetrafluoroborate and ii) a 0.25 cm² Pd foil purchased from Alfa Aesar was substituted for the gold plug and platinum black on the cathode, and a silver/silver chloride reference was used.

[0093] FIG. 11 shows a CV taken under these conditions. There is a large negative peak near zero volts with respect with SHE associated with iodine transformations and a negative going peak starting at about 0.8 V associated with conversion of CO₂. By comparison the data in Table 2 indicates that one needs to use a voltage more negative than -1.2 V to convert CO₂ on palladium in the absence of the Helper Catalyst. Thus, the helper catalyst has lowered the overpotential for CO₂ formation by about 0.5 V.

[0094] This example also demonstrates that the invention can be practiced with a second active element, palladium, and a second helper catalyst choline iodide. Further, those trained in the state of the art will note that there is nothing special

about the choice of palladium and choline iodide. Rather, this example shows that the results are general and not limited to the special case in example 1.

Specific Example 4

Using a Active Element, Helper Catalyst Mixture that includes Palladium and Choline Chloride to Lowering the Overpotential for Electrochemical Conversion of CO₂ to Formic Acid

[0095] The next example is to demonstrate that the invention can be practiced using a third Helper Catalyst, choline chloride.

[0096] The experiment used the Cell and procedures in Example 3, with the following exception: a 6.5% by weight choline chloride in water solution was substituted for choline iodide solution.

[0097] FIG. 12 shows a comparison of the cyclic voltammetry for a blank scan where i) the water-choline chloride mixture was sparged with argon and ii) a scan where the water-choline iodide mixture was sparged with CO₂. Notice the negative going peaks starting at about -0.6. This shows that CO₂ is being reduced at -0.6 V. By comparison the data in Table 2 indicates that one needs to use a voltage more negative than -1.2 V is needed to convert CO₂ on palladium in the absence of the Helper Catalyst. Thus, the overpotential for CO₂ conversion has been lowered by 0.6 V by the Helper Catalyst.

[0098] Another important point is that there is no strong peak for hydrogen formation. A bare palladium, catalyst would produce a large hydrogen peak at about -0.4 V at a pH of 7. While the hydrogen peak moves to -1.2 V in the presence of the helper catalyst. The Hori Review reports that palladium is not an effective catalyst for CO₂ reduction because the side reaction producing hydrogen is too large. The data in FIG. 12 show that the helper catalysts are effective in suppressing hydrogen formation.

[0099] We have also used CV to analyze the reaction products. Formic Acid was the only product detected. By comparison The Hori Review reports that the reaction is only 2.8% selective to formic acid in water. Thus the Helper Catalyst has substantially improved the selectivity of the reaction to formic acid.

[0100] This example also demonstrates that the invention can be practiced with a third helper catalyst choline chloride. Further, those trained in the state of the art will note that there is nothing special about the choice of palladium and choline chloride. Rather, this example shows that the results are general and not limited to the special case in example 1.

Specific Example 5

Using a Active Element, Helper Catalyst Mixture that includes nickel and Choline Chloride to Lowering the Overpotential for Electrochemical Conversion of CO₂ to CO

[0101] The next example is to demonstrate that the invention can be practiced using a third metal, nickel.

[0102] The experiment used the Cell and procedures in Example 4, with the following exception: a nickel foil from Alfa Aesar was substituted for the palladium foil.

[0103] FIG. 13 shows a comparison of the cyclic voltammetry for a blank scan where i) the water-choline chloride mixture was sparged with argon and ii) a scan where the water-choline chloride mixture was sparged with CO₂. Notice the negative going peaks starting at about -0.6. This shows that CO₂ is being reduced at -0.6 V. By comparison the data in Table 2 indicates that one needs to use a voltage more negative than -1.48 V is needed to convert CO₂ on nickel in the absence of the Helper Catalyst. Thus, the Helper Catalyst has lowered the overpotential for CO₂ conversion.

[0104] Another important point is that there is no strong peak for hydrogen formation. A bare nickel, catalyst would produce a large hydrogen peak at about -0.4 V at a pH of 7. While the hydrogen peak moves to -1.2 V in the presence of the helper catalyst. The Hori Review reports that nickel is not an effective catalyst for CO₂ reduction because the side reaction producing hydrogen is too large. The data in FIG. 13 show that the helper catalysts are effective in suppressing hydrogen formation.

[0105] Also the helper catalyst is very effective in improving the selectivity of the reaction. The Hori Review reports that hydrogen is the major product during carbon dioxide reduction on nickel in aqueous solutions. The hydrolysis shows 1.4% selectivity to formic acid, and no selectivity to carbon monoxide. By comparison, analysis of the reaction products by CV indicate that carbon monoxide is the major product during CO₂ conversion on nickel in the presence of the Helper Catalyst. There may be some formate formation. However, no hydrogen is detected. This example shows that the helper catalyst has tremendously enhanced the selectivity of the reaction toward CO and formate.

[0106] This example also demonstrates that the invention can be practiced with a third metal, nickel. Further, those trained in the state of the art will note that there is nothing special about the choice of nickel and choline chloride. Rather, this example shows that the results are general and not limited to the special case in example 1.

[0107] Those trained in the state of art should realize that since choline chloride, and choline iodide are active, other chlorine salts such as choline bromide, choline fluoride and choline acetate should be active too.

Specific Example 6

Demonstration that an Active Element (Gold), Helper Catalyst Mixture is useful in a CO₂ Sensor

[0108] This example demonstrates that the invention can be practiced with a fourth active element gold. It also demonstrates that the catalysts are useful in sensors.

[0109] The sensor will be a simple electrochemical device where an in an Active Element, Helper Catalyst Mixture is placed on an anode and cathode in an electrochemical device, then the resistance of the sensor is measured. If there no CO₂

present, the resistance will be high, but not infinite because of leakage currents. When CO₂ is present, the Active Element, Helper Catalyst Mixture may catalyze the conversion of CO₂. That allows more current to flow through the sensor. Consequently, the sensor resistance decreases. As a result, the sensor may be used to detect carbon dioxide.

[0110] An example sensor was fabricated on a substrate made from a 100 mm Silicon wafer (Silicon Quest, 500 μ m thick, <100> oriented, 1-5 Ω -cm nominal resistivity) which was purchased with a 500 nm thermal oxide layer. On the wafer, 170 Å chromium was deposited by DC magnetron sputtering ($\sim 10^{-2}$ Ton of argon background pressure). Next, 1000 Å of a Catalytically Active element, gold, was deposited on the chromium and the electrode was patterned via a standard lift-off photolithography process to yield the device shown schematically in FIG. 14.

[0111] At this point, the device consisted of an anode (200) and cathode (201) separated by a 6 μ m gap, wherein the anode and cathode were coated with a Catalytically Active element, gold. At this point the sensor could not detect CO₂.

[0112] Next 2 μ l of a Helper Catalyst, EMIMBF₄ (202) was added over the junction as shown FIG. 15. The device was mounted into a sensor test cell with wires running from the anode and cathode.

[0113] Next, the anode and cathode were connected to a SI 1287 Solatron electrical interface, and the catalysts were condition by sweeping from 0 volts to 5 volts at 0.1 V/sec and then back again. The process was repeated 16 times. Then the sensor was exposed to either nitrogen, oxygen, dry air or pure CO₂, and the sweeps were recorded. The last sweep is shown in FIG. 16. Notice that there is a sizable peak at an applied voltage of 4 volts in pure CO₂. That peak is associated with the electrochemical conversion of CO₂.

[0114] Notice that the peak is absent, when the sensor is exposed to oxygen or nitrogen, but it is clearly seen when the sensor is exposed to air containing less than 400 ppm of CO₂. Further the peak grows as the CO₂ concentration increases. Thus, the sensor can be used to detect the presence of CO₂.

[0115] We have also run the sensor in a galvanostatic mode, were we measured the voltage needed to maintain the current constant at 1 microamp, and measured the voltage of the device. FIG. 17 shows that less voltage is needed to maintain the current when CO₂ is added to the cell. This shows that the sensor that include an Active Element, Helper Catalyst Mixture responds to the presence of CO₂.

[0116] Table 4 compares the sensor here to those in the previous literature. Notice that the new sensor uses orders of magnitude less energy than commercial CO₂ sensors. This is a key advantage for many applications.

[0117] This example also illustrates that the invention can be practiced with a third active element, gold.

TABLE 4

A comparison of the power needed to run the present sensor to that needed to operate commercially available CO ₂ sensors.			
Sensor	Power	Sensor	Power
Specific Example 3	5×10^{-7} watts	GE Ventostat 8100	1.75 watts
Honeywell C7232	3 watts	Vaisala CARBOCAP GMP343	about 1 watt

[0118] The examples given above are merely illustrative and are not meant to be an exhaustive list of all possible

embodiments, applications or modifications of the invention. Thus, various modifications and variations of the described methods and systems of the invention will be apparent to those skilled in the art without departing from the scope and spirit of the invention. Although the invention has been described in connection with specific embodiments, it should be understood that the invention as claimed should not be unduly limited to such specific embodiments. Indeed, various modifications of the described modes for carrying out the invention which are obvious to those skilled in the chemical arts or in the relevant fields are intended to be within the scope of the appended claims.

[0119] The disclosures of all references and publications cited above are expressly incorporated by reference in their entireties to the same extent as if each were incorporated by reference individually.

1. A electrocatalyst comprised of at least one Catalytically Active Element and at least one Helper Catalyst wherein the catalyst is active for the electrochemical synthesis of formic acid using a reactant comprised of carbon dioxide.

2. The electrocatalyst in claim 1 where the Catalytically Active Element is comprised of one or more of Pb, Hg, Tl, In, Cd, Bi, Zr, Cr, Sn, W, Pd, Ru.

3. The electrocatalyst in claim 1 wherein The Helper Catalyst is comprised at least one of the following: phosphines, imidazoniums, pyridiniums, pyrrolidiniums, phosphoniums, sulfoniums, prolinates, methioninates, and cholines

4. The electrocatalyst in claim 1 wherein the Helper Catalyst is comprised of one or more of choline chloride, choline bromide, or choline iodide

5. A catalyst for the electrochemical conversion of CO₂ comprised of at least one Catalytically Active Element and at least one Helper Catalyst

6. The catalyst in claim 5 wherein the Catalytically Active Element comprised of at least one of the following chemical elements: V, Cr, Mn, Fe, Co, Ni, Cu, Sn, Zr, Nb, Mo, Ru, Rh, Pd, Ag, Cd, Hf, Ta, W, Re, Ir, Pt, Au, Hg, Al, Si, C, In, Sn, Tl, Pb, Bi, Sb, Te, U, Sm, Tb, La, Ce, Nd

7. The catalyst in claim 5 wherein the Helper Catalyst comprises at least one organic cation and or at least one organic anion.

8. The catalyst in claim 7 wherein the Helper Catalyst has a concentration of between about 0.0000062% and 99.9999% by weight.

9. The catalyst in claim 8 wherein The Helper Catalyst is comprised at least one of the following: phosphines, imidazoniums, pyridiniums, pyrrolidiniums, phosphoniums, sulfoniums, prolinates, methioninates, and cholines

10. The catalyst in claim 5 wherein the Helper Catalyst is a solvent, electrolyte or additive.

11. A process for the formation of formic acid wherein carbon dioxide reacts in an electrochemical cell containing a catalyst comprised of at least one Catalytically Active Element and at least one Helper Catalyst.

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