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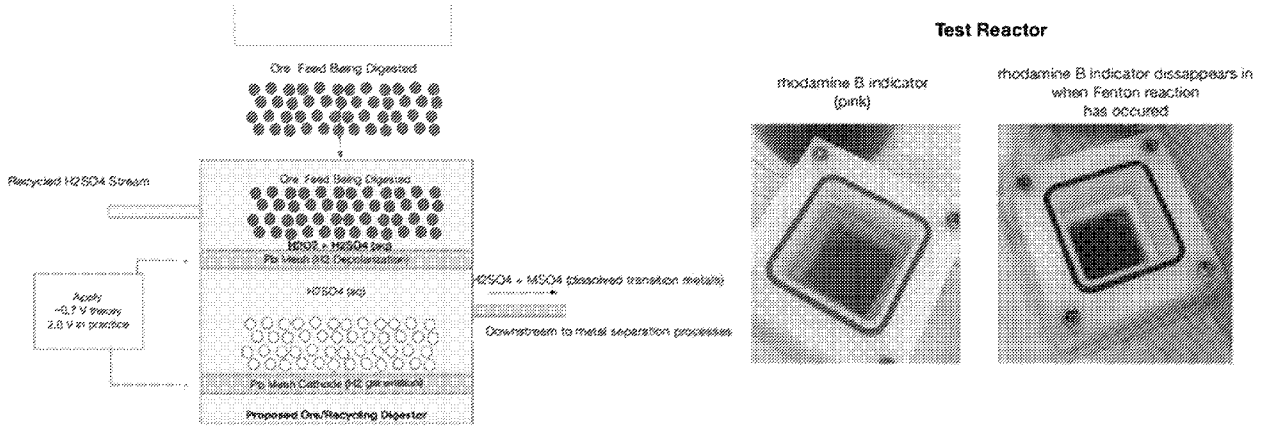

FIG. 1

(57) Abstract: A method, comprising: in the presence of an acid, applying a current between a first electrode and a second electrode so as to form an amount of hydrogen peroxide in situ so as to give rise to a digesting solution that comprises hydrogen peroxide and the acid; contacting the digesting solution and a metallic composition comprising a metal so as dissolve at least some of the metal comprised in the metallic composition, the metal optionally being a transition metal; and collecting at least some of the metal dissolved from the metallic composition. A system, comprising: a container; a first electrode and a second electrode, the first electrode and the second electrode being disposed within the container, at least one of the first electrode and the second electrode comprising PbO_2; and an amount of acid disposed in the container.

[Continued on next page]

WO 2025/029646 A1

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IN SITU ELECTROCHEMICAL HYDROGEN PEROXIDE GENERATION FOR HYDROMETALLURGICAL LITHIUM-ION BATTERY RECYCLING

RELATED APPLICATIONS

[0001] The present application claims priority to and the benefit of United States patent application no. 63/516,313, "In Situ Electrochemical Hydrogen Peroxide Generation For Hydrometallurgical Lithium-Ion Battery Recycling" (filed July 28, 2023). All foregoing applications are incorporated herein by reference in their entireties for any and all purposes.

TECHNICAL FIELD

[0002] The present disclosure relates to the field of hydrometallurgical recycling.

BACKGROUND

[0003] Engineered materials, from steel to semiconductors to battery active components, can begin with either minerals extracted from the Earth or recycled inputs from end-of-life (EOL) devices. Both classes of input material must be separated and purified to standards for the given application. Structural metals generally require less than 100 PPM of unintended dopants, and semiconductor and battery materials require under 1 PPM of labile impurities. Mineral extraction and recycling processes evolved over millennia to achieve these goals, and the convergence of climate, societal and economic concerns now warrants reducing the environmental impact of extraction and recycling while reducing cost.

[0004] Mineral refinement is a subset of the field of separation, where the atoms to be separated start in the solid phase. Ores (from the earth) and weathered engineered materials – such as scrap) – are typically oxidized, which can be in the form of metal oxides, metal sulfates, metal phosphates, or metal sulfides, as examples. The first order of refinement can be, in some instances, be to separate oxygen and sulfur species from the metal ion.

[0005] Pyrometallurgy ("pyro") is perhaps the oldest refinement strategy and is still the most common. Pyro involves heating a material to trigger thermally driven decomposition and separation, often aided by a reducing or oxidizing species to accelerate the process. Fe_2O_3 (s) reduction to Fe (s) is perhaps the most famous and ubiquitous pyro process, producing 2 GT of iron for steel every year worldwide. Pyro processes are still standard for battery

production in some geographies because of the processes' low cost, but these costs do not always fully account for environmental damage.

[0006] Hydrometallurgy involves using a caustic solvent – which can be H_2SO_4 (aq) – to dissolve oxidized species with an added oxidizing or reducing agent. For example, in copper extraction, H_2SO_4 interacts with naturally present acid-stable bacteria to trigger natural Fe^{2+}/Fe^{3+} oxidation-reduction cycles that greatly accelerate ore dissolution. But even with acceleration, the residence times for these processes can be on the order of 90 days, which means that leaching occupies a significant land area exposed to highly corrosive solvents for long periods. Accordingly, there is a long-felt need in the field for improved processing methods.

SUMMARY

[0007] So-called "overclocking" dissolution via aggressive chemistry is a relatively nascent approach at scale. A formula useful to accelerate dissolution is the combination of H_2SO_4 (aq) and H_2O_2 (aq) (dubbed "piranha" because it "eats everything"). Piranha solution is the "reference standard" for black mass digestion in battery recycling. While its use began because H_2SO_4 (aq) is known to dissolve oxides, and in combination with H_2O_2 (aq), the foregoing is also a known organic digester, and the combination also digested oxide materials at a higher rate than H_2SO_4 (aq) alone. H_2O_2 (aq), in the presence of ions in a solution capable of multiple valences, can form the exceptionally oxidizing $OH\cdot$ radical via the Fenton and Fenton-like reactions.

[0008] The Fenton reaction is a reaction where H_2O_2 (aq) combines with a small amount of iron (<100 ppm) in solution to produce $OH\cdot$ radicals. $OH\cdot$ radicals are exceptional oxidizers, second only to pure F_2 (g) amongst earth-abundant reagents. Unlike halides and halogens, when $OH\cdot$ reacts, it forms OH^- and then quickly combines with free protons in acid to form H_2O. Fenton reaction loops are genuinely green reagents, as the only byproduct is water. As an example, the textile industry uses the reaction to both bleach clothing and remove organic stains.

[0009] There are several ways to introduce H_2O_2 (g) into the Fenton reaction. The electro-Fenton process produces H_2O_2 by first using a depolarized electrolysis unit to produce H_2 and O_2 on demand from clean water, then recombining to form H_2O_2 (aq), finally feeding the H_2O_2 to an iron-bearing stream. In a depolarized H_2O_2 (aq) generator, H_2 (g) is formed at

the cathode and allowed to migrate to the anode, where it interrupts O_2 (g) formation, instead forming H_2O_2 (aq). Alternatively, O_2 (g) generated at the anode can be depolarized at the cathode for the same effect.

[0010] Generally, the H_2O_2 is generated separately from the iron-bearing stream as the H_2O_2 would be converted instantly to $OH\cdot$. In standard electro-Fenton processes, instant radical formation can have two adverse outcomes:

[0011] - The $OH\cdot$ does not last long enough to attack the organics and materials of choice

[0012] - The $OH\cdot$ attacks the fragile organic membranes and precious metal catalysts of the electrolyzer.

[0013] While iron is the typical homogenous catalyst for the Fenton and electro-Fenton processes, one can use "Fenton-like" transition metal catalysts such as Ni, Mn, Co, and others that have similar (if not as facile) production of $OH\cdot$ in the presence of H_2O_2. While Fe^{2+} is a suitable catalyst for Fenton reactions, Fe^{2+} is also but one option for such reactions. In recycling and pure mineral digestion, the quantities of H_2O_2 (g) required are ultimately not economical, and standard production routes of H_2O_2 are carbon intensive. Further, transport and mixing in piranha can be dangerous. Accordingly, there is a long-felt need in the art for improved methods of forming piranha solution as well as improved methods for hydrometallurgical recycling. In particular, existing hydrometallurgical recycling of lithium-ion batteries typically occurs under acidic, oxidative conditions using sulfuric acid and hydrogen peroxide reagents. These reagents are classified as oxidizers by the Occupational Safety and Health Administration, subject to unique transportation regulations.

[0014] In meeting the described needs, the disclosed technology provides, inter alia, an in-situ method to generate hydrogen peroxide in the extraction process of spent batteries using electrochemical methods. The peroxide can be produced, for example, via Pb high-surface area mesh electrodes in the greywater of the leaching reactor, using – for example – 200 mA/cm^2 of current densities and overpotentials of < 5V. Compared to existing technologies, these electrodes are comparatively stable in the impurity-laden graywater generally present during the leaching of spent batteries. Additionally, current systems require special reactors and apparatuses to maintain peroxide production, while this technology allows for H_2O_2 production modulation by tuning the current density and applied voltage.

This technology has numerous applications, namely in mineral and rare element recovery, recycling of batteries, and also mining hydrometallurgical processes.

[0015] In one aspect, the present disclosure provides a method, comprising: in the presence of an acid, applying a current between a first electrode and a second electrode so as to form an amount of hydrogen peroxide in situ so as to give rise to a digesting solution that comprises hydrogen peroxide and the acid; contacting the digesting solution and a metallic composition comprising a metal so as dissolve at least some of the metal comprised in the metallic composition, the metal optionally being a transition metal; and collecting at least some of the metal dissolved from the metallic composition.

[0016] Also provided is a system, comprising: a container; a first electrode and a second electrode, the first electrode and the second electrode being disposed within the container, at least one of the first electrode and the second electrode comprising PbO_2; and an amount of acid disposed in the container.

[0017] Further provided is a method, comprising: forming hydrogen peroxide in situ and contacting the hydrogen peroxide and an acid to form a digesting solution; contacting the digesting solution and a metallic composition that comprises a metal so as to dissolve the metal, the metal optionally being a transition metal; and collecting at least some of the dissolved metal.

BRIEF DESCRIPTION OF THE DRAWINGS

[0018] In the drawings, which are not necessarily drawn to scale, like numerals may describe similar components in different views. Like numerals having different letter suffixes may represent different instances of similar components. The drawings illustrate generally, by way of example, but not by way of limitation, various aspects discussed in the present document. In the drawings:

[0019] FIG. 1. Left, exemplary of operation of the disclosed technology. Right, an example of the successful production of piranha on demand in an example reactor via the consumption of H_2O_2 in 1 M H_2SO_4 (aq) / 0.1 M $FeSO_4$ (aq).

[0020] FIG. 2. Left, digesting $LiNi_{0.8}Mn_{0.1}Co_{0.1}O_2$ in 8M H_2SO_4 (aq). Note that digestion is incomplete after 24 hours. Right, the same battery sample in 2M H_2SO_4 (aq) + 14% H_2O_2 (aq); digestion complete in less than 1 hour.

[0021] FIG. 3 provides experimental results showing generation and consumption of hydrogen peroxide according to the disclosed technology (left) and an example system according to the present disclosure (right).

[0022] FIG. 4 provides example results from a system according to the present disclosure in which the nickel manganese cobalt (NMC) powder being processed is in contact with one of the Pb electrodes of the system.

[0023] FIG. 5 provides example results from a system according to the present disclosure in which the NMC powder being processed is in contact with one of the Pb electrodes of the system and a separator is disposed between the two electrodes of the system.

[0024] FIG. 6 provides example results from a system according to the present disclosure in which the NMC powder being processed is separated from the Pb electrodes of the system and a separator also is disposed between the two electrodes of the system.

DETAILED DESCRIPTION OF ILLUSTRATIVE EMBODIMENTS

[0025] The present disclosure may be understood more readily by reference to the following detailed description of desired embodiments and the examples included therein.

[0026] Unless otherwise defined, all technical and scientific terms used herein have the same meaning as commonly understood by one of ordinary skill in the art. In case of conflict, the present document, including definitions, will control. Preferred methods and materials are described below, although methods and materials similar or equivalent to those described herein can be used in practice or testing. All publications, patent applications, patents and other references mentioned herein are incorporated by reference in their entirety. The materials, methods, and examples disclosed herein are illustrative only and not intended to be limiting.

[0027] The singular forms “a,” “an,” and “the” include plural referents unless the context clearly dictates otherwise.

[0028] As used in the specification and in the claims, the term "comprising" can include the embodiments "consisting of" and "consisting essentially of." The terms “comprise(s),” “include(s),” “having,” “has,” “can,” “contain(s),” and variants thereof, as used herein, are intended to be open-ended transitional phrases, terms, or words that require the presence of the named ingredients/steps and permit the presence of other ingredients/steps. However, such description should be construed as also describing

compositions or processes as "consisting of" and "consisting essentially of" the enumerated ingredients/steps, which allows the presence of only the named ingredients/steps, along with any impurities that might result therefrom, and excludes other ingredients/steps.

[0029] As used herein, the terms "about" and "at or about" mean that the amount or value in question can be the value designated some other value approximately or about the same. It is generally understood, as used herein, that it is the nominal value indicated ±10% variation unless otherwise indicated or inferred. The term is intended to convey that similar values promote equivalent results or effects recited in the claims. That is, it is understood that amounts, sizes, formulations, parameters, and other quantities and characteristics are not and need not be exact, but can be approximate and/or larger or smaller, as desired, reflecting tolerances, conversion factors, rounding off, measurement error and the like, and other factors known to those of skill in the art. In general, an amount, size, formulation, parameter or other quantity or characteristic is "about" or "approximate" whether or not expressly stated to be such. It is understood that where "about" is used before a quantitative value, the parameter also includes the specific quantitative value itself, unless specifically stated otherwise.

[0030] Unless indicated to the contrary, the numerical values should be understood to include numerical values which are the same when reduced to the same number of significant figures and numerical values which differ from the stated value by less than the experimental error of conventional measurement technique of the type described in the present application to determine the value.

[0031] All ranges disclosed herein are inclusive of the recited endpoint and independently of the endpoints. The endpoints of the ranges and any values disclosed herein are not limited to the precise range or value; they are sufficiently imprecise to include values approximating these ranges and/or values.

[0032] As used herein, approximating language can be applied to modify any quantitative representation that can vary without resulting in a change in the basic function to which it is related. Accordingly, a value modified by a term or terms, such as "about" and "substantially," may not be limited to the precise value specified, in some cases. In at least some instances, the approximating language can correspond to the precision of an instrument for measuring the value. The modifier "about" should also be considered as disclosing the range defined by the absolute values of the two endpoints. For example, the expression "from about 2 to about 4" also discloses the range "from 2 to 4." The term "about" can refer

to plus or minus 10% of the indicated number. For example, "about 10%" can indicate a range of 9% to 11%, and "about 1" can mean from 0.9-1.1. Other meanings of "about" can be apparent from the context, such as rounding off, so, for example "about 1" can also mean from 0.5 to 1.4. Further, the term "comprising" should be understood as having its open-ended meaning of "including," but the term also includes the closed meaning of the term "consisting." For example, a composition that comprises components A and B can be a composition that includes A, B, and other components, but can also be a composition made of A and B only. Any documents cited herein are incorporated by reference in their entireties for any and all purposes.

[0033] Any embodiment or aspect provided herein is illustrative only and does not limit the scope of the present disclosure or the appended claims. Any part or parts of any one or more embodiments of aspects can be combined with any part or parts of any one or more other embodiments or aspects.

[0034] In the presence of a mild-to-strong acid (for example, H_2SO_4) solution, one can generate H_2O_2 (aq) with an electro-Fenton-like process in the presence of Fe^{2+} ions and other battery-relevant transition metals without destroying the reactor components and dissolve refractory species of choice (e.g., battery cathodes and ores). The Fe^{2+} ions can be present

[0035] Pb (s) is mainly insoluble in H_2SO_4 (for example, < 3 PPM @ 60°C) under oxidizing conditions, where it forms a dense film of PbO_2 rather than dissolving. The reduction of PbO_2 (s) in the presence of H_2SO_4 (aq) produces $PbSO_4$ (s). Without being bound to any particular theory or embodiment, failure of PbO_2 electrodes is due not to chemical dissolution but rather to mechanical shedding.

[0036] $PbSO_4$ (s) is prevented upon reduction of PbO_2 (s) in the presence of redox able ions such as Fe^{2+}/Fe^{3+} and, for example, Ni^{3+}/Ni^{4+}, $Mn^{2+}/Mn^{3+}/Mn^{4+}$, and Co^{3+}/Co^{4+}. Without being bound to any particular theory or embodiment, this means that Fenton active components, in the presence of PbO_2 (s), stabilize PbO_2 (s) against $PbSO_4$ (s) shedding while forming rock-digesting radical $OH^{\cdot}$. FIG. 1 provides a reactor design (left) and also indication the reactor has produced piranha (right).

[0037] The symbiotic stabilization of PbO_2 (s) electrodes in the presence of battery ions allows us the ability to create H_2O_2 (aq) in a reactor with H_2SO_4 (aq) on demand, where the battery metal ion itself is the Fenton and Fenton-like catalyst. The production of H_2O_2

(aq) in the presence of these ions leads to $OH^{\cdot}$, which in turn accelerates the dissolution of the input mass; the input mass can be, for example, ore or scrap battery cathode material.

[0038] In illustrative experiments, for over 100 hours of operating a process according to the present disclosure, there was:

[0039] - No Pb (aq) detectable in solution (meaning PbO_2 (s) is neither dissolving nor exfoliating)

[0040] - Apparent dissolution of Ni, Co, and Mn from the active materials when the reactor is "on."

[0041] - Minor dissolution of Ni, Co, and Mn when the reactor is off

[0042] Without being bound to any particular theory, the foregoing can be understood to indicate that one can dissolve input material via an electro-Fenton-like generated radical attack. The disclosed process thus has a range of applications, including, for example, green ore and scrap digestion at scale.

[0043] In particular, it has been shown that the disclosed process can produce meaningful quantities of H_2O_2 (aq) in the presence of PbO_2, standard leaching acids (i.e. H_2SO_4), and transition metal battery materials; this is shown in FIG. 1.

[0044] As shown, using standard piranha, one can dissolve ores and battery black-mass at competitive rates; such rates can be on the order of minutes or hours instead of on the order of days or weeks (FIG. 2). This digestion can be executed in a reaction without chemical separation membranes.

[0045] Greywater Looping

[0046] Current processes for mining minerals and recycling batteries are water-intensive. Leach pits lose significant amounts of water to evaporation, and external H_2O_2 / H_2SO_4 mixtures require DI clean water. The disclosed process reduces residence time from months to hours (or better) and does not require clean water, as the process can operate in greywater.

[0047] Additive Reagents

[0048] Unlike the traditional piranha process, the disclosed process can produce H_2O_2 within the digestion reactor with electricity. This reduces upstream greenhouse gas (GHG) emissions associated with H_2O_2 production as well as safety challenges in transporting and mixing piranha solution. Because one can use the transition metal ions as

Fenton and Fenton-like catalysts, one need not necessarily add or filter other metal contaminants.

[0049] Operational Cost

[0050] The disclosed process can be performed without one or both of membranes and precious metal catalysts. Instead, the operating input can be the electricity that drives the H_2O_2 (aq) formation. Thus, the disclosed technology can compete with or even surpass the operating expense advantage of equivalent pyro processes.

[0051] Aspects

[0052] The following Aspects are illustrative only and do not limit the scope of the present disclosure or the appended claims. Any part or parts of any one or more Aspects can be combined with any part or parts of any one or more other Aspects.

[0053] Aspect 1. A method, comprising: in the presence of an acid, applying a current between a first electrode and a second electrode so as to form an amount of hydrogen peroxide *in situ* so as to give rise to a digesting solution that comprises hydrogen peroxide and the acid; contacting the digesting solution and a metallic composition comprising a metal so as dissolve at least some of the metal comprised in the metallic composition, the metal optionally being a transition metal; and collecting at least some of the metal dissolved from the metallic composition. The digesting solution can, for example, be formed in the presence of the metallic composition.

[0054] Sulfuric acid is considered a particularly suitable acid for the disclosed technology. It should be understood, however, that the disclosed technology can operate using acids other than sulfuric acid. For example, any one or more of hydrochloric, hydrobromic, hydroiodic, perchloric, chloric, sulfuric, and nitric acid can be used.

[0055] Aspect 2. The method of Aspect 1, wherein at least one of the first electrode and the second electrode comprises PbO_2. As described herein, Pb-containing electrodes are considered especially suitable, but also are not required.

[0056] Aspect 3. The method of any one of Aspects 1-2, wherein the acid comprises sulfuric acid. As described elsewhere herein, sulfuric acid is considered a particularly suitable acid, but it should be understood, however, that the disclosed technology can operate using acids other than sulfuric acid. For example, any one or more of hydrochloric, hydrobromic, hydroiodic, perchloric, chloric, sulfuric, and nitric acid can be used.

[0057] Aspect 4. The method of any one of Aspects 1-3, wherein the metal comprises any one or more of nickel, manganese, and cobalt. The foregoing listing is not exhaustive, however, and iron can also be used in some embodiments. It should be understood that any one or more of Fe^{2+}/Fe^{3+}, Ni^{3+}/Ni^{4+}, $Mn^{2+}/Mn^{3+}/Mn^{4+}$, and Co^{3+}/Co^{4+} ions can be present. Such ions can be present in the metallic composition; such ions can also be provided separately.

[0058] Aspect 5. The method of any one of Aspects 1-4, further comprising collecting the metallic composition from a battery. The collecting can be accomplished by, for example, harvesting the metallic composition from used batteries.

[0059] Aspect 6. The method of any one of Aspects 1-5, wherein fluid motion is restricted (i) between the metallic composition and one of the first and second electrodes, (ii) between the first and second electrodes, or both (i) and (ii). Fluid motion can be restricted by, for example, a pervious medium – such as a membrane – or other fluid restrictor.

[0060] Aspect 7. The method of Aspect 6, wherein a pervious medium restricts the fluid motion. Such a medium can be a membrane, filter paper, a mat, a wool, and the like.

[0061] Aspect 8. The method of any one of Aspects 1-7, wherein the method is performed under such conditions that the first and second electrodes remain essentially structurally intact during performance of the method.

[0062] Aspect 9. The method of any one of Aspects 1-8, wherein the method is performed in a continuous manner.

[0063] Aspect 10. A system, comprising: a container; a first electrode and a second electrode, the first electrode and the second electrode being disposed within the container, at least one of the first electrode and the second electrode comprising PbO_2; and an amount of acid disposed in the container.

[0064] Aspect 11. The system of Aspect 10, wherein the acid comprises sulfuric acid.

[0065] Aspect 12. The system of any one of Aspects 10-11, further comprising an amount of a metallic composition disposed in the container. The metallic composition can be comprised in a feed to the system; such a feed can be an ore, scrap, battery parts, and the like. The metallic composition can also be present within the system, for example as a metal that is present or otherwise pre-loaded in the system.

[0066] Aspect 13. The system of Aspect 12, wherein the metallic composition comprises a transition metal.

[0067] Aspect 14. The system of any one of Aspects 12-13, further comprising a pervious medium (i) between the metallic composition and one of the first and second electrodes, (ii) between the first and second electrodes, or both (i) and (ii). Pervious media are described elsewhere herein; such media can be, for example, membranes, filter paper, mats, wools, and the like. Such a medium can be porous, fibrous, and the like.

[0068] Aspect 15. The system of any one of Aspects 10-14, further comprising an outlet for communicating dissolved material evolved in the container. The outlet can be in fluid communication with a metal separation location; metal separation can be performed according to methods known in the art.

[0069] Aspect 16. A method, comprising: forming hydrogen peroxide *in situ* and contacting the hydrogen peroxide and an acid to form a digesting solution; contacting the digesting solution and a metallic composition that comprises a metal so as to dissolve the metal, the metal optionally being a transition metal; and collecting at least some of the dissolved metal.

[0070] Aspect 17. The method of Aspect 16, wherein the digesting solution is free or essentially free of exogenous hydrogen peroxide. This is not, however, a requirement. The digesting solution can include the hydrogen peroxide formed in situ as well as hydrogen peroxide that occurs naturally in the solution.

[0071] Aspect 18. The method of any one of Aspects 16-17, wherein forming the hydrogen peroxide *in situ* is effected electrochemically by applying a current between first and second electrodes, the first and second electrodes comprising PbO_2.

[0072] Aspect 19. The method of any one of Aspects 16-18, wherein the metallic composition is obtained from a battery. The metal can be, for example, any one or more of nickel, manganese, and cobalt.

[0073] Aspect 20. The method of any one of Aspects 16-19, wherein the dissolved metal comprises any one or more of nickel, manganese, and cobalt.

[0074] FIG. 1 provides an example depiction of the disclosed technology. As shown in the left panel of FIG. 1, the disclosed technology can include providing a feed – such as an ore, battery components, and the like – to a reactor. The reactor can include a region in which the feed is contact with a digesting solution, for example, piranha solution.

The hydrogen peroxide can, as described, be formed in situ. In this way, one can form the digesting solution in situ without the need to transport the hydrogen peroxide to the use location.

[0075] As shown, the reactor can include electrodes; an electrode can be present as a mesh or in other pervious form, although this is not a requirement. An electrode can comprise PbO_2; in some embodiments, an electrode can consist of PbO_2. A potential can be applied to the electrodes; such a potential can be, for example, from -5 V to 5 V, for example from -0.8 V to 2 V. Metal dissolved from the feed can be communicated from the reactor for further processing; as shown in FIG. 1, dissolved metal (M) from the feed can be communicated from the reactor for further processing, such as for metal separation. Also as shown, acid – which can be recycled acid – can be provided to the reactor. Such recycled acid can be separated from the metal/acid solution that is communicated from the reactor for further processing.

[0076] The reactor can have present a metal – for example, any one or more of Fe, Ni, Li, Mn, and Co – that supports production of $OH\cdot$ in the presence of H_2O_2. Such a metal can be present within the reactor; such a metal can also be comprised in the feed to the reactor. The reactor can, as described, be operated to form H_2O_2 in situ and then form $OH\cdot$ from the H_2O_2 in the presence of acid, thereby facilitating the extraction of metals – such as transition metals – from the feed to the reactor. As described, H_2O_2 can be produced from fresh water fed to the reactor, but the H_2O_2 can also be produced from greywater, for example the greywater that results during the leaching of spent batteries. H_2O_2 can also be produced from a carrier fluid – such as greywater or other fluid – that carries the feed into the reactor. A reactor can be operated in a batch mode, a semi-batch mode, or even in a continuous mode.

[0077] Although FIG. 1 depicts the presence of Pb electrodes, it should be understood that this is exemplary only and that other materials besides Pb can be used. Similarly, although FIG. 1 depicts the use of sulfuric acid, other acids can be used with and/or in place of sulfuric acid, as it is not a requirement that sulfuric acid be present.

[0078] FIG. 2. Left, digesting $LiNi_{0.8}Mn_{0.1}Co_{0.1}O_2$ in 8M H_2SO_4 (aq). Note that digestion is incomplete after 24 hours. Right, the same battery sample in 2M H_2SO_4 (aq) + 14% H_2O_2 (aq); digestion complete in less than 1 hour.

[0079] FIG. 3 provides experimental results showing generation and consumption of hydrogen peroxide according to the disclosed technology (left) and an example system

according to the present disclosure (right). Ass shown, Rhodamine B – or other indicator – can be used to monitor generation and consumption of H_2O_2.

[0080] FIG. 4 provides example results from a system according to the present disclosure in which the nickel manganese cobalt (NMC) powder being processed is in contact with one of the PbO_2 electrodes of the system. As shown, a stirrer or other agitator can be present to facilitate system operation.

[0081] FIG. 5 provides example results from a system according to the present disclosure in which the NMC powder being processed is in contact with one of the electrodes of the system and a separator is disposed between the two electrodes of the system. Such a separator can be pervious; as an example, such a separator can be filter paper or other pervious separator. Without being bound to any particular theory or embodiment, the presence of a separator can reduce the overpotential, particularly when the separator is present between electrodes.

[0082] FIG. 6 provides example results from a system according to the present disclosure in which the NMC powder being processed is separated from the electrodes of the system and a separator also is disposed between the two electrodes of the system. Without being bound to any particular theory or embodiment, the presence of a separator can reduce the overpotential, particularly when the separator is present between electrodes and when the separator is present between the feed material and an electrode, as shown in FIG. 6.

[0083] References

[0084] 1. Dutta T, Kim K-H, Uchimiya M, Kwon EE, Jeon B-H, Deep A, Yun S-T (2016) Global demand for rare earth resources and strategies for green mining. Environmental research, 150:182–190. https://doi.org/10.1016/j.envres.2016.05.052

[0085] 2. Schlesinger M, King M, Sole K, Davenport W (2011) Extractive Metallurgy of Copper. https://doi.org/10.1016/C2010-0-64841-3

[0086] 3. Gielen D, Saygin D, Taibi E, Birat J-P (2020) Renewables-based decarbonization and relocation of iron and steel making: A case study. Journal of Industrial Ecology, 24(5):1113–1125. https://doi.org/10.1111/jiec.12997

[0087] 4. Schmidt HG (2022) Safe Piranhas: A Review of Methods and Protocols. ACS Chemical Health & Safety, 29(1):54–61. https://doi.org/10.1021/acs.chas.1c00094

[0088] 5. Mauriz E, Calle A, Montoya A, Lechuga LM (2006) Determination of environmental organic pollutants with a portable optical immunosensor. Talanta, 69(2):359–364. https://doi.org/10.1016/j.talanta.2005.09.049

[0089] 6. Gaines L, Richa K, Spangenberger J (2018) Key issues for Li-ion battery recycling. MRS Energy & Sustainability, 5:E14. https://doi.org/10.1557/mre.2018.13

[0090] 7. Jung YS, Lim WT, Park J-Y, Kim Y-H (2009) Effect of pH on Fenton and Fenton-like oxidation. Environmental technology, 30(2):183–190. https://doi.org/10.1080/09593330802468848

[0091] 8. Babuponnusami A, Muthukumar K (2014) A review on Fenton and improvements to the Fenton process for wastewater treatment. Journal of Environmental Chemical Engineering, 2(1):557–572. https://doi.org/10.1016/j.jece.2013.10.011

[0092] 9. Seo DC, Jeon I, Jeong ES, Jho JY (2020) Mechanical Properties and Chemical Durability of Nafion/Sulfonated Graphene Oxide/Cerium Oxide Composite Membranes for Fuel-Cell Applications. Polymers, 12(6)https://doi.org/10.3390/polym12061375

[0093] 10. Wang N, Zheng T, Zhang G, Wang P (2016) A review on Fenton-like processes for organic wastewater treatment. Journal of Environmental Chemical Engineering, 4(1):762–787. https://doi.org/10.1016/j.jece.2015.12.016

[0094] 11. Kołodziej B, Adamski Z (1985) Effect of manganese (II) added to the electrolyte on the properties of lead anodes used in oxidation of ferrous sulphate to ferric sulphate. Journal of Applied Electrochemistry, 15(5):705–710. https://doi.org/10.1007/BF00620566

What is Claimed:

1. A method, comprising:

   in the presence of an acid, applying a current between a first electrode and a second electrode so as to form an amount of hydrogen peroxide *in situ* so as to give rise to a digesting solution that comprises hydrogen peroxide and the acid;

   contacting the digesting solution and a metallic composition comprising a metal so as dissolve at least some of the metal comprised in the metallic composition, the metal optionally being a transition metal; and

   collecting at least some of the metal dissolved from the metallic composition.

2. The method of claim 1, wherein at least one of the first electrode and the second electrode comprises PbO_2.

3. The method of any one of claims 1-2, wherein the acid comprises sulfuric acid.

4. The method of any one of claims 1-2, wherein the metal comprises any one or more of nickel, manganese, and cobalt.

5. The method of any one of claims 1-2, further comprising collecting the metallic composition from a battery.

6. The method of any one of claims 1-2, wherein fluid motion is restricted (i) between the metallic composition and one of the first and second electrodes, (ii) between the first and second electrodes, or both (i) and (ii).

7. The method of claim 6, wherein a pervious medium restricts the fluid motion.

8. The method of any one of claims 1-2, wherein the method is performed under such conditions that the first and second electrodes remain essentially structurally intact during performance of the method.

9. The method of any one of claims 1-2, wherein the method is performed in a continuous manner.

10. A system, comprising:

a container;

a first electrode and a second electrode,

the first electrode and the second electrode being disposed within the container,

at least one of the first electrode and the second electrode comprising PbO_2; and

an amount of acid disposed in the container.

11. The system of claim 10, wherein the acid comprises sulfuric acid.

12. The system of any one of claims 10-11, further comprising an amount of a metallic composition disposed in the container.

13. The system of claim 12, wherein the metallic composition comprises a transition metal.

14. The system of claim 12, further comprising a pervious medium (i) between the metallic composition and one of the first and second electrodes, (ii) between the first and second electrodes, or both (i) and (ii).

15. The system of any one of claims 10-11, further comprising an outlet for communicating dissolved material evolved in the container.

16. A method, comprising:

forming hydrogen peroxide *in situ* and contacting the hydrogen peroxide and an acid to form a digesting solution;

contacting the digesting solution and a metallic composition that comprises a metal so as to dissolve the metal, the metal optionally being a transition metal; and

collecting at least some of the dissolved metal.

17. The method of claim 16, wherein the digesting solution is free or essentially free of exogenous hydrogen peroxide.

18. The method of any one of claims 16-17, wherein forming the hydrogen peroxide *in situ* is effected electrochemically by applying a current between first and second electrodes, the first and second electrodes comprising PbO_2.

19. The method of any one of claims 16-17, wherein the metallic composition is obtained from a battery.

20. The method of any one of claims 16-17, wherein the dissolved metal comprises any one or more of nickel, manganese, and cobalt.

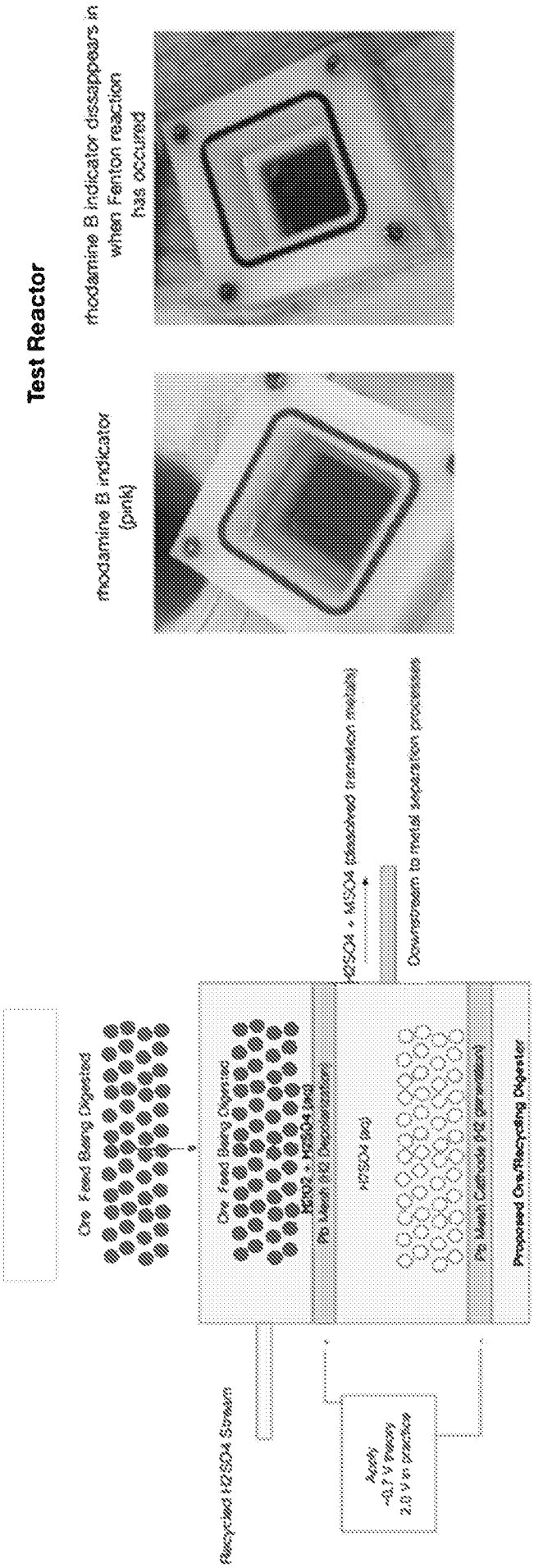

Test Reactor
rhodamine B indicator (pink)
rhodamine B indicator dissappears in when Fenton reaction has occured
Ore Feed Barrel Digested
Ore Feed Barrel Digested
Recycled H2SO4 Stream
Downstream to metal separation processes
Proposed Ore/Recycling Digester

FIG. 1

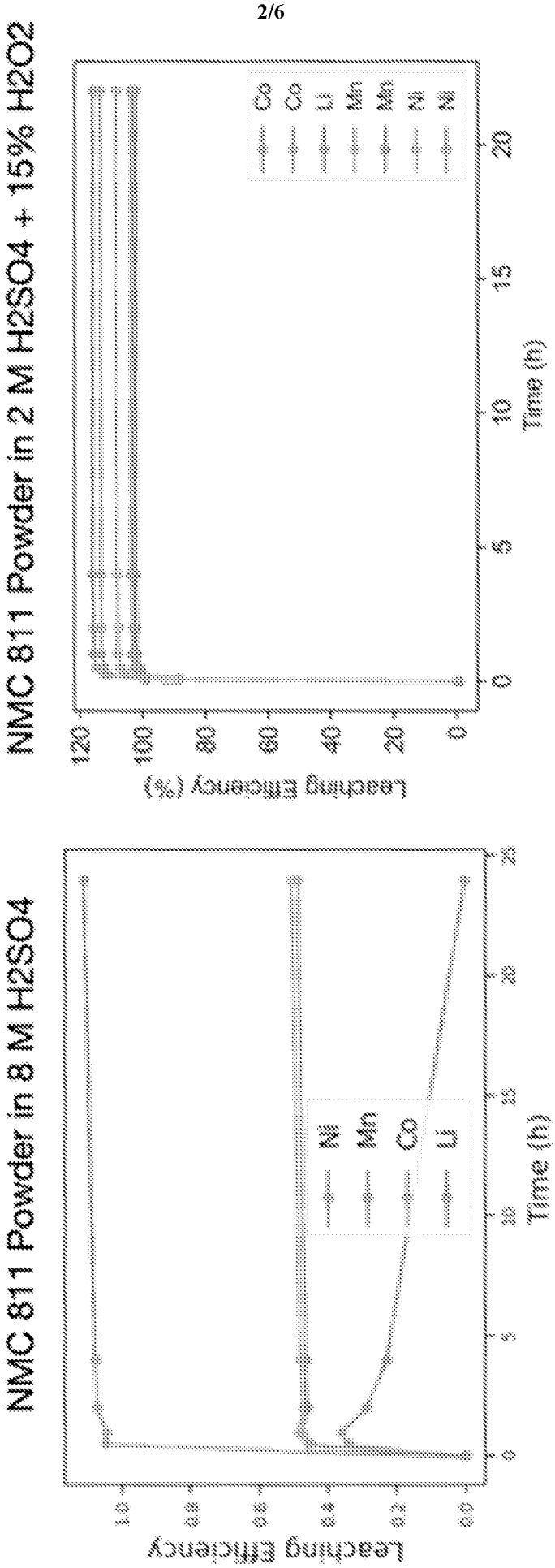
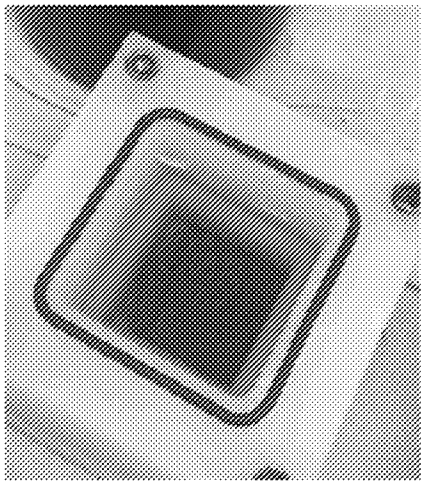
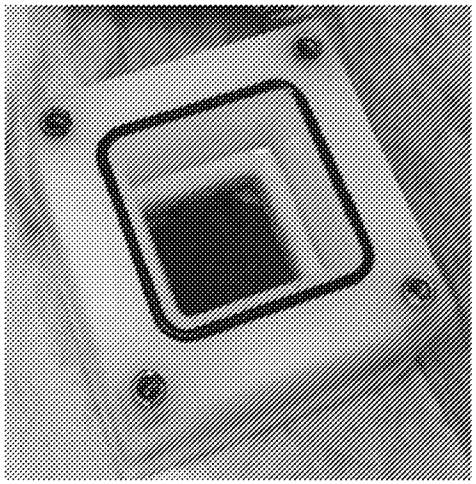

NMC 811 Powder in 2 M H2SO4 + 15% H2O2
Leaching Efficiency (%)
Time (h)
Co
Li
Mn
Ni
NMC 811 Powder in 8 M H2SO4
Leaching Efficiency
Time (h)
Ni
Mn
Co
Li

FIG. 2

In situ electrochemical generation of hydrogen peroxide

- Initial titration experiments using Rhodamine B indicator show generation and consumption of H2O2 (color disappears)





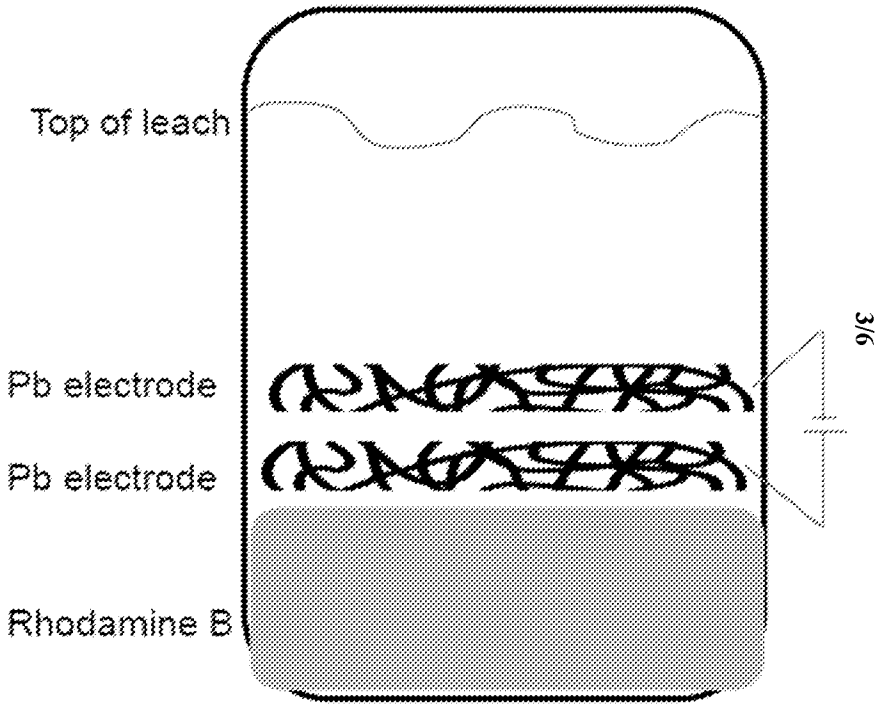


FIG. 3

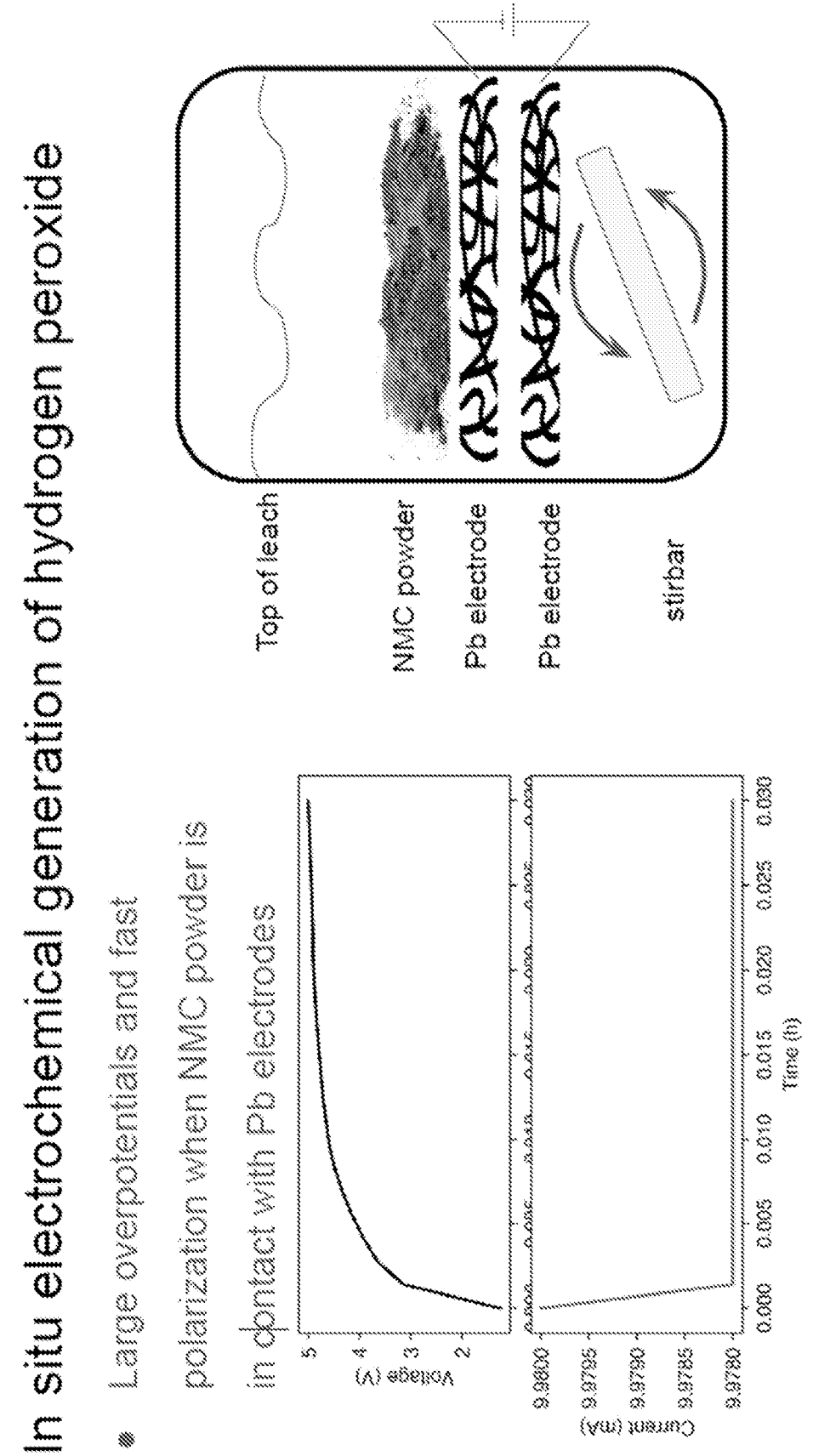

In situ electrochemical generation of hydrogen peroxide
Large overpotentials and fast
polarization when NMC powder is
in contact with Pb electrodes
Top of leach
NMC powder
Pb electrode
Pb electrode
stirbar
Voltage (V)
Current (mA)
Time (h)

FIG. 4

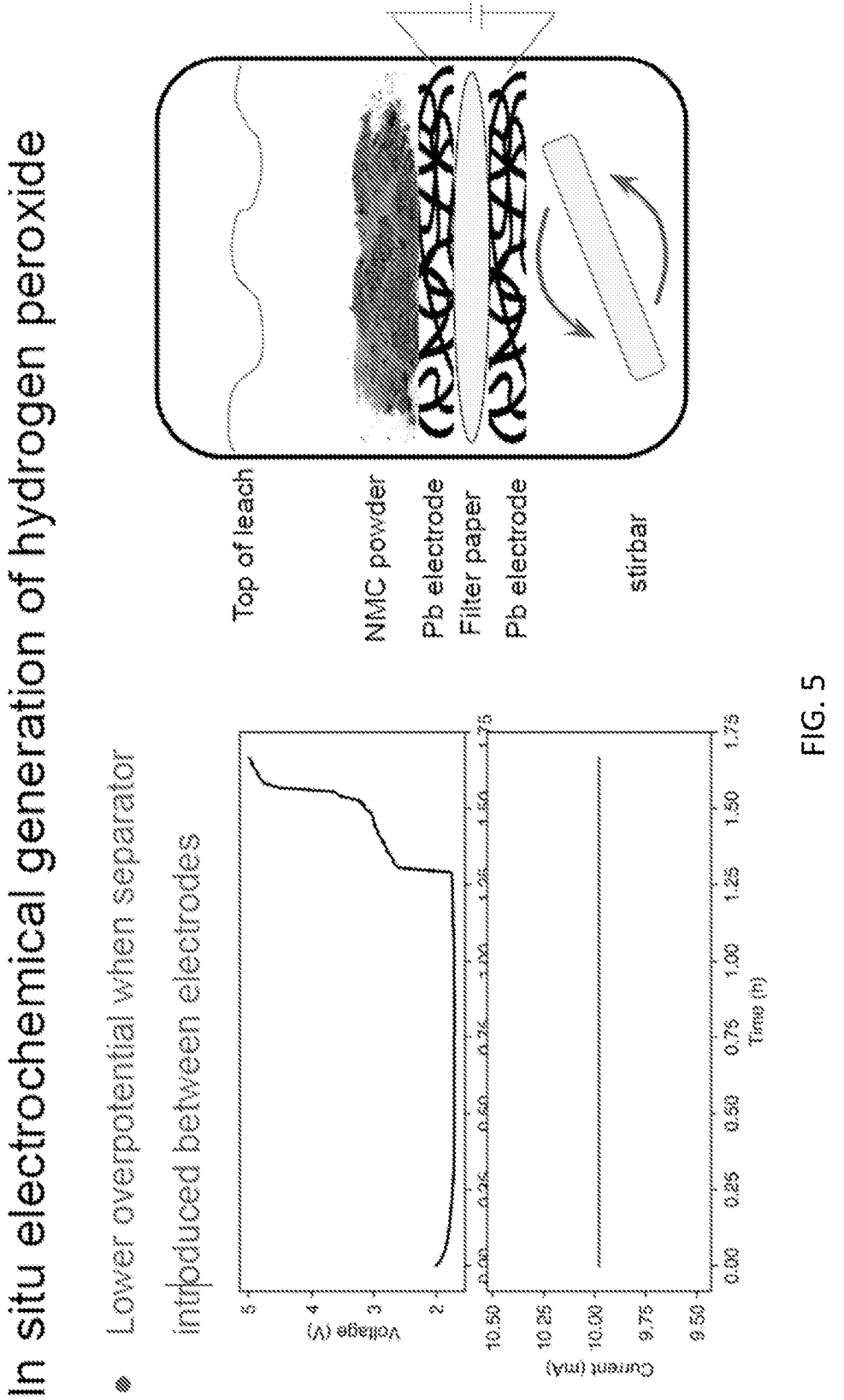
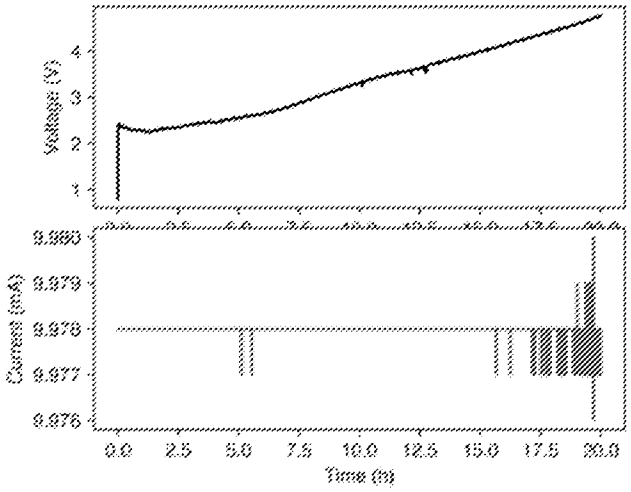

In situ electrochemical generation of hydrogen peroxide
Lower overpotential when separator introduced between electrodes
Top of leach
NMC powder
Pb electrode
Filter paper
Pb electrode
stirbar
Voltage (V)
Current (mA)
Time (h)

FIG. 5

In situ electrochemical generation of hydrogen peroxide

- Lowest overpotential stable over 20 hours at 0.833 mA/g Pb using glass fiber membrane to separate electrodes from NMC powder



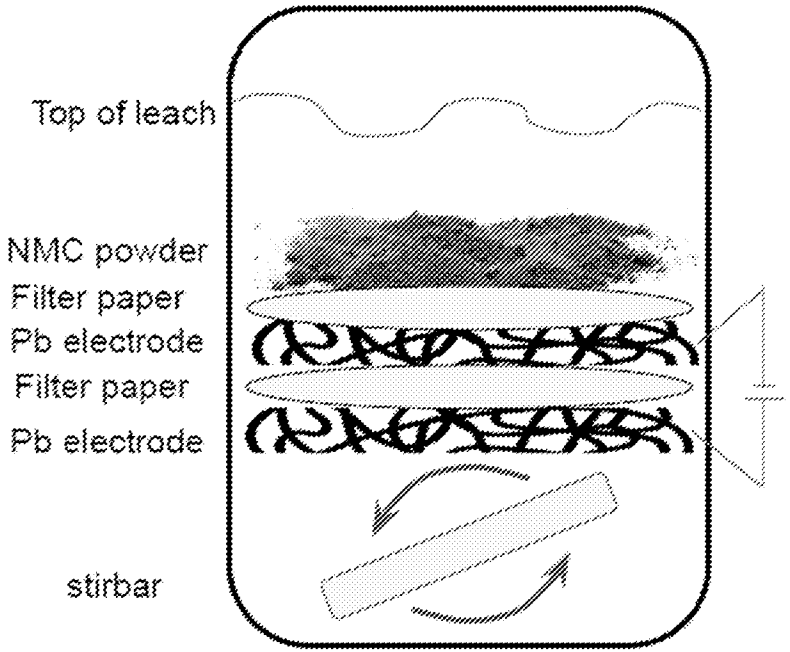


FIG. 6

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2024/039806

A. CLASSIFICATION OF SUBJECT MATTER

IPC: ***H01M 10/52*** (2024.01); ***C25B 1/30*** (2024.01); ***C22B 1/00*** (2024.01); ***C22B 3/00*** (2024.01); *C22B 26/12* (2024.01)

CPC: ***H01M 10/52; C25B 1/30; C22B 1/005; C22B 23/0407; C22B 23/0415;*** *C22B 26/12*

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

See Search History Document

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

See Search History Document

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

See Search History Document

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2023/0147264 A1 (3R-CYCLE OY) 11 May 2023 (11.05.2023) abstract, [0025], [0095], [0125], [0215], [0295]	1, 6/1, 7/6/1), 8/1, 9/1, 16, 17
Y	US 2021/0391606 A1 (Worcester Polytechnic Institute) 16 December 2021 (16.12.2021) abstract, Fig 3, [0031], [0036]-[0037]	1-9, 16-20
Y	US 3,884,778 A (Eng et al.) 20 May 1975 (20.05.1975) abstract, col 10 lines 49-55	1-9, 16-20
A	US 2021/0032721 A1 (DUSENFELD GMBH) 04 February 2021 (04.02.2021) entire document	1-9, 16-20
A	US 2023/0160036 A1 (Ecopro Innovation Co Ltd) 25 May 2023 (25.05.2023) entire document	1-9, 16-20

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

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"D" document cited by the applicant in the international application
"E" earlier application or patent but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
18 November 2024 (18.11.2024)	**05 December 2024 (05.12.2024)**

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

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2024/039806

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	Chaenko et al., "Indirect Electrosynthesis of Peracetic Acid Using Hydrogen Peroxide Generated in Situ in a Gas Diffusion Electrode" 22 March 2011, Russ J Electrochem 47, 230–233 (2011). https://doi.org/10.1134/S1023193511020030 entire document	1-9, 16-20
A	Kornienko et al., "Use of Aqueous Hydrogen Peroxide Solutions Prepared by Cathodic Reduction of Oxygen for Indirect Oxidation of Chemical Substances in Situ: Achievements and Prospects" 28 March 2014, Russ J Appl Chem 87, 1-15 (2014). https://doi.org/10.1134/S1070427214010017 entire document	1-9, 16-20

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2024/039806

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

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

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

Group I: Claims 1-9, 16-20, directed to a method comprising: forming hydrogen peroxide in situ.

Group II: Claims 10-15, directed to a system comprising: a container.

The groups of inventions listed above do not relate to a single general inventive concept under PCT Rule 13.1 because, under PCT Rule 13.2, they lack the same or corresponding special technical features for the following reasons:

Special Technical Features:

Group I requires a method, comprising: in the presence of an acid, applying a current between a first electrode and a second electrode so as to form an amount of hydrogen peroxide in situ so as to give rise to a digesting solution that comprises hydrogen peroxide and the acid; contacting the digesting solution and a metallic composition comprising a metal so as dissolve at least some of the metal comprised in the metallic composition, the metal optionally being a transition metal; and collecting at least some of the metal dissolved from the metallic composition; not required by group II.

Group II requires a system, comprising: a container; a first electrode and a second electrode, the first electrode and the second electrode being disposed within the container, at least one of the first electrode and the second electrode comprising PbO2; and an amount of acid disposed in the container; not required by group I.

Common Technical Features:

Groups I and II share the technical feature of two electrodes in the presence of an acid. However, these shared technical features do not represent a contribution over prior art, because the shared technical feature is being anticipated by document titled “Indirect Electrosynthesis of Peracetic Acid Using Hydrogen Peroxide Generated in Situ in a Gas Diffusion Electrode” to Chaenko et al. (hereinafter "Chaenko"). Chaenko teaches two electrodes in the presence of an acid (abstract, “Indirect electrochemical oxidation of acetic to peracetic acid in aqueous solutions using hydrogen peroxide generated in situ from O2 in a gas diffusion electrode was studied”; pg 231 col 1 para 2-3, “The experiments were carried out in an electrochemical cell, in which the cathode and anode compartments were separated by an MFSK cation exchange membrane... The gas diffusion electrodes were flat discs made of a mixture of carbon black A 437E (60 wt %) and FP4D (40 wt %) with a total porosity of 65-70% and a thickness of 0.8-0.9 mm. ?2 was fed from the reagent chamber to the gas diffusion cathode on its rear side. The resulting H2O2 was entrained from the pore volume of the electrode to the catholyte containing acetic acid. As electrolytes, we used acetic acid solutions”).

Accordingly, the inventions listed as Groups above lack unity of invention under PCT Rule 13 because they do not share a same or corresponding special technical feature providing contribution over prior art.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2024/039806

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

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

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

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☑ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.: **1-9, 16-20**

Remark on Protest

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

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

☐ No protest accompanied the payment of additional search fees.