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(54) **ELECTROCHEMICAL HYDROGENOLYSIS OF CARBONYL GROUPS IN ALDEHYDES AND KETONES USING ZINC CATHODES**

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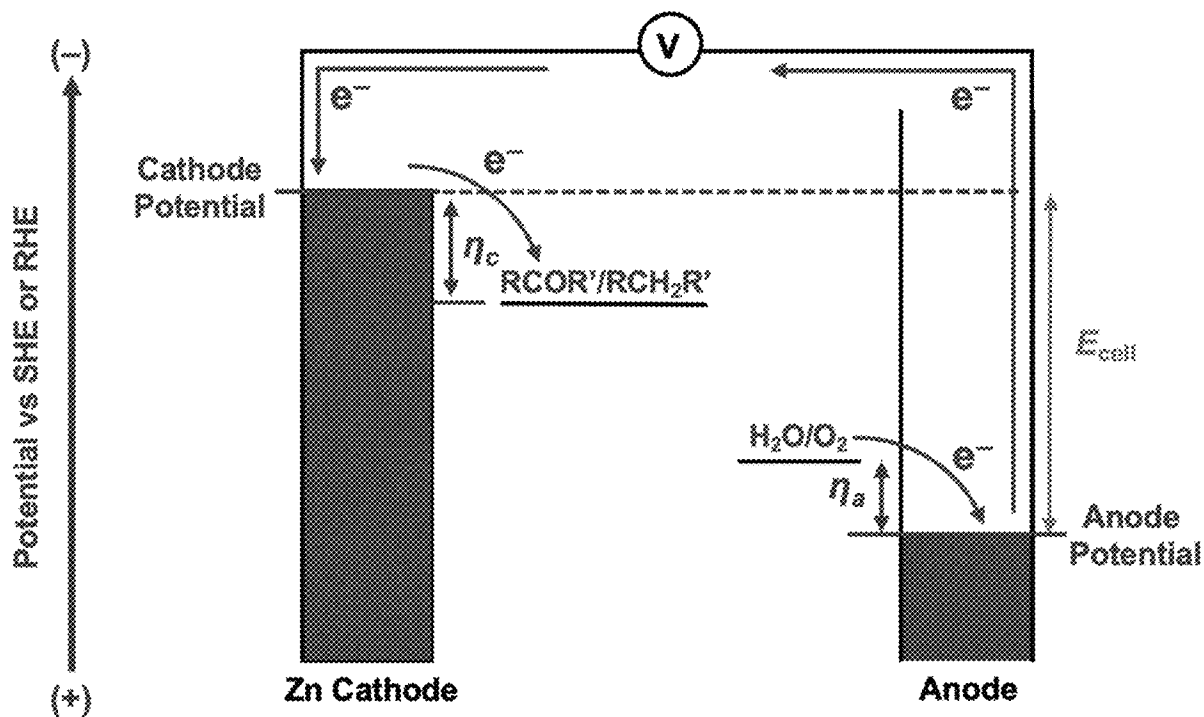
(57) **ABSTRACT**

Electrochemical cells and methods for the reduction of aldehydes and ketones via selective hydrogenolysis of their carbonyl bonds are provided. The electrochemical cells and methods use zinc-containing electrocatalytic cathodes that promote electrochemical hydrogenolysis of the carbonyl bond of the aldehyde or ketone over hydrogenation in an acidic electrolyte solution. As a result, the carbonyl-groups of the aldehydes and ketones are reduced into alkyl groups with high relative selectivities.
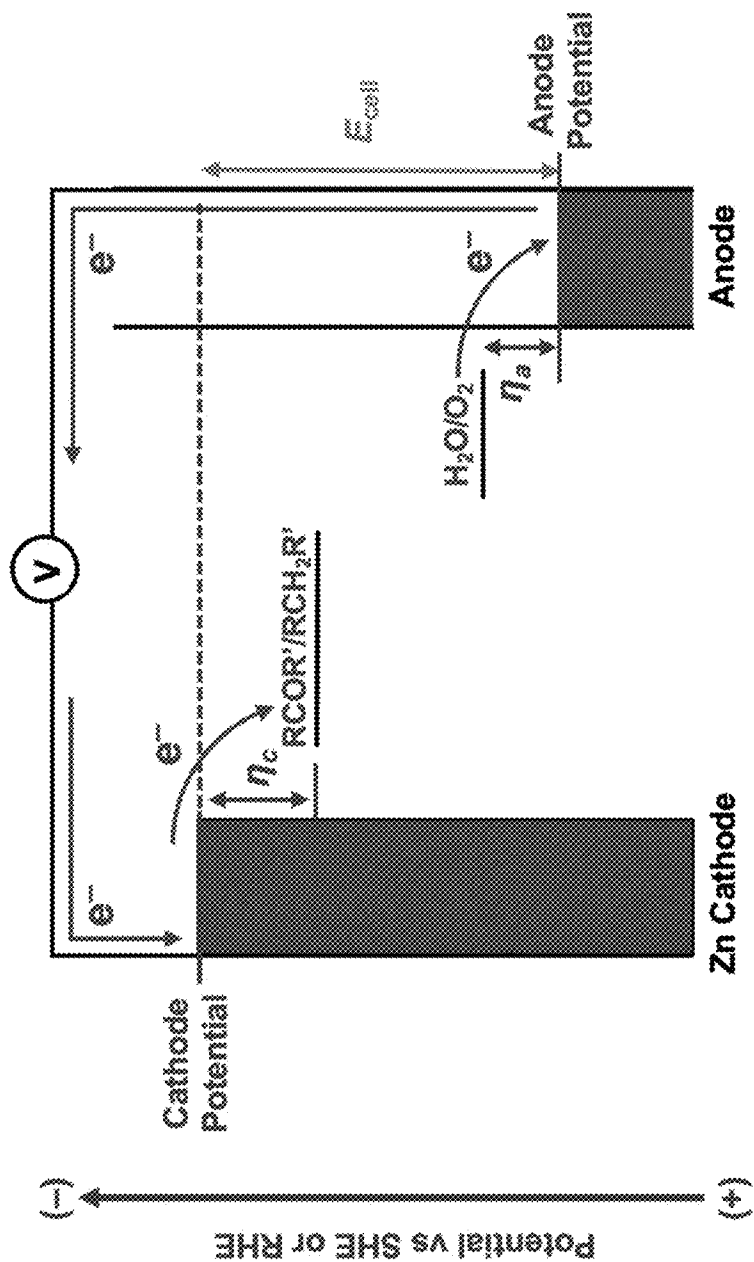
FIG. 1A

FIG. 1B

FIG. 2A

Aldehydes:

(i) Aryl aldehydes:

(ii) Alkyl aldehydes:

FIG. 2B

Ketones:

(i) Aryl ketones:

(ii) Alkyl ketones:

FIG. 2C

FIG. 3A

4-hydroxybenzaldehyde
(4-HBAL)

$2e^-$, $2H^+$
Hydrogenation

4-hydroxybenzyl alcohol

$4e^-$, $4H^+$, $-H_2O$
Hydrogenolysis

4-methylphenol

FIG. 3B

4-hydroxyacetophenone
(4-HAP)

$2e^-$, $2H^+$
Hydrogenation

4-(1-hydroxyethyl)phenol

$4e^-$, $4H^+$, $-H_2O$
Hydrogenolysis

4-ethylphenol
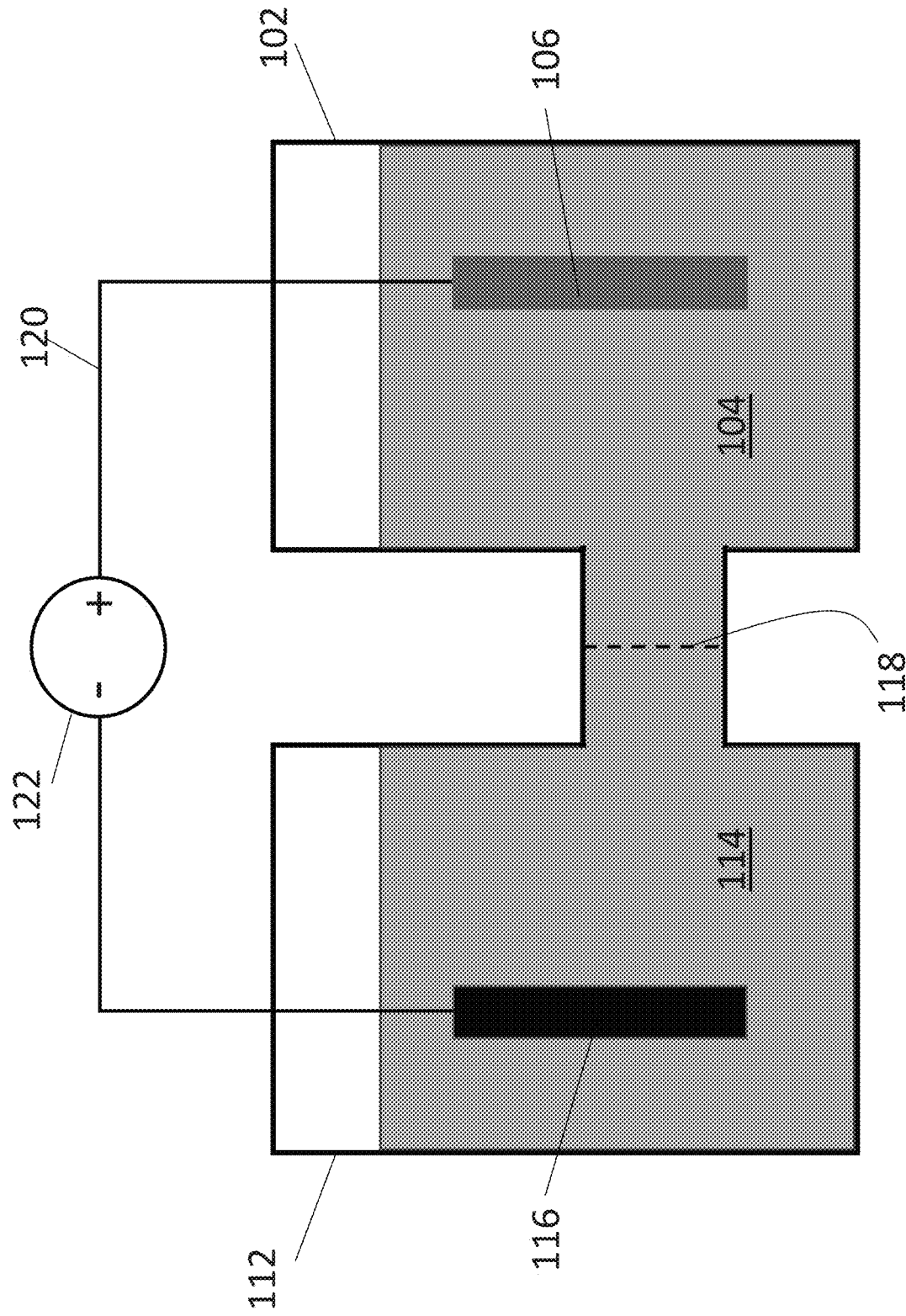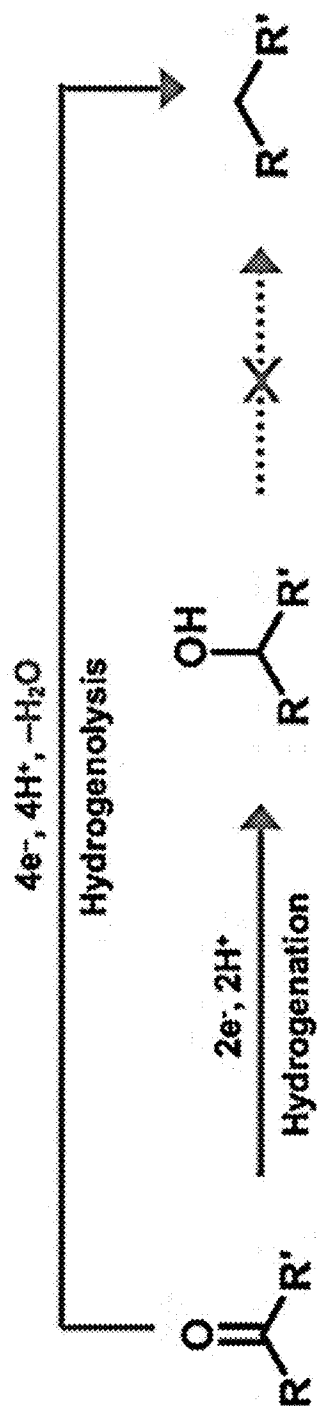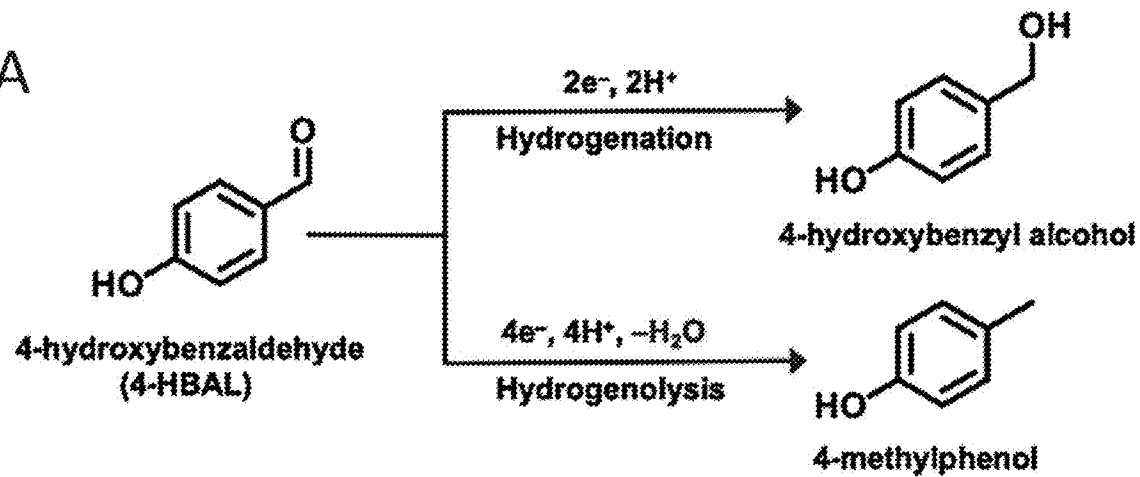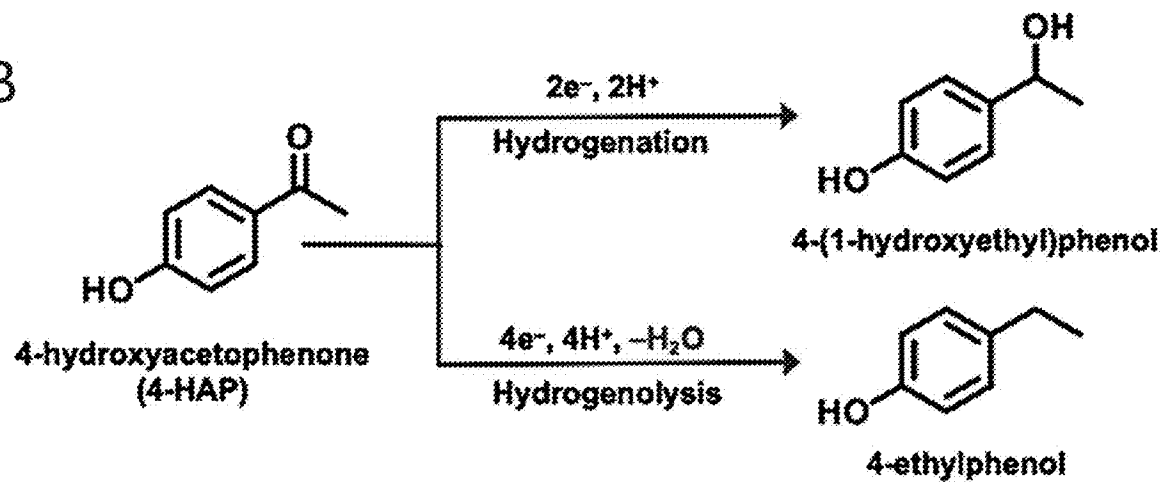
FIG. 4A

FIG. 4B

FIG. 4C

FIG. 5A

FIG. 5B
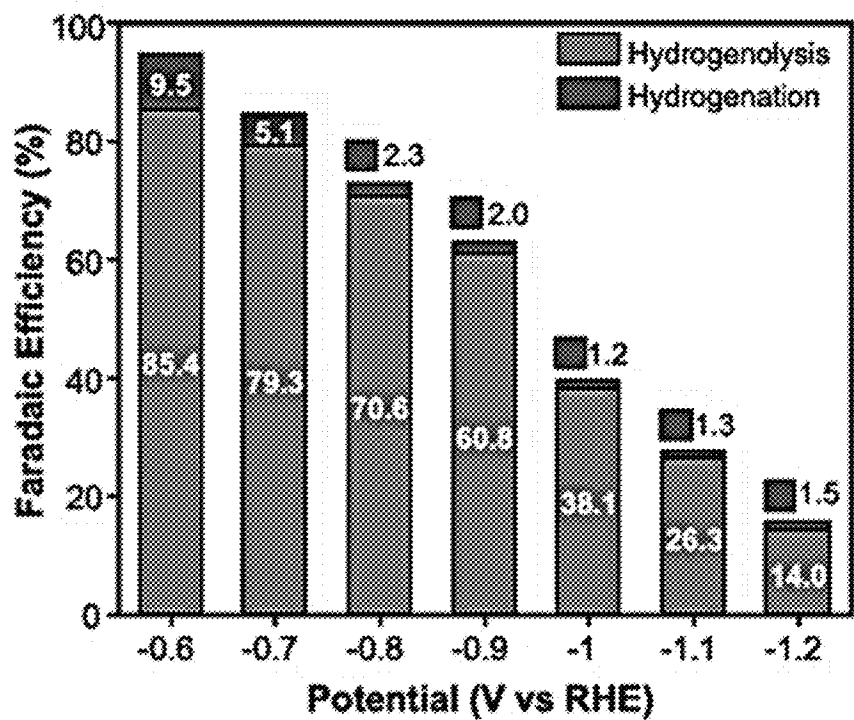
FIG. 5C

FIG. 5D

FIG. 5F

FIG. 5E

FIG. 5G

Current Density (mA/cm²)

Potential (V vs RHE)

Hydrognolysis
Hydrogenation
Other

FIG. 5H

Current Density (mA/cm²)

Potential (V vs RHE)
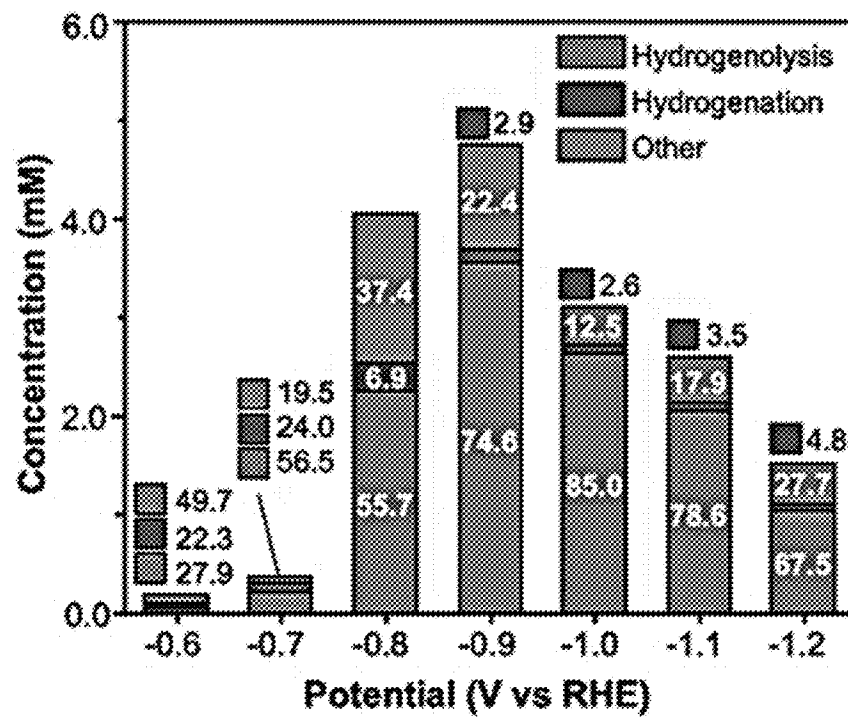
Hydrognolysis
Hydrogenation
Other
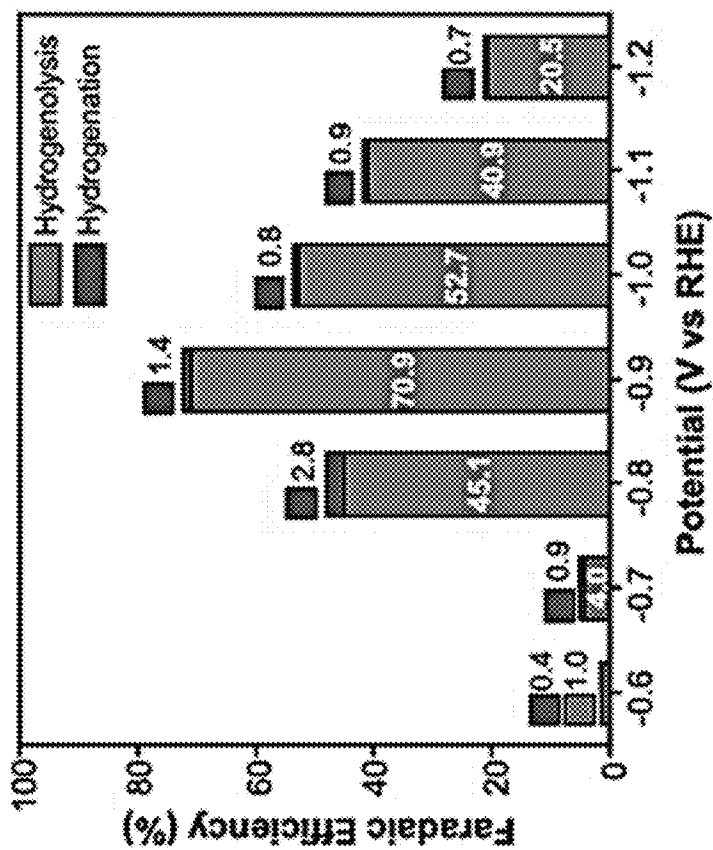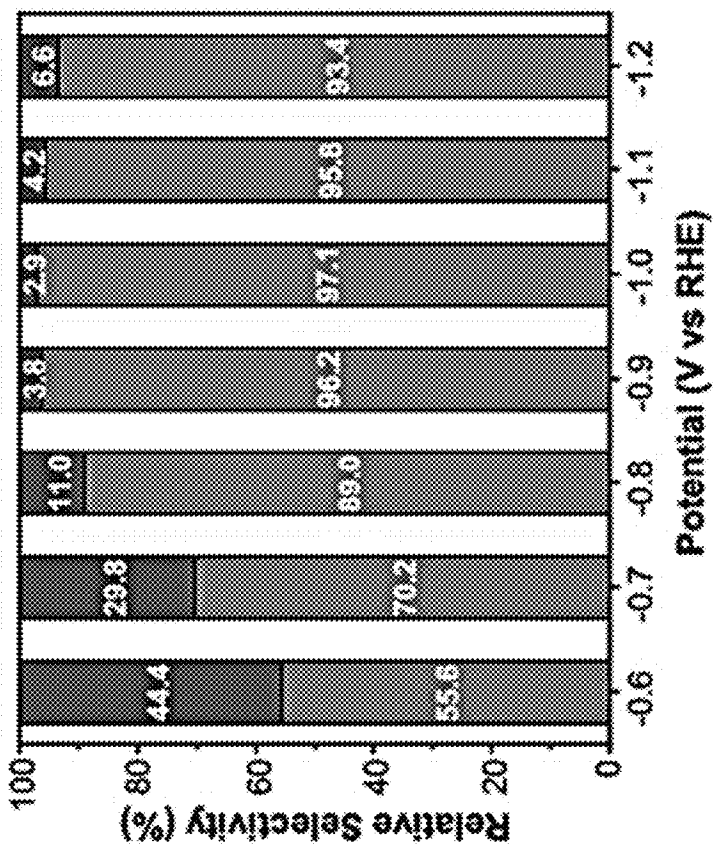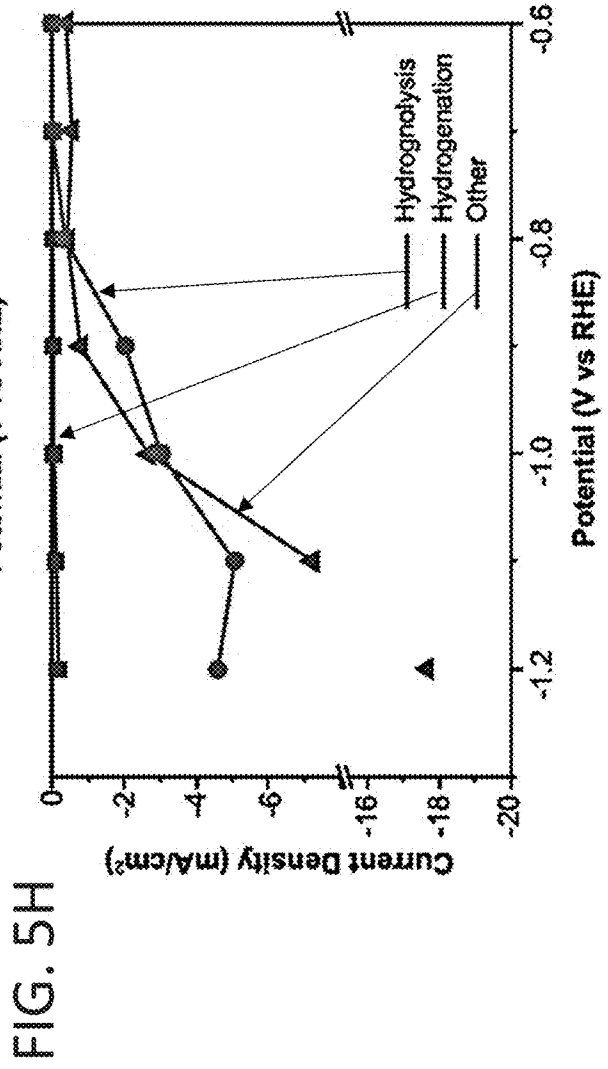
FIG. 6B
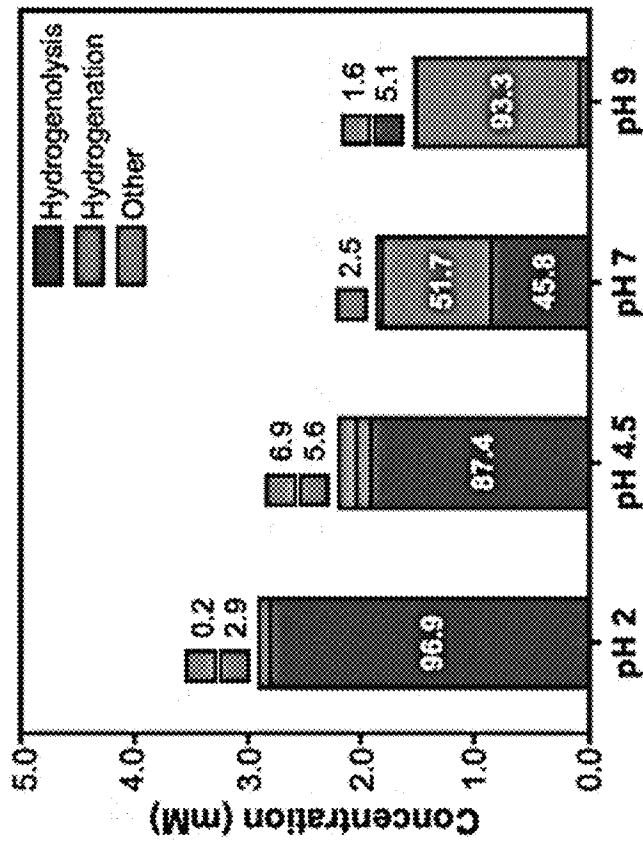
FIG. 6A

FIG. 6D

FIG. 6C

FIG. 6F

FIG. 6E

ELECTROCHEMICAL HYDROGENOLYSIS OF CARBONYL GROUPS IN ALDEHYDES AND KETONES USING ZINC CATHODES

REFERENCE TO GOVERNMENT RIGHTS

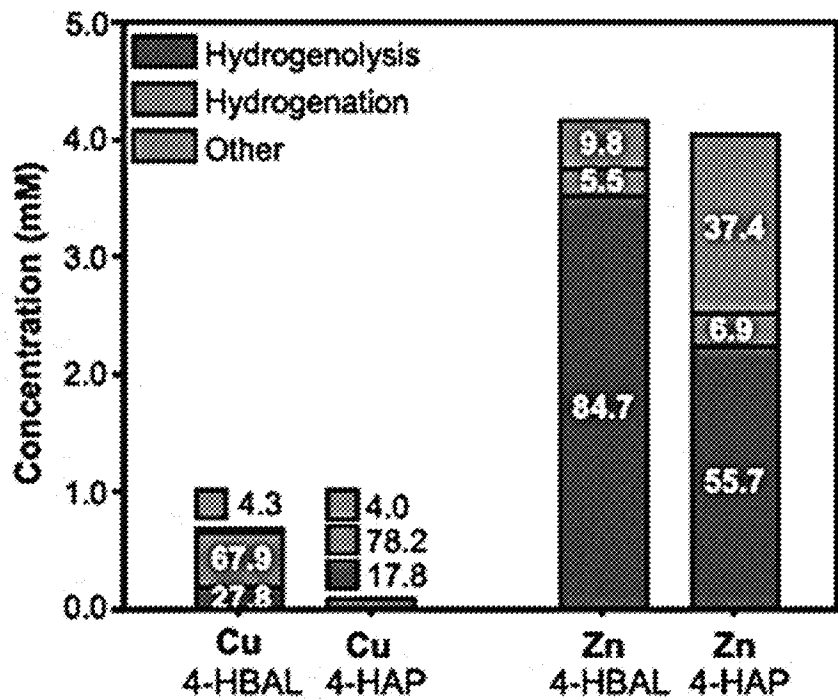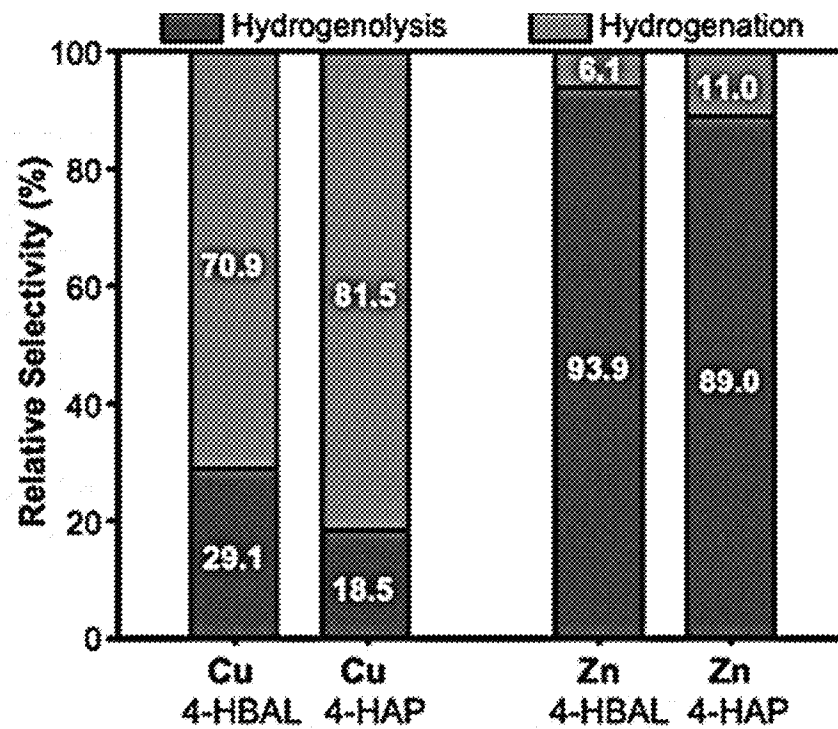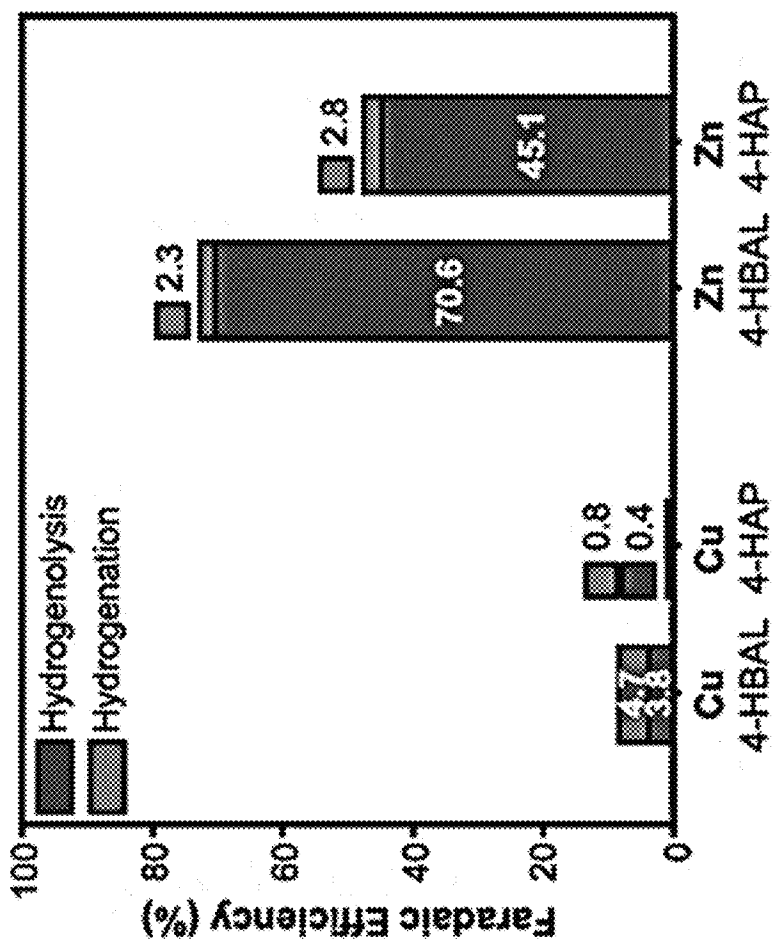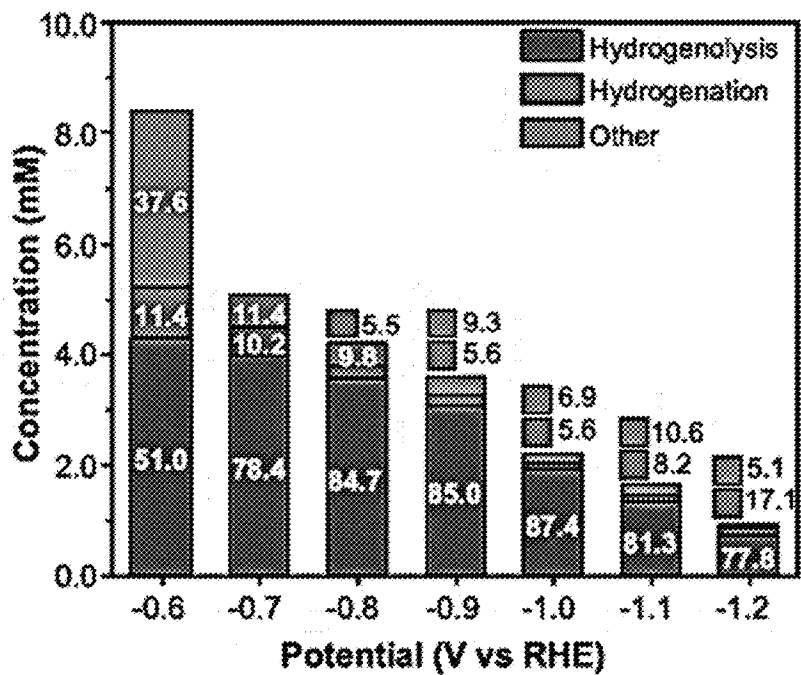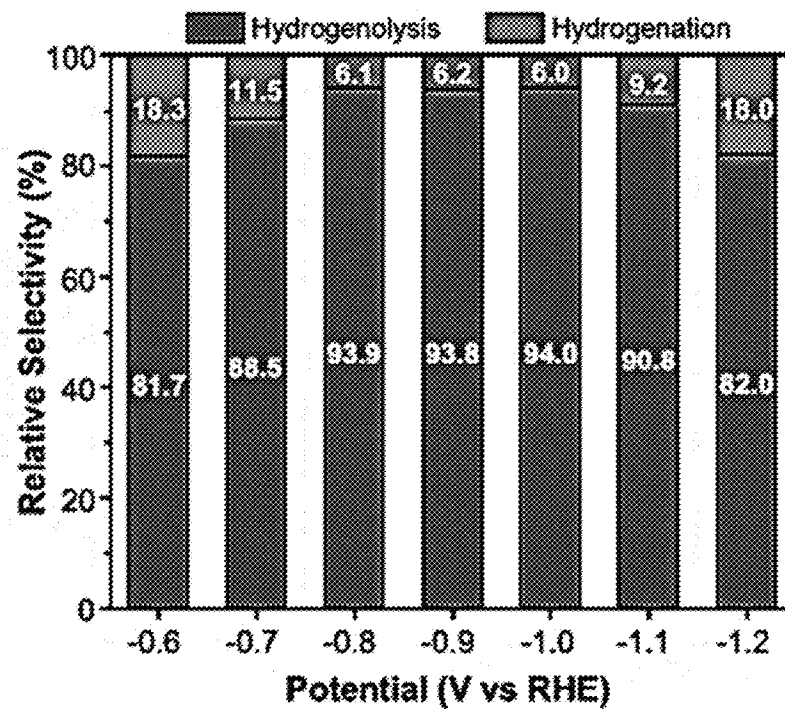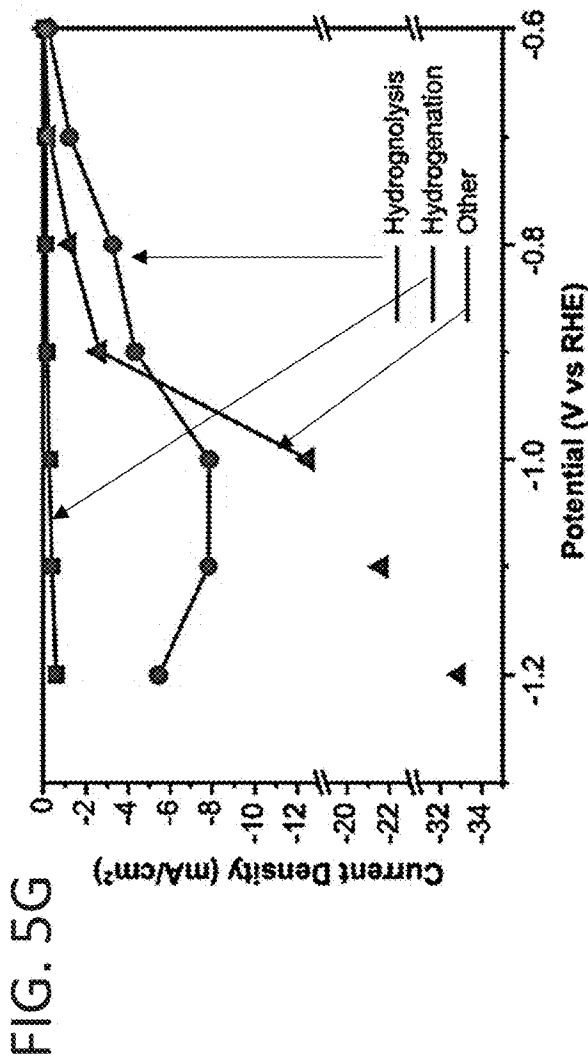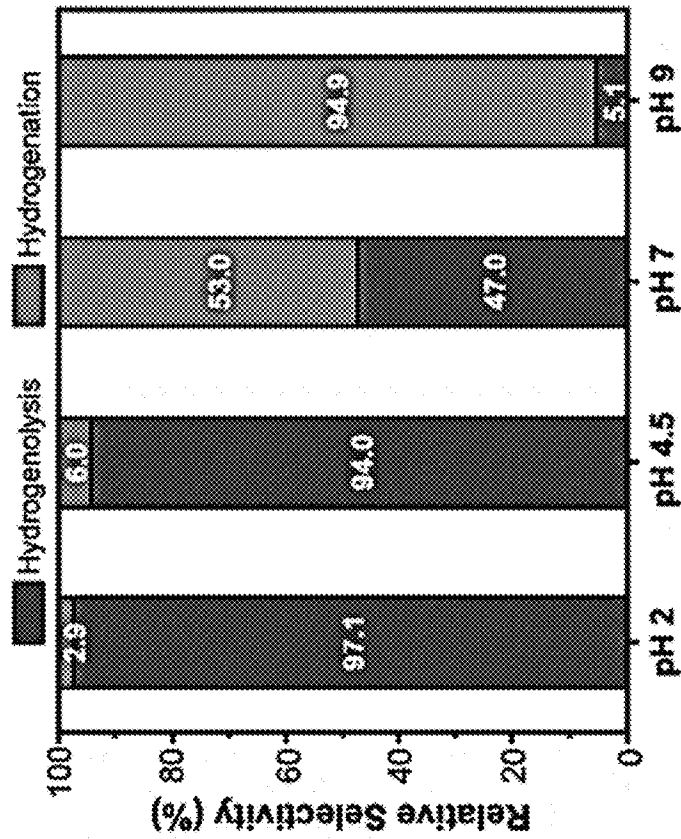[0001] This invention was made with government support under DE-SC0020983 awarded by the US Department of Energy. The government has certain rights in the invention.

BACKGROUND

[0002] Development of routes for the sustainable production of fuels and building block chemicals using renewable sources has received considerable attention due to the rising cost and diminishing supply of fossil resources. Lignocellulosic biomass, which is inexpensive, nonedible, and the most abundant class of biomass, has been studied widely as feedstock for the production of sustainable fuels and chemicals. Among various approaches to utilize lignocellulosic biomass, fast pyrolysis has been one of the most extensively developed. Fast pyrolysis, a rapid heating process in the absence of oxygen, decomposes and liquefies biomass to bio-oil. The resulting bio-oil typically contains a variety of small organic molecules with oxygenated moieties such as aldehyde and ketone groups. The presence of carbonyl groups lowers the energy density of the bio-oil and also makes it unstable toward polymerization, even under ambient temperature storage conditions. Therefore, deoxygenation of the compounds in bio-oil is critical to increase its energy density and storage lifetime. Furthermore, deoxygenation is a key reduction reaction used for production of various commodity and fine chemicals (i.e., pharmaceuticals) using petrochemicals as well as biomass-derived chemicals.

[0003] Deoxygenation can be achieved via conventional thermocatalytic hydrodeoxygenation with pressurized H_2 at elevated temperatures, which has been used for petroleum upgrading.

[0004] Electrochemical reduction provides an attractive alternative approach that is compatible with ambient temperature and pressure. In electrochemical reduction, the H atoms needed for organic reduction are generated in-situ by the electrochemical reduction of water molecules (or hydronium ions) instead of from H_2 gas, thus eliminating the steps involving the production, storage, delivery, and use of H_2. However, most of the electrochemical reduction processes developed to date for aldehydes and ketones are limited to hydrogenation of the unsaturated C=O bond, which results in the formation of alcohols. (Lopez-Ruiz, J. A. et al. *ACS Catal.* 9, 9964-9972 (2019); and Roylance, J. J. et al., *ACS Catal.* 6, 1840-1847 (2016).) 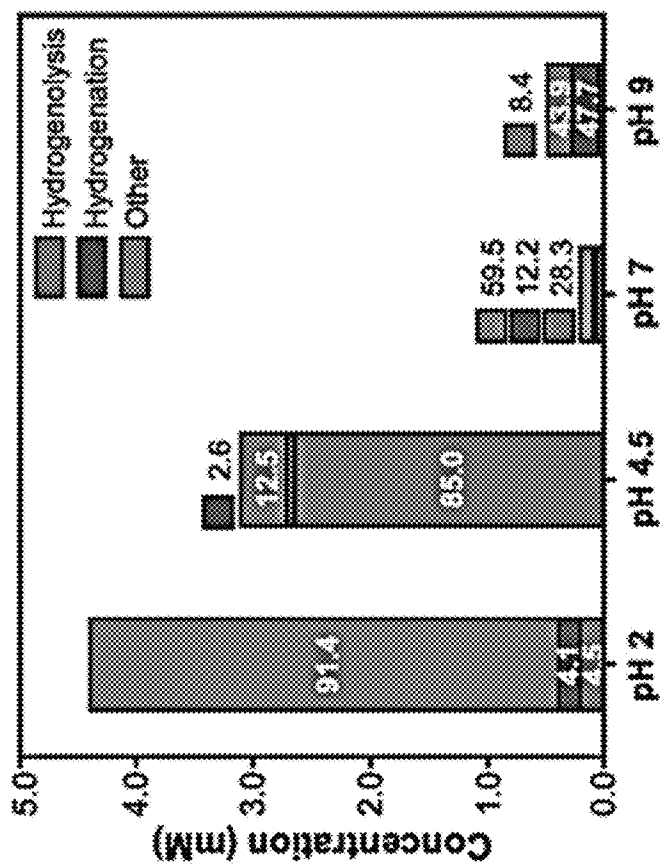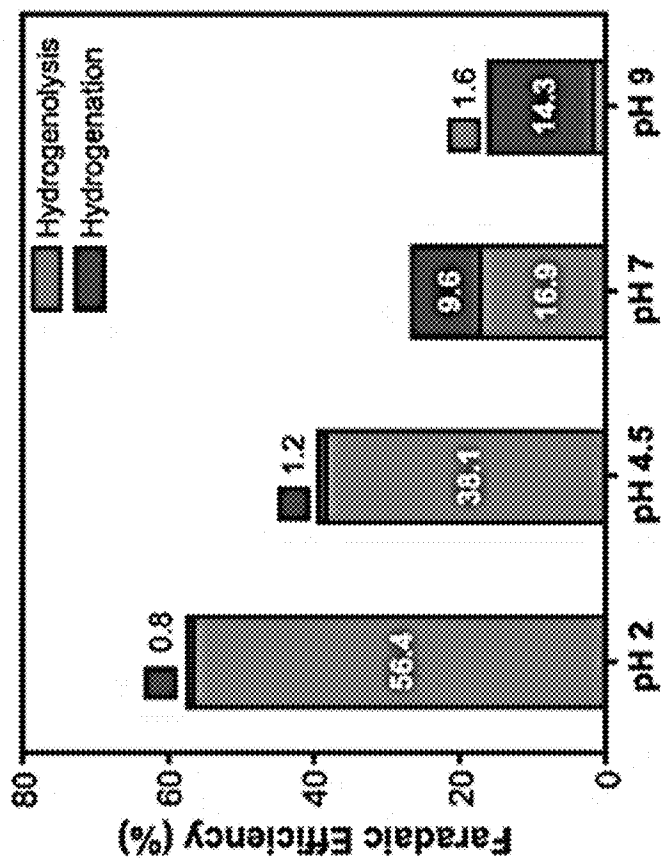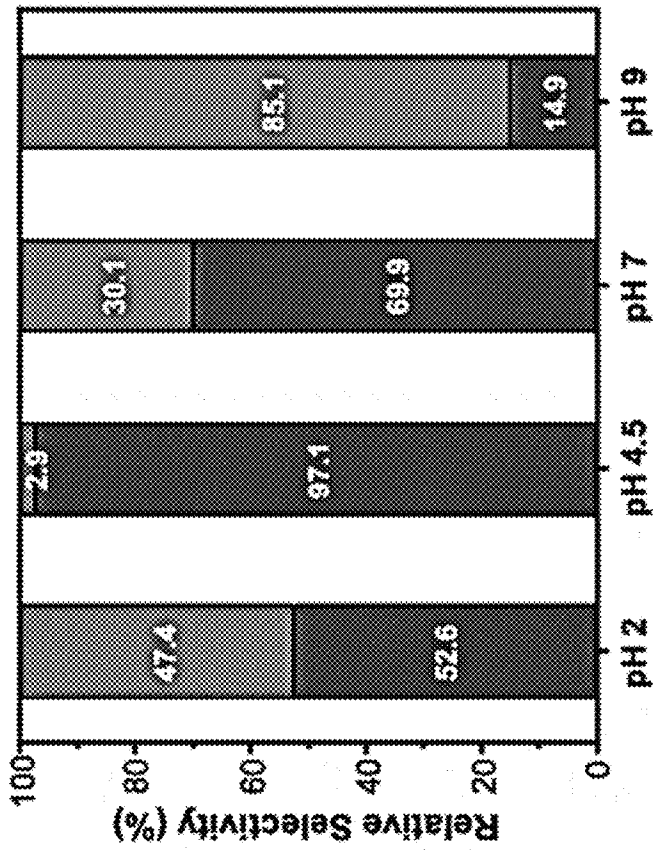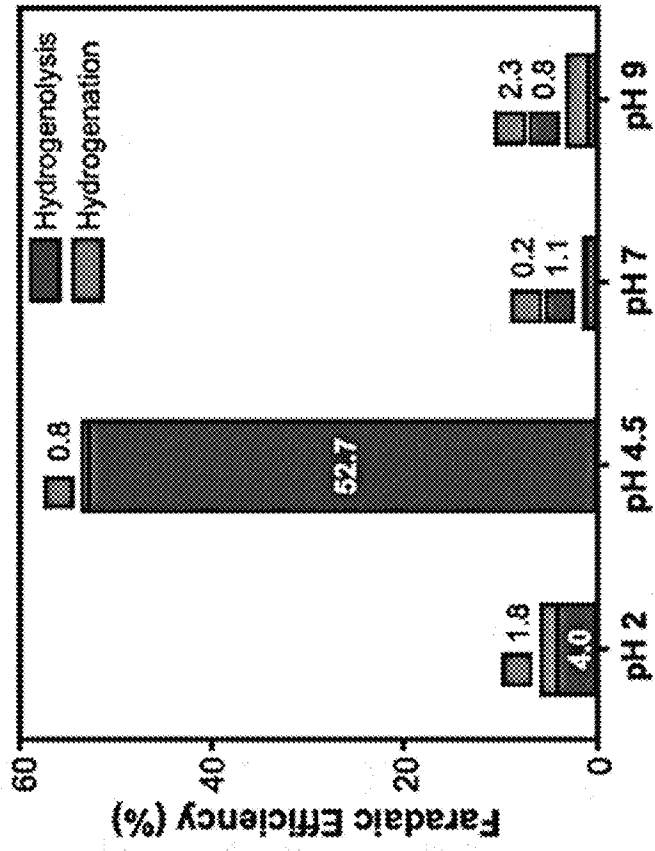Electrochemical hydrogenolysis that combines hydrogenation and C—O bond cleavage to form the corresponding hydrocarbons has been rarely shown except in the case of furfural and furfural derivatives like 5-hydroxymethylfurufurfural (HMF). (Bender, M. T. et al., *ACS Catal.* 12, 12349-12368 (2022); May, A. S. et al., *ACS Catal.* 10, 3212-3221 (2020).)

[0005] Recent electrochemical reduction studies of furfural and HMF show that hydrogenolysis is more difficult than hydrogenation. (Chadderdon, X. H. et al. *J. Am. Chem. Soc.* 139, 14120-14128 (2017). Lee, D. K. et al. *ChemSusChem* 14, 4563-4572 (2021); Yuan, X. et al., *ChemSusChem* 15, (2022).) Furthermore, these studies suggest that once an alcohol is produced by hydrogenation of the carbonyl group, electrochemical cleavage of the C—O bond is extremely difficult (much more difficult than cleavage of the intact C—O bond). Thus, hydrogenation is not an initial step of hydrogenolysis but rather a competing reaction to hydrogenolysis in electrochemical reduction of carbonyl groups. The studies of furfural and HMF reduction found that Cu can achieve high hydrogenolysis selectivities. (Bender et al., 2022; Yuan, X. et al., *ChemSusChem* 15, (2022); and May et al., 2020.) However, Cu's ability to perform selective hydrogenolysis appears to be limited to furfural-based molecules given the lack of studies reporting selective hydrogenolysis of other molecules with Cu.

SUMMARY

[0006] Methods for the electrochemical reduction of aryl-aldehydes, aryl-ketones, alkyl-aldehydes, and/or alkyl ketones via selective hydrogenolysis of their carbonyl bonds are provided. The methods use zinc-containing electrocatalytic cathodes that promote electrochemical hydrogenolysis of the carbonyl group of the aldehyde or ketone over hydrogenation in an acid-containing solution.

[0007] One example of a method for the electrochemical reduction of the aldehydes or ketones uses an electrochemical cell that includes: a cathode comprising zinc in a catholyte solution, the catholyte solution comprising one or more carbonyl compounds selected from aryl-aldehydes, aryl-ketones, alkyl-aldehydes, alkyl-ketones, or a combination thereof, and an acid, wherein at least one of the one or more carbonyl compounds is not an aryl-aldehyde in which a carbonyl carbon is directly bonded to a furan ring; an anode in an anolyte solution comprising a chemical species to be oxidized; and an electrical circuit connecting the cathode and the anode.

[0008] The electrochemical reduction is carried out by applying an electrical potential difference between the cathode and the anode that induces the electrochemical reduction of a carbonyl group in the aryl-aldehyde, aryl-ketone, alkyl-aldehyde, or alkyl-ketone into an alkyl group via hydrogenolysis at the cathode, and also induces the electrochemical oxidation of the chemical species to be oxidized at the anode.

[0009] Other principal features and advantages of the invention will become apparent to those skilled in the art upon review of the following drawings, the detailed description, and the appended claims.

BRIEF DESCRIPTION OF THE DRAWINGS

[0010] Illustrative embodiments of the invention will hereafter be described with reference to the accompanying drawings, wherein like numerals denote like elements.

[0011] FIG. 1A shows the electrochemical hydrogenolysis of aldehydes and ketones using a Zn cathode. In the electrochemical hydrogenolysis, electrons gained by an oxidation reaction at the anode are used for the reduction of the carbonyl groups of the aldehydes and ketones (RCOR' where R'=H for an aldehyde) at the Zn cathode, meaning Zn is not used as the electron source (reductant). The potential of the electrons gained at the anode becomes sufficiently negative for the carbonyl reduction by electrical energy input. Water oxidation is used in the figure as an example anode reaction. (η_a: anodic overpotential, η_c:

cathodic overpotential, E_{cell}: cell voltage, SHE: standard hydrogen electrode, and RHE: reversible hydrogen electrode).

[0012] FIG. 1B shows a schematic diagram of an electrochemical cell for the electrochemical reduction of aldehydes and ketones.

[0013] FIG. 2A shows electrochemical hydrogenation and hydrogenolysis reactions (R'═H for an aldehyde). FIG. 2B shows the structures of various aryl-aldehydes and alkyl-aldehydes. FIG. 2C shows the structures of various aryl-ketones and alkyl-ketones.

[0014] FIGS. 3A-3B show electrochemical hydrogenation and hydrogenolysis reactions. FIG. 3A shows 4-HBAL and FIG. 3B shows 4-HAP.

[0015] FIGS. 4A-4C show comparison of constant-potential reduction results for Cu and Zn at −0.8 V vs a reversible hydrogen electrode (RHE) in a pH 4.5 solution containing 10 mM 4-HBAL or 4-HAP. FIG. 4A shows concentrations of hydrogenation, hydrogenolysis, and other products after passing an amount of charge equivalent to 2 e⁻ per starting molecule. The white text gives the corresponding absolute selectivities (%). FIG. 4B shows relative selectivities for the hydrogenation and hydrogenolysis products. FIG. 4C shows Faradaic efficiencies (FEs) for the hydrogenation and hydrogenolysis products.

[0016] FIGS. 5A-5H show the effect of potential, showing constant-potential reduction results on Zn in a pH 4.5 solution containing 10 mM (FIGS. 5A-5C) 4-HBAL or (FIGS. 5D-5F) 4-HAP. FIGS. 5A, 5D show concentrations of hydrogenation, hydrogenolysis, and other products after passing an amount of charge equivalent to 2 e⁻ per starting molecule. The white text gives the corresponding absolute selectivities (%). FIGS. 5B, 5E show relative selectivities for the hydrogenation and hydrogenolysis products. FIGS. 5C, 5F show FEs for the hydrogenation and hydrogenolysis products. FIG. 5G shows the effect of potential applied to (FIG. 5G) Cu and (FIG. 5H) Zn on total current density (gray) and partial current densities for hydrogenolysis and hydrogenation for 4-HBAL.

[0017] FIGS. 6A-6F show the effect of pH, showing constant-potential reduction results on Zn at −1.0 V vs RHE in solutions containing 10 mM (FIGS. 6A-6C) 4-HBAL or (FIGS. 6D-6F) 4-HAP at various pHs. FIGS. 6A, 6D show concentrations of hydrogenation, hydrogenolysis, and other products after passing an amount of charge equivalent to 2 e⁻ per starting molecule. The white text gives the corresponding absolute selectivities (%). FIGS. 6B, 6E show relative selectivities for the hydrogenation and hydrogenolysis products. FIGS. 6C, 6F show FEs for the hydrogenation and hydrogenolysis products.
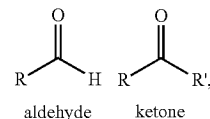
DETAILED DESCRIPTION

[0018] Electrochemical cells for the reduction of aldehydes and ketones via selective hydrogenolysis are provided. The electrochemical cells use zinc-containing electrocatalytic cathodes that promote electrochemical hydrogenolysis of the carbonyl group of the aldehyde or ketone over hydrogenation in an acid-containing solution. As a result, the electrochemical cells can reduce the carbonyl groups of aldehydes and ketones into alkyl groups with high selectivities. Moreover, because zinc is used as a cathode that is cathodically protected during the electrochemical reduction, the zinc is not oxidized or consumed as a reactant during the hydrogenolysis of the carbonyl group. Instead,

the electrons used for the reduction of the carbonyl compounds at the cathode come from the oxidation reaction occurring at the anode, as shown in FIG. 1A. An electrical potential applied between the cathode and the anode provides the electrons gained at the anode with a sufficiently negative potential to carry out hydrogenolysis at the cathode.

[0019] One illustrative embodiment of an electrochemical cell for carrying out the electrochemical reduction of aldehydes and ketones is shown in FIG. 1B. The electrochemical cell includes a cathode compartment 102 containing a catholyte solution 104 in which zinc-containing cathode 106 is submerged. The electrochemical cell further comprises an anode compartment 112 containing an anolyte solution 114 in which an anode 116 is submerged. Cathode compartment 102 and anode compartment 112 are separated by an ion-permeable membrane 118. Cathode 106 and anode 116 are in electrical communication through a circuit, which, in a simple form comprises an electrically conductive wire 120 connecting cathode 106 to anode 116 and a voltage source 122 configured to apply an electrical potential between cathode 106 and anode 116.

[0020] Cathode 106 contains zinc (Zn), which reduces the carbonyl group of the aldehyde or the ketone to an alkyl group via hydrogenolysis (FIG. 2A, "Hydrogenolysis"). The cathode may comprise metallic zinc Zn^0 (including pure zinc metal, zinc-containing metal alloys, and/or zinc metal mixed with other non-zinc containing compounds) or a zinc compound. Zinc compounds contain zinc as zinc ions that may, or may not be, reduced to metallic zinc under the applied potential. Zinc compounds include zinc oxides, zinc sulfides, zinc selenides, zinc tellurides, and zinc phosphides. The zinc-containing cathodes can have a variety of morphologies. For example, they can be planar, substantially planar, or nanostructured and they can be porous or non-porous. A high surface area is generally desirable but is not absolutely necessary. Examples of suitable cathode structures include zinc or zinc-containing foils, foams, and meshes. The cathodes may, optionally, also include a support on which the metallic zinc and/or zinc compounds are supported and/or a binder, such as an organic polymer, that holds particles of the metallic zinc and/or the zinc compounds together.

[0021] Catholyte solution 104 includes one or more carbonyl compounds selected from aldehydes, ketones, or a combination thereof. The aldehydes and ketones are carbonyl (C═O) group-containing organic molecules that can be represented by the formulas:

$$\underset{\text{aldehyde}}{\overset{\overset{\displaystyle O}{\|}}{R{\diagup}{\diagdown}H}} \qquad \underset{\text{ketone}}{\overset{\overset{\displaystyle O}{\|}}{R{\diagup}{\diagdown}R'}},$$

where the R and R' groups comprise aryl and/or alkyl groups, as described in more detail below.

[0022] The aldehydes may be aryl-aldehydes or alkyl-aldehydes. As used herein, the term aryl-aldehyde refers to an aldehyde in which the carbonyl carbon is bonded directly to a carbon atom that is part of an aromatic ring of the R group. As used herein, the term alkyl-aldehyde is used broadly to refer to an aldehyde in which the carbonyl carbon

is bonded to a carbon atom that is not part of an aromatic ring of the R group. While the carbonyl carbon of an alkyl-aldehyde is bonded to a carbon that is not part of an aromatic ring, said alkyl aldehyde may include one or more aryl moieties within its R group that are not directly bonded to the carbonyl carbon. Similarly, while the carbonyl carbon of an aryl-aldehyde is bonded to a carbon atom that is part of an aromatic ring, said aryl group may include one or more non-aromatic moieties within its R group that are not directly bonded to the carbonyl carbon. For purpose of illustration, the structures of a few example aryl-aldehydes and alkyl-aldehydes are shown in FIG. 2B

[0023] The ketones may be aryl-ketones or alkyl-ketones. As used herein, the term aryl-ketone refers to a ketone in which the carbonyl carbon is bonded directly to a carbon atom that is part of an aromatic ring of the R group and also to a carbon atom that is part of an aromatic ring of the and R' group, or in which the carbonyl carbon is bonded directly to a carbon atom that is part of an aromatic ring of only the R group. If the carbonyl carbon is bonded to a carbon atom that is part of an aromatic ring of the R group and also to a carbon atom that is not part of an aromatic ring of the R' group, the carbonyl carbon may be bonded to, for example, a carbon atom in an alkyl group or in an alkenyl group of the R' group. As used herein, the term alkyl-ketone is used broadly to refer to a ketone in which the carbonyl carbon is bonded directly to a carbon atom that is not part of an aromatic ring of the R group and to a carbon atom that is not part of an aromatic ring of the R' group. However, in the aryl-ketones, the R and R' groups may also comprise one or more non-aromatic groups that are not directly bonded to the carbonyl carbon. Similarly, in the alkyl-ketones, the R and R' groups may also comprise one or more aryl moieties that are not directly bonded to the carbonyl carbon. For purposes of illustration, the structures of a few example aryl-ketones and alkyl-ketones are shown in FIG. 2C.

[0024] Aryl groups that may be present in the R and R' groups of the aldehydes and ketones include homocyclic (all-carbon) aromatic rings, heterocyclic aromatic rings, or both. The aryl groups include at least one aromatic ring, which may be a single ring or part of a multicyclic aromatic group containing two or more fused or unfused aromatic rings. By way of illustration, an aromatic ring of an aryl-aldehyde or aryl-ketone, or an aryl moiety that is part of an R or R' group of an alkyl-aldehyde or alkyl-ketone, may be, for example, a phenyl group or a naphthyl group. In addition to the aldehyde and/or ketone groups, there may be other substituents on the aromatic rings, such as hydroxyl groups (i.e., —OH), ether groups (e.g., —OCH$_3$), ester groups, halide groups, boron, amine groups, amide groups, alkyl groups, and/or vinyl groups (FIGS. 2B and 2C).

[0025] Non-aromatic groups of the aldehydes or ketones can be cyclic or acyclic or may include both cyclic and acyclic portions, and the acyclic groups can be linear or branched. For the purposes of this disclosure, and as the name would suggest, any group with a carbon atom that is not part of an aromatic ring is considered a non-aromatic group. Thus, non-aromatic groups that may form at least a portion of an R or R' group include, but are not limited to alkyl groups, including C$_1$ to C$_{12}$ alkyl groups and C$_1$ to C$_6$ alkyl groups, and alkenyl groups (FIGS. 2B and 2C).

[0026] A wide variety of aryl-aldehydes, aryl-ketones, alkyl-aldehydes, and alkyl-ketones can be electrochemically reduced to their corresponding aryl-alkanes and alkyl-al-

kanes via hydrogenolysis of the carbonyl bond with a high relative selectivity using the electrochemical cells and methods described herein. Some embodiments of the electrochemical reductions use aryl-aldehydes or aryl-ketones derived from lignocellulosic biomass as a feedstock, where lignocellulosic biomass refers to plant biomass containing cellulose, hemicellulose, and lignin. For example, the depolymerization of lignin produces aryl-aldehydes and aryl-ketones, such as vanillin (4-hydroxy-3-methoxybenzaldehyde), syringaldehyde (4-hydroxy-3,5-dimethoxybenzaldehyde), acetovanillone (4'-hydroxy-3'-methoxyacetophenone), and acetosyringone (3',5'-dimethoxy-4'-hydroxyacetophenone), which can be electrochemically deoxygenated to produce high-quality bio-oils having low oxygen contents using the electrochemical cell and methods described herein.

[0027] However, it is desirable to omit from the catholyte solution aryl-aldehydes for which the aromatic ring opens during the hydrogenolysis of the carbonyl group and, thus, the final product is not the corresponding aryl-alkane. Examples of such molecules include aryl-aldehydes in which the aromatic ring to which the carbonyl carbon is bonded is a furan ring, such as furfurals and furfural derivatives. Thus, while aryl-aldehydes for which aromatic ring opening occurs concurrently with carbonyl group hydrogenolysis may, optionally, be present in the catholyte solution, when present they are present in combination with one or more alkyl-aldehydes and/or alkyl-ketones, and/or with one or more aryl-aldehydes and/or aryl-ketones for which hydrogenolysis of the carbonyl group occurs while conserving the aryl structure.

[0028] Other embodiments of the electrochemical reductions use aryl-aldehydes, aryl-ketones, alkyl-aldehydes, and/or alkyl-ketones that are useful in a variety of industries, including the pharmaceutical industry.

[0029] Aromatic compounds other than aryl-aldehydes and aryl-ketones also can be present in the initial catholyte solution. However, in some embodiments of the cells, the aryl-aldehydes and aryl-ketones that are initially present (i.e., that are present before the onset of the electrochemical reduction) are the predominant aromatic compounds present in the starting electrolyte solution. Thus, in some embodiments of the electrochemical cells, aryl-aldehydes and/or aryl-ketones make up at least 50 mol. % of aromatic compounds that are initially present in the catholyte solution. This includes embodiments in which aryl-aldehydes and/or aryl-ketones make up at least 70 mol. %, at least 80 mol. %, at least 90 mol. %, at least 95 mol. %, or at least 99 mol. % of the aromatic compounds present in the initial catholyte solution.

[0030] Catholyte solution 104 may be an aqueous solution (i.e., a solution in which water is the only solvent for the aldehyde and ketone solutes), a non-aqueous solution (i.e., a solution in which one or more organic solvents are the only solvents for the aldehyde and ketone solutes), or a mixed solution in which water and one or more organic solvents are present as co-solvents for the aldehyde and ketone solutes. The nature of the catholyte solution and the particular solvents used will depend on the particular aldehydes and ketones being reduced. By way of illustration only, organic solvents that may be used in a non-aqueous catholyte solution or a mixed catholyte solution include acetonitrile,

propyl alcohol, methanol, ethanol, propylene carbonate, tetrahydrofuran, and dimethyl sulfoxide, and/or dimethyl-formamide.

[0031] The catholyte solution includes at least one source for protons (e.g., at least one acid) that will be used provide the H atoms needed for the hydrogenolysis. The proton source renders the solution acidic and a higher acidity tends to promote hydrogenolysis of the carbonyl bond over hydro-genation. For aqueous catholyte solutions, the addition of the acid will render the solution acidic and the acidic can be determined readily based on pH. Thus, acidic aqueous catholyte solutions are defined as catholyte solutions having a pH of less than 7.0. In some illustrative embodiments of the electrochemical cells and methods, the catholyte solution has a pH in the range from 0 to 5.0. This includes embodi-ments in which the catholyte solution has a pH in the range from 1.0 to 4.5. Strong or weak acids may be used to provide protons and render the catholyte solutions acidic.

[0032] When not using a strongly acidic catholyte solution (pH<1), the acidic catholyte solutions may be a buffered solution that include a weak acid and its conjugate base in order to maintain a constant level of acidity or a level of acidity that does not change rapidly or significantly during the operation of the electrochemical cell. Non-limiting examples of weak acids that can be used include sodium hydrogen sulfate, acetic acid, phosphric acid, and citric acid. For the purposes of this disclosure, acids with a pKa of 1 and greater are considered weak acids. (The pKa values corre-spond to the pKa values in the catholyte solution at a temperature of 25° C.)

[0033] For non-aqueous or mixed catholyte solutions, it is more difficult to determine pH. For these catholyte solutions, sufficiently strong acids are added as a proton source and the acid concentration will be optimized such that the hydrog-enolysis reaction becomes a dominant reaction. (The pKa value of an acid varies based on the type of non-aqueous solvent used, so specific pKa ranges are not provided here.) Examples of acids that may be used in non-aqueous or mixed catholyte solutions include, but not limited to, p-tolu-ene sulfonic acid, triflic acid, trifluoromethanesulfonic acid, methanesulfonic acid, hydrochloric acid, and sulfuric acid.

[0034] Optionally, the catholyte solution may include additional salts as supporting electrolytes to provide a desired solution conductivity or ionic strength.

[0035] In embodiments of the electrochemical cells and methods in which the aldehydes or ketones or their reduction products can be consumed by oxidation reactions at the anode and/or in which the species being oxidized or their oxidation products at the anode can be consumed by reduc-tion reactions at the cathode, a divided cell, such as the one shown in FIG. 1B, can be used. In a divided cell, the aldehydes and ketones can be retained in the cathode com-partment and/or the species being oxidized can be retained in the anode compartment. However, if the anode reaction and cathode reaction do not interfere with each other (i.e., consuming the reactants or products of the other electrode), the electrochemical reductions can be carried out in an undivided cell in which the anode and cathode are both submerged in the same electrolyte solution (i.e., a single solution may be used as the catholyte solution and the anolyte solution).

[0036] The material of anode 116 and the reactant atoms or molecules (the chemical species to be oxidized) present in anolyte solution 114, if a divided cell is used, will depend upon the oxidation reaction that takes place at the anode ("the anode reaction") during the electrochemical reduction. Examples of anode reactions that can be carried out include, but are not limited to, water oxidation (i.e., wherein water is the chemical species being oxidized) oxidation of non-aqueous solvents, oxidation of sacrificial metals, oxidative upgrading of biomass-derived molecules, such as furfurals including 5-hydroxymethyl furfural, glucose, and glycerol, and other organic molecules to produce commodity and fine chemicals.

[0037] Anolyte solution 114 may be an aqueous solution (i.e., a solution in which water is the only solvent for the solute to be oxidized), a non-aqueous solution (i.e., a solu-tion in which one or more organic solvents are the only solvents for the solute to be oxidized), or a mixed solution in which water and one or more organic solvents are present as co-solvents for the solute to be oxidized. The nature of the anolyte solution, the particular solvents used, and the pH of the anolyte solution will depend on the particular chemical species being oxidized, the composition of the catholyte, and type of the membranes used.

[0038] To operate the electrochemical cell, voltage source 122 is used to create a potential difference between zinc-containing cathode 106 and anode 116, such that a flow of electrons from the anode to the cathode through an external wire results. The electrons obtained from the oxidation reaction occurring at anode 116 is used at the surface of cathode 106 for the reduction of aldehydes and ketones in the catholyte solution 104 (FIG. 1B. The electrochemical reduction product resulting from the reduction of the car-bonyl group in the aldehyde of an aryl-aldehyde or the ketone group of an aryl-ketone is referred to as an aryl-alkane. Similarly, the electrochemical reduction product resulting from the reduction of the carbonyl group in the aldehyde of an alkyl-aldehyde or the ketone group of an alkyl-ketone is referred to as an alkyl-alkane. Once the aryl-alkane and/or alkyl-alkane is produced, it may be removed from the catholyte solution.

[0039] Importantly, because the electrons used for carbo-nyl reduction come from the oxidation reaction at the anode and not from the oxidation of zinc in the cathode (FIG. 1A), the Zn-containing cathode is not a chemical reductant and is not continuously consumed. This renders the electrochemi-cal reduction of the aldehydes and ketones using zinc-containing cathodes sustainable and represents a substantial advantage over organic reductions that utilize Zn as a chemical reductant or the electrochemical deoxygenation of aldehyde or ketone carbonyl groups using a Zn anode, where the Zn is continuously consumed.

[0040] The Zn-containing cathodes in the electrochemical cells promote hydrogenolysis over hydrogenation of the carbonyl group of the aldehyde or ketone. This selectivity for carbonyl hydrogenolysis can be measured in terms of a "relative selectivity" for hydrogenolysis, which is defined as the amount (based on moles) of carbonyl hydrogenolysis product divided by the combined total amount (based on moles) of carbonyl hydrogenolysis and carbonyl hydroge-nation products. (See equation (2) in the Example.) The pH of the catholyte solution, the applied potential, and the catholyte solvent can be chosen to achieve a relative selec-tivity for hydrogenolysis that is sufficient for a given appli-cation or that is maximized. Generally, increasing the acidity (e.g., decreasing the pH) of the catholyte solution increases the relative selectivity for hydrogenolysis. Increasing the

applied potential also tends to increase the relative selectivity; however, at very high applied potentials, an increase in the hydrogen evolution reaction (HER), which competes with the carbonyl hydrogenation and hydrogenolysis, makes the effect of potential on the relatively selectivity for hydrogenolysis unpredictable.

[0041] The hydrogenolysis products may be produced with high FE, where FE is the ratio of charge used to produce the hydrogenolysis product to the total charge used. (See equation (3) of the Example.) High FE for hydrogenolysis may be obtained when the potential is negative enough to perform hydrogenolysis as the dominant carbonyl reduction reaction but is not sufficiently negative to make the HER (or the reduction of other solvent) a dominant reaction. The optimal potential to maximize the FE for hydrogenolysis depends on the reactivity of the carbonyl compound toward hydrogenolysis, pH of the solution, and the type of solvent.

[0042] The competing HER reaction can be suppressed by using concentrated carbonyl compound solutions and continuously feeding the aldehydes or ketones into the catholyte compartment in order to keep their concentration substantially constant in the catholyte solution during the operation of the electrochemical cell.

[0043] The electrochemical reductions can be carried out at room temperature ("RT"; 23° C.) or near room temperature (e.g., 20° C.<T<26° C.). However, the electrochemical reductions can be carried out at temperatures outside of this range.

[0044] As can be understood from the discussion above, the electrochemical reduction of aldehydes and ketones via carbonyl hydrogenolysis can be carried out with high relative selectivity and high FE by the selection of appropriate pH conditions, applied voltages, and/or solvents. Thus, by tailoring these parameters, the electrochemical reduction of a wide range of aldehydes and/or ketones can be achieved with a relative selectivity for carbonyl hydrogenolysis of at least 50% (e.g., 50% to 100%) and an FE of at least 20% (e.g., 30% to 90%, or higher). This includes electrochemical reductions of aldehydes and/or ketones that are conducted with a relative selectivity for carbonyl hydrogenolysis of at least 60%, at least 70%, at least 80%, and at least 90% and/or electrochemical reductions of aldehydes and/or ketones that are conducted with an FE for carbonyl hydrogenolysis of at least 30%, at least 50%, at least 60%, at least 70%, at least 80%, and at least 90%.

[0045] In addition to producing the carbonyl hydrogenolysis product at a high selectivity relative to the hydrogenation product and high FEs, the electrochemical cells can produce the carbonyl hydrogenolysis product at a high absolute selectivity—that is, at a high selectivity relative to all other electrochemical reduction products of the aldehyde or ketone (See equation (1) of the Example). The absolute selectivity will depend on the particular aldehydes and ketones being used and the chosen electrolyte and operating conditions. By way of illustration only, electrochemical reductions can be carried out with an absolute selectivity for the carbonyl hydrogenolysis product of at least 50%, based on moles (e.g., 50% to 100%). This includes electrochemical reductions of aldehydes and/or ketones that are conducted with an absolute selectivity for carbonyl hydrogenolysis of at least 60%, at least 70%, at least 80% and at least 90%.

EXAMPLE

[0046] This Example demonstrates the successful electrochemical reduction of aryl-aldehydes and aryl-ketones on Zn that results in remarkable hydrogenolysis selectivities compared with those attainable on Cu. The effects of applied potential and pH on the selectivity for hydrogenolysis of carbonyl compounds on Zn were investigated to demonstrate the advantages of electrochemical reduction.

Results

[0047] In this Example, 4-hydroxybenzaldehyde (4-HBAL) and 4-hydroxyacetophenone (4-HAP) were chosen as representative aromatic aldehyde and ketone model compounds to demonstrate the unique hydrogenolysis ability of Zn (FIGS. 3A-3B). The presence of a hydroxy group in these molecules increased the solubility and decreased the volatility of these compounds and their corresponding hydrogenolysis products in aqueous media, making them exemplary carbonyl compounds that can be reduced in aqueous media. Additionally, the presence of a hydroxy group in these molecules made them good models for the reactive oxygenated aromatic compounds present in bio-oil, as many of those contain a hydroxy group.

[0048] Comparison of Cu and Zn. First, the electrocatalytic abilities of Cu and Zn were compared for the constant potential reduction of 4-HBAL and 4-HAP in a pH 4.5 buffered solution containing 10 mM 4-HBAL or 4-HAP at −0.8 V vs the reversible hydrogen electrode (RHE). The concentrations of each product obtained after passing an amount of charge equivalent to 2 e⁻ per starting molecule are shown in FIG. 4A. The white numbers in this bar graph give the absolute selectivities for each product calculated using Eq. 1. For mass balance, the difference between the amount of consumed reactant and the sum of the detectable products is indicated as "other" in FIG. 4A. This "other" is due to the formation of side products that cannot be easily identified or quantified (e.g., ill-defined dimers, oligomers, or some other reduced species).

$$\text{Absolute Selectivity (\%)} = \frac{\text{mol of specific product}}{\text{mol of consumed reactant}} \times 100\% \quad (1)$$

$$\text{Relative Selectivity (\%)} = \quad (2)$$

$$\frac{\text{mol of hydrogenation or hydrogenolysis product}}{\text{mol of hydrogenation product +}} \times 100\%$$
$$\text{mol of hydrogenolysis product}$$

$$FE\ (\%) = \frac{\text{mol of e-consumed to produce specific product}}{\text{mol of e-passed}} \times 100\% \quad (3)$$

[0049] This working embodiment of the invention focuses specifically on the selectivities toward hydrogenation versus hydrogenolysis. Thus, relative selectivities, which compare the amount of hydrogenation or hydrogenolysis product to the combined amount of hydrogenation and hydrogenolysis products (Eq. 2), can be very informative (FIG. 4B). The FEs for production of these two products (Eq. 3) are shown in FIG. 4C.

[0050] When Cu was used as the cathode, the yields and FEs of the reduction products were generally very low because the hydrogen evolution reaction (HER) is preferred to organic reduction on Cu at −0.8 V vs RHE. In particular, 4-HAP hardly reacted. Nonetheless, it was evident that for both compounds, hydrogenation was the dominant reaction over hydrogenolysis on Cu; the relative selectivities for

hydrogenolysis were only 27.8% and 17.8% for 4-HBAL and 4-HAP, respectively (FIG. 4B).

[0051] When Zn was used as the cathode under the same conditions, a striking difference was observed. Firstly, because Zn is less catalytic for HER than Cu, significantly higher conversion of 4-HBAL and 4-HAP was observed at −0.8 V vs RHE. Secondly, for both 4-HBAL and 4-HAP, hydrogenolysis was the dominant reaction with a relative selectivity of approximately 90% for both 4-HBAL and 4-HAP (FIG. 4B). The FE for hydrogenolysis of 4-HBAL was 70.6% and the FE for hydrogenolysis of the less reactive 4-HAP was as high as 45.1%.

[0052] The Effect of Potential. Next, the effect of potential on the selectivities and FEs was investigated for hydrogenation and hydrogenolysis on Zn. The results obtained with constant potential reduction of 4-HBAL and 4-HAP at various potentials are shown in FIGS. 5A-5H. For 4-HBAL, the amount of hydrogenolysis product produced and corresponding FE decreased gradually with increasing overpotential because HER was promoted (FIGS. 5A, 5C). Considering only the FE for hydrogenolysis, −0.6 V vs RHE was the best potential (85.4%). However, the highest relative selectivity for hydrogenolysis was achieved at −1.0 V vs RHE (94.0%) (FIG. 5B). For 4-HAP, which is significantly less reactive than 4-HBAL, a more negative potential was needed to achieve the highest organic conversion and maximal hydrogenolysis selectivity (FIG. 5D). The highest FE for hydrogenolysis was achieved at −0.9 V vs RHE (70.9%) (FIG. 5F) and the highest relative hydrogenolysis selectivity was obtained at −1.0 V vs RHE (97.1%) (FIG. 5E).

[0053] The effect of potential on the rate of hydrogenolysis and hydrogenation is best examined by plotting the potential-dependent partial current for each reaction (FIGS. 5G, 5H). The results show that when the overpotential increased, the hydrogenolysis current increased considerably until −1.0 V vs RHE for 4-HBAL and −1.1 V vs RHE for 4-HAP. The hydrogenation current also increased with increasing overpotential but not as considerably as the hydrogenolysis current, which resulted in an increase in the relative hydrogenolysis selectivity with increasing overpotential in this potential region (FIGS. 5B, 5D). As the overpotential increased further, the hydrogenolysis current decayed as HER became the dominant reaction, but the hydrogenation current continued to increase. This resulted in a slight decrease in the relative selectivity for hydrogenoly-

sis in the very high overpotential region (>−1.0 V vs. RHE) (FIGS. 5B, 5D). This very high overpotential region with dominant HER is not of great interest for both mechanistic and practical applications.

[0054] The potential dependent study clearly shows that increasing overpotential is favorable for increasing the rate (FIGS. 5G, 5H) and relative selectivity (FIGS. 5B, 5D) for hydrogenolysis on Zn until HER becomes the dominant reaction. This also highlights the advantage of electrochemical reduction having the applied potential as an additional reaction parameter. For example, when 4-HBAL and 4-HAP were reduced by using the Zn electrode as a chemical reductant under the open circuit condition while all other conditions remained the same, even after 24 hours, the amounts of 4-HBAL and 4-HAP consumed (4.13 mM and 0.01 mM, respectively) and the relative selectivities for hydrogenolysis (66.0% and 29.2%, respectively) were considerably lower than those obtained by electrochemical reduction (FIGS. 5A-5H).

[0055] The Effect of pH. The effect of pH on hydrogenolysis and hydrogenation was investigated by performing organic reductions at the same potential (−1.0 V vs RHE) in pH 2, 4.5, 7, and 9 solutions (FIGS. 6A-6F). The potential of −1.0 V vs RHE was chosen because the highest relative selectivity for hydrogenolysis was achieved at this potential (FIGS. 5A-5H). For the reduction of 4-HBAL, as pH increased, the selectivity for hydrogenolysis consistently decreased, making pH 2 optimal for hydrogenolysis. The same general trend was observed for 4-HAP with one notable difference. At pH 2, ill-defined polymerization reactions occurred, and the majority of 4-HAP (91.4%) was consumed in these undesirable reactions. Since hydrogenation and hydrogenolysis of 4-HAP were minor reactions whose selectivities could be considerably affected by these dominant yet unidentified reactions, discussing their relative selectivities at pH 2 is not meaningful. For the pH range of 4.5-9, as pH increased, the selectivity for hydrogenolysis of 4-HAP also decreased, as in the case of 4-HBAL, making pH 4.5 optimal for the hydrogenolysis of 4-HAP. The general trend observed here is that hydrogenolysis is promoted under lower pH conditions.

[0056] Other examples of aromatic aldehydes that can undergo hydrogenolysis with hydrogenolysis selectivities (>80%) for other aromatic aldehydes that can be obtained from depolymerization of lignin, are shown in Table 1.
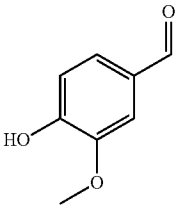
TABLE 1

Results obtained from reduction of vanillin and syringaldehyde using a
Zn electrode at −1.0 V vs RHE in a pH 4.5 solution containing 10 mM reactant after passing
an amount of charge equivalent to 2 e⁻ per starting molecule.

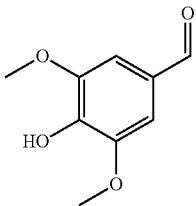| Molecule	Consumed (mM)	Selectivity (%)		Relative Selectivity (%)		FE (%)	
		Hydrogenation	Hydrogenolysis	Hydrogenation	Hydrogenolysis	Hydrogenation	Hydrogenolysis
vanillin	1.95 mM	12.5%	82.5%	13.2%	86.8%	2.5%	32.2%

TABLE 1-continued

Results obtained from reduction of vanillin and syringaldehyde using a
Zn electrode at −1.0 V vs RHE in a pH 4.5 solution containing 10 mM reactant after passing
an amount of charge equivalent to 2 e⁻ per starting molecule.

Molecule	Consumed (mM)	Selectivity (%) Hydroge-nation	Selectivity (%) Hydroge-nolysis	Relative Selectivity (%) Hydroge-nation	Relative Selectivity (%) Hydroge-nolysis	FE (%) Hydroge-nation	FE (%) Hydroge-nolysis
syringaldehyde	2.04 mM	17.8%	78.5%	18.4%	81.6%	3.6%	32.0%

[0057] The Use of Non-aqueous Solvents. While the examples shown above used aqueous solutions, the electrolyte solution for electrochemical reductions does not need to be an aqueous solution. Instead, it can be a mixture of aqueous and non-aqueous solutions or just a non-aqueous solution. The use of an electrolyte solution that contains a non-aqueous solvent (e.g., acetonitrile, propyl alcohol) makes it possible to use organic molecules that are not soluble in an aqueous solution (either as reactants or products) for electrochemical reductions, significantly broadening the types of molecules that can be used in the present methods. Table 2 shows results obtained from the electrochemical reduction of various aldehydes and ketones (10 mM each) in an electrolyte solution composed of 1:1 ratio (by volume) of water and acetonitrile, which contains 10 mM p-tolualdehyde, and 0.75 M sodium perchlorate. It is noted that the molecules shown as reactants in Table 2 and their reduction products have limited solubilities in an aqueous medium. The use of acetonitrile as a co-solvent solubilizes these reactants and their reduction products, and the hydrogenolysis product is obtained as the major product in this mixed medium. With the electrolyte solution containing a non-aqueous solvent, herein is reported the potential against the Ag/AgCl (4 M KCl) reference electrode instead of RHE because pH and therefore the RHE potential is ill-defined with the non-aqueous solvent.

TABLE 2

Results obtained from the reduction of various carbonyl compounds (10
mM) using a Zn electrode in a solution composed of 1:1 ratio (by volume) of water and
acetonitrile containing 0.1M p-toluenesulfonic acid and 0.75M sodium perchlorate after
passing an amount of charge equivalent to 2 e⁻ per starting molecule. The reduction of all
carbonyl compounds were carried out at −1.26 V vs. Ag/AgCl except for the last two
compounds, 4-hydroxyphenylacetone and 3-(3-(trifluoromethyl)phenyl)propanal, which were
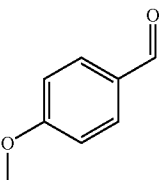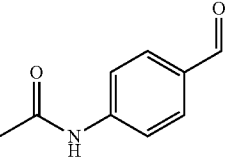reduced at −1.46 V vs. Ag/AgCl.

Molecule	Consumed (mM)	Selectivity (%) Hydroge-nation	Selectivity (%) Hydroge-nolysis	Relative Selectivity (%) Hydroge-nation	Relative Selectivity (%) Hydroge-nolysis	FE (%) Hydroge-nation	FE (%) Hydroge-nolysis
p-anisaldehyde	4.29 mM	5.6%	84.1%	6.3%	93.7%	2.4%	72.2%
4-acetamido benzaldehyde	1.94 mM	7.8%	89.0%	8.0%	92.0%	1.5%	34.5%

TABLE 2-continued

Results obtained from the reduction of various carbonyl compounds (10 mM) using a Zn electrode in a solution composed of 1:1 ratio (by volume) of water and acetonitrile containing 0.1M p-toluenesulfonic acid and 0.75M sodium perchlorate after passing an amount of charge equivalent to 2 e⁻ per starting molecule. The reduction of all carbonyl compounds were carried out at −1.26 V vs. Ag/AgCl except for the last two compounds, 4-hydroxyphenylacetone and 3-(3-(trifluoromethyl)phenyl)propanal, which were reduced at −1.46 V vs. Ag/AgCl.
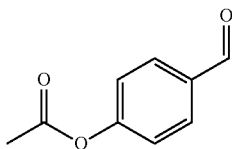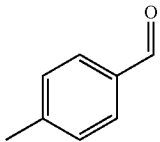
Molecule	Consumed (mM)	Selectivity (%) Hydrogenation	Selectivity (%) Hydrogenolysis	Relative Selectivity (%) Hydrogenation	Relative Selectivity (%) Hydrogenolysis	FE (%) Hydrogenation	FE (%) Hydrogenolysis
4-acetoxybenzaldehyde	1.37 mM	13.2%	85.0%	13.4%	86.6%	1.8%	23.3%
p-tolualdehyde	2.65 mM	3.4%	93.9%	3.5%	96.6%	0.9%	49.8%
benzaldehyde	1.89 mM	5.3%	80.9%	6.2%	93.8%	1.0%	30.6%
acetophenone	4.10 mM	8.7%	83.4%	9.4%	90.1%	3.6%	68.4%
4-hydroxyphenylacetone	0.63 mM	~0%	58.3%	~0%	>99%	~0%	7.3%
3-(3-(trifluoromethyl)phenyl)propanal	2.24 mM	~0%	47.2%	~0%	>99%	~0%	21.2%

Methods

[0058] Materials. 4-hydroxybenzaldehyde (98%, Sigma-Aldrich), 4-hydroxyacetophenone (99%, Sigma-Aldrich), benzaldehyde (98%, Alfa Aesar), acetophenone (98%, Sigma Aldrich), vanillin (99%, Sigma Aldrich), syringaldehyde (98%, Sigma Aldrich), p-tolualdehyde (97%, Sigma-Aldrich), 4-acetamidobenzaldehyde (98%, TCI), 4-acetoxy-benzaldehyd (99%, Chem-Impex), p-anisaldehyde (98%, Sigma-Aldrich), 4-hydroxybenzyl alcohol (99%, Sigma

Aldrich), p-cresol (99%, Sigma Aldrich), 4-(1-hydroxy-ethyl)phenol (97%, Ambeed), 4-ethylphenol (99%, Sigma Aldrich), 2-methoxy-4-methylphenol (98%, TCI), 2,6-dimethoxy-4-methylphenol (97%, TCI), benzyl alcohol (99%, MP Biomedicals), toluene (99.8%, Sigma-Aldrich), 1-phenylethanol (98%, Sigma Aldrich), ethylbenzene (99.8%, Acros Organics), 4-methylbenzyl alcohol (98%, Sigma-Aldrich), p-xylene (≥99%, Sigma Aldrich), 4-methoxybenzyl alcohol (96%, Sigma Aldrich), 4-methylanisole (99%, Sigma Aldrich), 4-acetamidobenzyl alcohol (99%, Chem-Impex), 4'-methylacetanilide (98+ %, Thermoscientific), 4-acetoxybenzyl alcohol (95%, AstaTech), 4-hydroxyphenylacetone (97%, TCI), 3-(3-(trifluoromethyl)phenyl)propanal (98%, Ambeed), p-tolyl acetate (98%, TCI), Na_2SO_4 (ACS grade, Dot Scientific Inc.), sodium acetate 99.0%, Sigma-Aldrich), $NaH_2PO_4.2H_2O$ (≥99%, Sigma Aldrich), H_3BO_3 (≥99.5%, Sigma-Aldrich), NaOH (≥97%, Sigma-Aldrich), KOH (≥85%, Sigma-Aldrich), H_2SO_4 (95-98%, Sigma-Aldrich), Zn foil (99.98%, Thermo Scientific), Cu foil (99.9%, Nimrod Copper Co.). All chemicals were used without further purification after purchase. Deionized water (Barnstead E-pure water purification system, resistivity >18 MΩ cm) was used to prepare all solutions.

[0059] Electrode Preparation. The Cu and Zn working electrodes were prepared by cutting metal foils into 3 cm×1.3 cm strips and masking the front and back side of the metal foil with Teflon tape such that a circular area of 1 cm² was exposed on the front side. The Pt counter electrodes were prepared by sputter coating a 20 nm Ti adhesion layer followed by 100 nm of Pt on precleaned glass slides. Prior to any electrochemical test, all metal electrodes underwent a procedure to remove the surface oxide layer. Zn electrodes were immersed in 37 wt. % HCl for about 10 s. Cu electrodes were immersed in 10 wt. % H_2SO_4 solution for about 10 s. After these procedures, the electrodes were rinsed with deionized water (Barnstead 18 MΩ) and dried with a N_2 flow.

[0060] Electrolyte Solution Preparation. Electrochemical reduction experiments in aqueous media were performed in various pH solutions; pH 2 (0.5 M Na_2SO_4—$NaHSO_4$ buffer), pH 4.5 (0.5 M sodium acetate-acetic acid buffer), pH 7 (0.5 M $NazHPO_4$—NaH_2PO_4 buffer) and pH 9 (0.5 M potassium borate-boric acid buffer). The pH 4.5 and pH 9 solutions additionally contained 0.5 M Na_2SO_4 to make their solution conductivity and ionic strengths comparable to those of pH 2 and 7 solutions. For vanillin and syringaldehyde, a pH 4.5 (0.5 M sodium acetate-acetic acid buffer) was used. For other molecules that do not readily dissolve in aqueous media (i.e., those shown in Table 2), a 1:1 (by volume) water:acetonitrile solution that contained 0.1 M p-toluenesulfonic acid and 0.75 M sodium perchlorate was used. The concentration of organic reactant in all cases was 10 mM.

[0061] The electrolyte solution used for the reduction of the carbonyl group-containing compounds shown in Table 2 was a 1:1 (by volume) water: acetonitrile solution that contain 0.1 M p-toluenesulfonic acid, and 0.75 M sodium perchlorate. The concentration of carbonyl compounds was 10 mM.

[0062] Constant Potential Electrolysis. The constant potential electrolysis of 4-HBAL (or other starting molecules such as 4-HAP, vanillin, and syringaldehyde) was performed in an H-type cell divided by a glass frit using Zn or Cu electrodes as the working electrode (WE), Ag/AgCl (in 4 M KCl) as the reference electrode (RE), and Pt as the counter electrode (CE). The cathode compartment contained 10 mL of the buffer solution containing 10 mM 4-HBAL (or

other starting molecules) while the anode compartment contained the same amount of the same buffer solution without the carbonyl compound. All constant potential reductions were performed with stirring until 19.3 C of charge (2 e⁻ per starting molecule) was passed. The constant potential electrolysis of other carbonyl-containing compounds shown in Table 2 was performed in a sealed H-type cell divided by a glass frit using the same RE and CE described above. The WE was a piece of 3 cm×1 cm zinc foil, for which a size of 1.5 cm×1 cm was submerged unmasked into the catholyte, exposing a surface area of 3 cm². The cathode compartment contained 30 mL of the mixed electrolyte containing 10 mM p-anisaldehyde (or other starting molecules) while the anode compartment contained the same amount of the same mixed electrolyte without the carbonyl compound. All constant potential reductions were performed with stirring until 57.9 C of charge (2 e⁻ per starting molecule) was passed.

[0063] The chemical reduction reactions (with no applied potential) of 4-HBAL or 4-HAP were performed by immersing a masked Zn foil (1 cm² exposed surface area) into 10 mL of a pH 4.5 buffered solution containing 10 mM 4-HBAL or 4-HAP. In these reactions, Zn was used as a chemical reductant. The solution with Zn foil immersed was stirred for 24 h, and then aliquots were taken for analysis without further treatment.

[0064] Product Analysis. Quantification of electrolysis results was achieved using high performance liquid chromatography (HPLC, Prominence-i LC 2030C 3D, Shimadzu) equipped with a Restek Roc C18 column (150×4.6 mm, 5 μm). The flow rate was 1 mL min⁻¹ 1 with a column temperature of 40° C., and the mobile phase was composed of solvent A (water, 0.1% phosphoric acid) and solvent B (acetonitrile, 0.1% phosphoric acid). The HPLC gradient started at 20% solvent B for 2 min, then increased to 80% solvent B over a 7 min time period and held at 80% solvent B for another 1 min. Integration of PDA absorbances at multiple wavelengths was compared to calibration curves of all identified products to quantify each product. After the required charge passed, aliquots were taken from the cathode compartment for HPLC analysis without further treatment.

[0065] Due to the limited commercial availability, the hydrogenation products for vanillin and syringaldehyde was quantified by ¹H-NMR using a Bruker Avance III 400 MHZ nuclear magnetic resonance (NMR) spectrometer. NMR samples were prepared by adding 0.450 mL of the electrolysis solution and 0.050 mL of D_2O with 12.5 mM of a dimethyl sulfone as an internal standard to an NMR tube. NMR analyses were conducted with a relaxation delay of 30 s and using a WATERGATE method with excitation sculpting to remove the background signal due to the water solvent.

[0066] The word "illustrative" is used herein to mean serving as an example, instance, or illustration. Any aspect or design described herein as "illustrative" is not necessarily to be construed as preferred or advantageous over other aspects or designs. Further, for the purposes of this disclosure and unless otherwise specified, "a" or "an" can mean only one or can mean "one or more." Embodiments of the inventions consistent with either construction are covered.

[0067] The foregoing description of illustrative embodiments of the invention has been presented for purposes of illustration and of description. It is not intended to be exhaustive or to limit the invention to the precise form disclosed, and modifications and variations are possible in light of the above teachings or may be acquired from

practice of the invention. The embodiments were chosen and described in order to explain the principles of the invention and as practical applications of the invention to enable one skilled in the art to utilize the invention in various embodiments and with various modifications as suited to the particular use contemplated. It is intended that the scope of the invention be defined by the claims appended hereto and their equivalents.

1. A method for the electrochemical reduction of an aldehyde or a ketone in an electrochemical cell comprising:
   a cathode comprising zinc in a catholyte solution, the catholyte solution having a pH of 3 or less and comprising one or more carbonyl compounds selected from aryl-aldehydes, aryl-ketones, alkyl-aldehydes, alkyl-ketones, or a combination thereof, and an acid, wherein at least one of the one or more carbonyl compounds is not an aryl-aldehyde in which a carbonyl carbon is directly bonded to a furan ring;
   an anode in an anolyte solution comprising a chemical species to be oxidized; and
   an electrical circuit connecting the cathode and the anode;
   the method comprising:
   applying an electrical potential difference between the cathode and the anode that induces the electrochemical reduction of a carbonyl group in the one or more aryl-aldehydes, aryl-ketones, alkyl-aldehydes, or alkyl-ketones into an alkyl group via hydrogenolysis at the cathode, wherein the selectivity for the hydrogenolysis of the carbonyl group is higher than that of the hydrogenation of the carbonyl group, and also induces the electrochemical oxidation of the chemical species to be oxidized at the anode.

2. The method of claim 1, wherein the catholyte solution comprises at least one of the aryl-aldehydes or at least one of the aryl-ketones.

3. The method of claim 2, wherein the aryl-aldehyde, the aryl-ketone, or the combination thereof is derived from lignocellulosic biomass.

4. The method of claim 1, wherein the catholyte solution is an aqueous solution.

5. The method of claim 4, wherein the catholyte solution has a pH of two or less.

6. The method of claim 5, wherein the catholyte solution has a pH of less than 1.

7. The method of claim 1, wherein the catholyte solution is made by forming a first solution comprising the one or more carbonyl compounds and adding the acid to the first solution.

8. The method of claim 1, wherein the catholyte solution comprises water and an organic co-solvent.

9. The method of claim 1, wherein the catholyte solution is a non-aqueous solution.

10. The method of claim 9, comprising acetonitrile as a non-aqueous solvent.

11. The method of claim 9, wherein the acid has a pKa of less than 1.

12. The method of claim 1, wherein the zinc of the cathode is present as metallic zinc (Zn^0).

13. The method of claim 1, wherein the cathode comprises a zinc compound comprising Zn^{2+} ions.

14. (canceled)

15. The method of claim 1, wherein the electrochemical reduction has a relative selectivity for the hydrogenolysis of the carbonyl group over hydrogenation of the carbonyl group of at least 80%.

16. The method of claim 14, wherein the electrochemical reduction has an absolute selectivity for the hydrogenolysis of the carbonyl group of at least 50%.

17. The method of claim 12, wherein electrochemical reduction has a Faradaic efficiency for the hydrogenolysis of the carbonyl group of at least 20%.

18. The method of claim 17, wherein the catholyte solution is an aqueous solution having a pH of 2 or less.

19. The method of claim 18, wherein the electrochemical reduction has an absolute selectivity for the hydrogenolysis of the carbonyl group of at least 50%.

20. The method of claim 2, wherein the at least one aryl-aldehyde or the at least one aryl-ketone comprises a phenyl ring directly bonded to a carbonyl carbon of the aryl-aldehyde or the aryl-ketone.

21. The method of claim 1, wherein the catholyte solution further comprises water.

22. The method of claim 1, one or more carbonyl compounds selected from aryl-aldehydes, aryl-ketones, alkyl-aldehydes, alkyl-ketones, or a combination thereof, and an acid, wherein at least one of the one or more carbonyl compounds is not an aryl-aldehyde in which a carbonyl carbon is directly bonded to a furan ring makes up at least 50 mol. % of aromatic compounds present in the catholyte solution prior to the application of the potential difference.

23. The method of claim 1, one or more carbonyl compounds selected from aryl-aldehydes, aryl-ketones, alkyl-aldehydes, alkyl-ketones, or a combination thereof, and an acid, wherein at least one of the one or more carbonyl compounds is not an aryl-aldehyde in which a carbonyl carbon is directly bonded to a furan ring are not derived from lignocellulosic biomass.

24. The method of claim 23, one or more carbonyl compounds selected from aryl-aldehydes, aryl-ketones, alkyl-aldehydes, alkyl-ketones, or a combination thereof, and an acid, wherein at least one of the one or more carbonyl compounds is not an aryl-aldehyde in which a carbonyl carbon is directly bonded to a furan ring comprise p-anisaldehyde, 4-acetamido benzaldehyde, 4-acetoxybenzaldehyde, p-tolualdehyde, benzaldehyde, acetophenone, 4-hydroxyphenylacetone, or 3-(3-(trifluoromethyl)phenyl) propanal.

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