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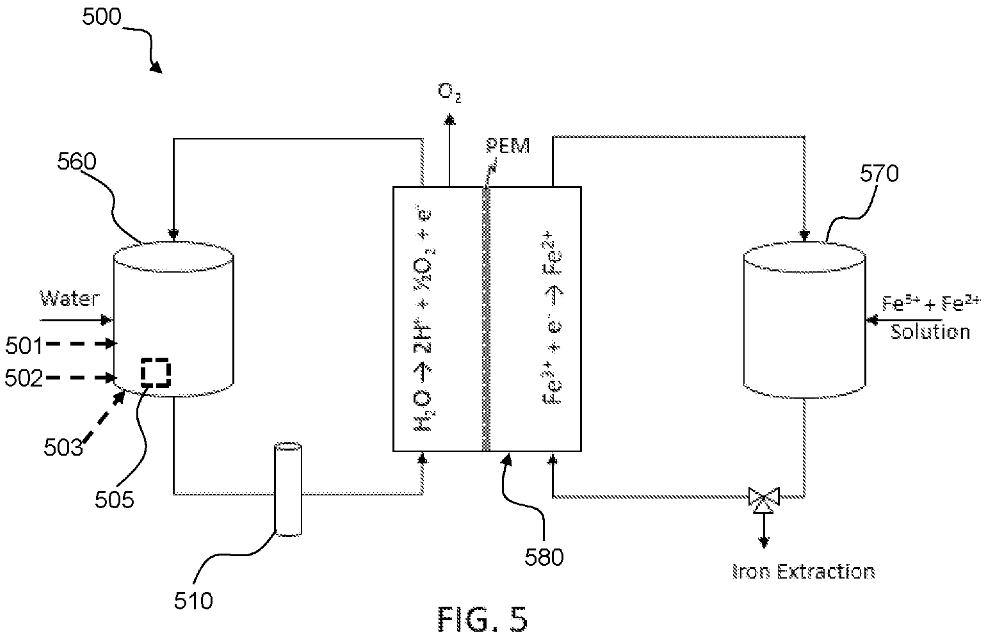

FIG. 5

(57) **Abstract:** Aspects disclosed herein include a method for stabilizing a lead anode, the method comprising: operating an electrochemical cell comprising performing electrochemical reduction at a first cathode and electrochemical oxidation at a first anode; wherein: the electrochemical cell comprises a first anodic chamber having a first anolyte in contact with the first anode, a first cathodic chamber having a first catholyte in contact with the first cathode, and a first separator separating the first anolyte from the first catholyte; the first anode is a lead electrode; each of the first anolyte and the first catholyte independently comprises aqueous iron cations and aqueous anions; and the first anolyte comprises the aqueous iron cations at a concentration selected from the range of 0.01 M to 0.5 M.

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STABILIZED LEAD DIOXIDE ANODE AND METHODS OF USING

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application claims the benefit of and priority to U.S. Provisional Patent Application Serial No. 63/410,092, filed September 26, 2022, which is incorporated herein by reference in its entirety for all purposes to the extent not inconsistent herewith.

BACKGROUND OF INVENTION

[0002] Lead electrodes are useful as oxygen-evolution anodes, for oxygen evolution reactions (OER), in various electrochemical systems. However, persistent issues have complicated the use of lead electrodes in many such processes. Two major problems are: (1) mechanical delamination of lead oxide and lead sulfate material from the electrode, causing dimensional instability, loss of catalyst material and loss of electrode conductivity, ultimately limiting electrode lifetime; and (2) manganese oxide deposits collecting on and around the electrode, requiring regular clean-up to prevent occlusion of PbO_2 catalyst sites and uneven current distributions. For example, manganese metal is typically included in zinc electrowinning anolyte to minimize dissolution and incorporation of lead into the plated zinc. Manganese may also be present due it being an impurity in the original process feedstock, such as an ore.

[0003] Where OER at an anode is necessary, a typical solution in the art, for avoiding the above challenges, is to not use lead anodes, which are inexpensive, and rather utilize more expensive OER anodes such as iridium-based anode materials. In addition to being expensive, iridium-based anode materials have their own sets of challenges, such as limited global supply.

[0004] To take advantage of inexpensive lead anodes for OER, the above mentioned challenges, and others, are addressed by the methods, systems, and associated aspects, disclosed herein.

SUMMARY OF THE INVENTION

[0005] Aspects disclosed herein include a method for stabilizing a lead anode, the method comprising: operating an electrochemical cell comprising performing electrochemical reduction at a first cathode and electrochemical oxidation at a first anode; wherein: the electrochemical cell comprises a first anodic chamber having a first anolyte in contact with the first anode, a first cathodic chamber having a first catholyte in contact with the first cathode, and a first separator separating the first anolyte from the first catholyte; the first anode is a lead electrode; each of the first anolyte and the first catholyte independently comprises aqueous iron cations and aqueous anions; and the first anolyte comprises the aqueous iron cations at a concentration of at least 0.01 M.

[0006] Aspects disclosed herein include a method for stabilizing a lead anode, the method comprising: operating an electrochemical cell comprising performing electrochemical reduction at a first cathode and electrochemical oxidation at a first anode; and recycling a second electrolyte from a metal electroplating cell to the first anolyte, the second electrolyte having aqueous iron cations; wherein: the electrochemical cell comprises a first anodic chamber having a first anolyte in contact with the first anode, a first cathodic chamber having a first catholyte in contact with the first cathode, and a first separator separating the first anolyte from the first catholyte; the first anode is a lead electrode; each of the first anolyte and the first catholyte independently comprises aqueous iron cations and aqueous anions; and the first anolyte comprises the aqueous iron cations at a concentration of at least 0.01 M but no more than 0.5 M, optionally no more than 0.45 M, optionally no more than 0.445 M, optionally no more than 0.44 M, optionally no more than 0.4 M. Optionally, in aspects herein, the first anolyte comprises the aqueous iron cations at a concentration of at least 0.01 M but no more than 0.4 M (in some aspects, no more than 0.44 M;in some aspectsno more than 0.445 M). Optionally, in aspects herein, the first anolyte comprises the aqueous iron cations at a concentration of at least 0.02 M but no more than 0.4 M. Optionally, in aspects herein, the first anolyte comprises the aqueous iron cations at a concentration of at least 0.03 M but no more than 0.4 M. Optionally, in aspects herein, the first anolyte comprises the aqueous iron cations at a concentration of at least 0.04 M but no more than 0.4 M. Optionally, in aspects herein, the first anolyte comprises the aqueous iron cations at a concentration of at least 0.05 M but no more than 0.4 M. Optionally, in aspects herein, the first anolyte comprises the aqueous iron cations at a concentration of at least 0.1 M but no more than 0.4 M.

[0007] Aspects disclosed herein include a method for stabilizing a lead anode, the method comprising: operating an electrochemical cell comprising performing electrochemical reduction at a first cathode and an oxygen evolution reaction (OER) at a first anode; wherein: the electrochemical cell comprises a first anodic chamber having a first anolyte in contact with the first anode, a first cathodic chamber having a first catholyte in contact with the first cathode, and a first separator separating the first anolyte from the first catholyte; the first anode is a lead electrode; each of the first anolyte and the first catholyte independently comprises aqueous iron cations and aqueous anions; and the first anolyte comprises aqueous iron sulfate at a concentration of at least 0.01 M.

[0008] Anion exchange membranes (AEMs) may “leak” cations driven towards the negative electrode by diffusion and electrical field. Therefore, maintaining iron sulfate concentration within a target range (also referred to herein as a stabilizing-concentration range of iron cations) requires adding aqueous iron cations to replace aqueous iron lost by said leakage. Optionally, for example, in some aspects, replenishing or maintaining a stabilizing or target concentration range of iron cations in the anolyte may be achieved by flowing the anolyte, or portion thereof, over a solid iron salt, such as ferrous and/or ferric sulfate, ferric and/or ferrous oxide, metallic iron, one or more ores such as magnetite, or any combination thereof. Optionally, for example, in some aspects, replenishing or maintaining a stabilizing or target concentration range of iron cations in the anolyte may be achieved by adding to or dosing the anolyte with an aqueous solution having aqueous iron cations (also referring to herein as an aqueous dosing-solution or liquid iron source). Optionally, for example, in some aspects, metallic iron may be provided to the catholyte or the catholyte may be exposed to metallic iron to consume protons (acid) that leak through the AEM from the anolyte.

[0009] Aspects disclosed herein include a method comprising: operating an electrochemical cell comprising performing electrochemical reduction at a first cathode and electrochemical oxidation at a first anode; wherein: the electrochemical cell comprises a first anodic chamber having a first anolyte in contact with a first anode, a first cathodic chamber having a first catholyte in contact with a first cathode, and a first separator separating the first anolyte from the first catholyte; the first anode is a lead electrode; and each of the first anolyte and the first catholyte independently comprises aqueous iron cations and aqueous anions; and wherein the method further comprises: dissolving solid manganese oxide in the first anolyte in the presence of aqueous ferrous ions.

[0010] Aspects disclosed herein include a method comprising: operating an electrochemical cell comprising performing electrochemical reduction at a first cathode and electrochemical oxidation at a first anode; wherein: the electrochemical cell comprises a first anodic chamber having a first anolyte in contact with a first anode, a first cathodic chamber having a first catholyte in contact with a first cathode, and a first separator separating the first anolyte from the first catholyte; the first anode is a lead electrode; and each of the first anolyte and the first catholyte independently comprises aqueous iron cations and aqueous anions; and wherein the method further comprises: reverse-biasing the first anode for a finite time comprising electrochemically reducing aqueous ferric ions to aqueous ferrous ions at the first anode in the presence of the first anolyte.

[0011] Aspects disclosed herein include a method comprising: operating an electrochemical cell comprising performing electrochemical reduction at a first cathode and electrochemical oxidation at a first anode; wherein: the electrochemical cell comprises a first anodic chamber having a first anolyte in contact with a first anode, a first cathodic chamber having a first catholyte in contact with a first cathode, and a first separator separating the first anolyte from the first catholyte; each of the first anode and the first cathode is independently a lead electrode; and each of the first anolyte and the first catholyte independently comprises aqueous iron cations and aqueous anions.

[0012] Without wishing to be bound by any particular theory, there may be discussion herein of beliefs or understandings of underlying principles relating to the devices and methods disclosed herein. It is recognized that regardless of the ultimate correctness of any mechanistic explanation or hypothesis, an embodiment of the invention can nonetheless be operative and useful.

BRIEF DESCRIPTION OF THE DRAWINGS

[0013] **FIG. 1** is a schematic diagram illustrating a cross-sectional view of a three-dimensional porous substrate with layers of lead on one or both faces.

[0014] **FIG.** 2 is a schematic diagram illustrating a cross-sectional view of a bipolar electrode structure.

[0015] **FIG.** 3 is a schematic diagram illustrating a cross-sectional view of a bipolar stack comprising a series of bipolar electrodes between end-plates.

[0016] **FIG. 4** is a schematic diagram illustrating a cross-sectional view of a bipolar electrode structure, showing some example reactions that may optionally be catalyzed by the respective electrodes according to some aspects.

[0017] **FIG. 5** is a schematic diagram illustrating an acid generating ferric reduction cell optionally including an oxygen evolution anode comprising lead.

[0018] **FIG. 6** is a schematic diagram illustrating an iron electroplating cell optionally including an oxygen evolution anode comprising lead.

[0019] **FIG. 7** is a schematic diagram illustrating a two-step iron conversion system with various sub-systems including an oxygen evolution reaction at the first anode, according to various aspects herein.

[0020] **FIG. 8** is a schematic diagram illustrating a two-step iron conversion system with various sub-systems including an oxygen evolution reaction at the anode of the acid regeneration subsystem (the first anode) and an oxygen evolution reaction at the anode of the plating cell (the second anode), according to various aspects herein.

[0021] **FIG. 9** is a schematic diagram illustrating a two-step iron conversion system with various sub-systems, including an oxygen evolution reaction at the anode of the acid regeneration subsystem (the first anode), and further demonstrating possible fluid flows between subsystems.

[0022] **FIG. 10** is a schematic diagram illustrating a two-step iron conversion system with various sub-systems, including an oxygen evolution reaction at the anode of the acid regeneration subsystem (the first anode) and an oxygen evolution reaction at the anode of the plating cell (the second anode), and further demonstrating possible fluid flows between subsystems.

[0023] **FIG. 11** is a schematic diagram illustrating an ore dissolution subsystem including an acid regenerating cell.

[0024] **FIGs. 12A-12C** are scanning electron microscope (SEM) images of electrode surfaces before electrochemical cycling in acid (**FIG. 12A**), an equivalent electrode surface but after electrochemical cycling in sulfuric acid free of dissolved iron (**FIG. 12B**), and an equivalent electrode surface but after electrochemical cycling in the presence of aqueous iron sulfate, or sulfuric acid with dissolved iron ions (**FIG. 12C**).

The lead electrode exposed to acid, free of aqueous iron cations, has a surface with large $PbSO_4$ crystals, which dimensionally destabilize the lead electrode. The lead electrode exposed to acid with aqueous iron cations has much smaller $PbSO_4$ crystals, corresponding to a dimensionally more stable lead electrode.

[0025] **FIG. 13** is a series of schematic diagrams illustrating potential mechanisms, according to some aspects, occurring when a lead electrode is exposed to sulfuric acid free of aqueous cations (left images) compared to when a lead electrode is exposed to sulfuric acid with aqueous iron cations, or ferric and/or ferrous sulfate (right images). Generally, in the absence of iron sulfate, large surface-destabilizing $PbSO_4$ crystals are formed; the destabilizing effect is heightened when oxygen bubbles evolve from the surface. In contrast, generally, according to some aspects, the presence of iron sulfate prevents or significantly hampers or slows formation of large $PbSO_4$ crystals leading to a stable and robust surface, including when oxygen bubbles are evolving from the surface. In some aspects, the presence of iron sulfate may result in formation of a protective layer, optionally comprising an Fe-Pb-S-O composition (e.g., $Fe_xPb_ySO_4$), on the lead electrode surface.

[0026] **FIG. 14** is a series of SEM images of Pb and PbO_2 surfaces after having been soaked H_2SO_4, $PbSO_4$, or $Pb_2(SO_4)_3$, as labeled, for 12 hours followed by air drying (no liquid rinse). It is clear that PbO_2, in particular, exposed to sulfuric acid in absence of iron sulfate, has a significantly rougher surface having large crystals of $PbSO_4$, compared to the other shown surfaces.

[0027] **FIG. 15** is a series of SEM images of Pb surfaces exposed to 1 M ferric sulfate (top images) or 0.1 M sulfuric acid (bottom images) for one day of 50% duty cycling at approximately 30 mA/cm^2 or approximately 50 mA/cm^2.

STATEMENTS REGARDING CHEMICAL COMPOUNDS AND NOMENCLATURE

[0028] In general, the terms and phrases used herein have their art-recognized meaning, which can be found by reference to standard texts, journal references and contexts known to those skilled in the art. The following definitions are provided to clarify their specific use in the context of this disclosure.

[0029] As used herein, the term “electrolyte” refers to an aqueous solution containing one or more dissolved ionic species. An electrolyte may be acidic, basic or neutral in pH, notwithstanding examples herein are described with reference to acidic electrolyte.

[0030] As used herein, the term “anolyte” refers to an electrolyte that is in contact with an “anode” electrode. Similarly, the term “catholyte” refers to an electrolyte that is in contact with a “cathode” electrode. In some examples and aspects, anolyte and catholyte may be maintained as distinct un-mixed solutions, typically separated from one another by a separator membrane within an electrochemical cell and by separate fluid conduits outside of a cell. However, in some cases, the terms “anolyte” and “catholyte” may refer to a single electrolyte, such as in an un-divided electrochemical cell.

[0031] In the art of electrochemical cells, such as with respect to electrolytic cells, an anode refers to an electrode at which electrochemical oxidation occurs and a cathode refers to an electrode at which electrochemical reduction occurs. As used herein, reverse-biasing an anode refers to applying a voltage such that electrochemical reduction occurs at the anode. Herein, in a case of reverse-biasing the anode, although reduction occurs at the anode during reverse-biasing, the anode is not renamed but is rather characterized as being reverse-biased for the purpose of consistent electrode identification. Optionally, but not necessarily, an anode may be reverse-biased by applying a negative potential to the anode or by applying a potential that is less or more negative than the potential on the respective counter electrode (e.g., cathode), such that electrons may flow from an electrical circuit into the reverse-biased anode thereby facilitating electrochemical reduction at the reverse-biased anode in the presence of an electrolyte. Optionally, but not necessarily, reverse-biasing an anode particularly refers to a potential on the anode being such that ferric ions are reduced to ferrous ions at said anode.

[0032] The term “lead electrode” refers to an electrode having lead and/or lead oxide exposed to an electrolyte, such as an anolyte. A lead electrode optionally comprises bulk lead or is optionally substantially formed of bulk lead. Optionally, a lead electrode may comprise one or more layers of lead and/or lead oxide on a different material serving as mechanical and electrical support and/or substrate, such that lead and/or lead oxide is exposed to an electrolyte. As an oxygen evolution reaction (OER) proceeds, a lead metal surface of a lead electrode will oxidize to lead oxide (PbO_x), or in some aspects first to lead sulfate ($PbSO_4$) in the presence of sulfate ions, and then to lead oxide (PbO_x). Accordingly, a lead electrode may also include some $PbSO_4$. A lead electrode may comprise intentional dopant and/or alloying species to modify its electrochemical or other properties. As used herein, the formula PbO_x represents lead oxide inclusive of lead dioxide (PbO_2) and further inclusive of nonstoichiometric oxygen deficient variations of lead (di)oxide, such as wherein x is greater than or equal to 1 and less than or equal to 2. As used herein, the formula PbO_2 is shorthand for lead dioxide and is intended to be inclusive of nonstoichiometric oxygen deficient variations thereof such that the compounds represented by the formula PbO_2 include those represented by PbO_x.

[0033] The terms "aqueous iron cations" and "aqueous iron ions", as used herein including the claims, is intended to refer to all aqueous iron cations, of any oxidation state, such as at least aqueous ferrous ($Fe^{2+}{}_{(aq)}$) ions and aqueous ferric ($Fe^{3+}{}_{(aq)}$) ions.

[0034] The term "solid manganese oxide" refers to any solid manganese oxide or undissolved precipitate of manganese oxide. The terms "solid $MnO_{2-\delta}$", "solid MnO_x", "solid MnO_2", are used interchangeably to likewise refer to any solid or undissolved precipitate of MnO_x, wherein x is greater than or equal to 1 and less than or equal to 2. The term "manganese oxide" refers to manganese dioxide (MnO_2) and further including oxygen-deficient or non-stoichiometric manganese dioxide such as may be represented in the art by formula $MnO_{2-\delta}$ and/or formula MnO_x, wherein δ is greater than or equal to 0 and less than or equal to 1 and wherein x is greater than or equal to 1 and less than or equal to 2. Optionally, the term "manganese oxide" is further inclusive of any other manganese oxide species such as, but not limited to, manganese(II) oxide (MnO), manganese(II,III) oxide (Mn_3O_4), manganese(III) oxide (Mn_2O_3), manganese(VI) oxide (MnO_3), manganese(VII) oxide (Mn_2O_7), Mn_5O_8, Mn_7O_{12} and Mn_7O_{13}, and any oxygen deficient or non-stoichiometric variation thereof. As used herein, the formula MnO_2 is shorthand for manganese dioxide and is intended to be further inclusive of nonstoichiometric oxygen deficient variations thereof such that the compounds represented by the formula MnO_2 include those represented by MnO_x, wherein x is greater than or equal to 1 and less than or equal to 2.

[0035] The term "manganese sulfate" refers to $MnSO_4$. Optionally, term "manganese sulfate" refers to $MnSO_4$ and furthermore other manganese sulfate species.

[0036] The term “spent” electrolyte is intended to be consistent with the term as used in Applicant’s PCT patent application # PCT/US2022/021732, titled “2-Step Iron Conversion System,” published September 29, 2022, as PCT Patent Pub. No. WO2022204394, hereinafter referred to as “PCT’732”, which is incorporated herein by reference and which is also included as Appendix A in U.S. Provisional Patent App. No. 63/410,092, filed September 26, 2022, hereinafter referred to as “Provis’092”, which the benefit of and priority to is claimed herein and which is also incorporated herein by reference in its entirety. Generally, a spent electrolyte, which may be a spent catholyte and/or a spent anolyte, is an electrolyte that has already been used for electrochemical reduction and/or electrochemical oxidation in an electrochemical cell and is then removed from its respective electrochemical cell. For example, a spent catholyte (or, anolyte) is one that has been part of an electrochemical reduction (or, oxidation) reaction in an electrochemical cell and is subsequently removed from the electrochemical cell. In the course of respective electrochemical reaction(s) (reduction or oxidation) occurring in presence of an electrolyte (catholyte or anolyte), one or more reagents (e.g., iron ions) may be depleted and/or one or more products may be accumulated in said electrolyte. Therefore, a spent electrolyte may be optionally characterized as an electrolyte in which one or more reagents have been depleted and/or one or more products have been accumulated, in the course of the respective electrochemical reaction(s), to a technically and/or commercially undesired or non-preferable amount for the same respective electrochemical reaction(s), wherein the spent electrolyte is thus removed from its respective electrochemical cell. For example, a catholyte in an iron electroplating cell, such as a second catholyte of a second electrochemical cell according to aspects in PCT’732 and in Provis’092, may become depleted of ferrous ions in the course of electroplating iron to such a degree wherein it would be preferable to remove the (spent) catholyte from the electroplating cell. The removed (spent) catholyte, having ferrous ions but at a concentration too low for electroplating, may optionally then be recycled, directly or indirectly, to a first anolyte of an electrochemical cell according to aspects disclosed herein. Removing and recycling a spent electrolyte may be performed as part of a batch process or a continuous process.

[0037] As used herein, the terms “pure iron” and “high purity iron” are used in a relative sense to refer to a metallic iron material that is more pure than an iron source material, and contains an acceptably low quantity of one or more impurities.

[0038] As used herein, the terms “iron source material” and “iron feedstock” are used synonymously to refer to iron-containing materials that may be used as inputs into the various systems and methods described herein. “Iron source materials,” “iron feedstocks,” and “solid-iron containing materials” may include iron in any form, such as iron salts (e.g., iron(ii) sulfate, iron(III) sulfate, iron(ii) chloride, iron(III) chloride, iron oxides, hydroxides, oxyhydroxides, carbonates, or other iron-containing compounds, ores, rocks or minerals, including any mixtures thereof, in naturally-occurring states or beneficiated or purified states. The term “iron-containing ore” or simply “iron ore” may include materials recognized, known, or referred to in the art as iron ore(s), rock(s), natural rock(s), sediment(s), natural sediment(s), mineral, and/or natural mineral(s), whether in naturally-occurring states or in beneficiated or otherwise purified or modified states. Some aspects of processes and systems described herein may be particularly useful for iron ores including hematite, goethite, magnetite, limonite, siderite, ankerite, turgite, bauxite, or any combination thereof.

[0039] Optionally, an iron source material or iron feedstock may comprise an iron metal material, such as, but not limited to, iron dust (e.g., fine particulate produced as a byproduct of ironmaking or steelmaking processes in blast furnaces, oxygen furnaces, electric arc furnaces, etc.), iron powder, scrap steel, and/or scrap cast iron. “Iron source materials” and “iron feedstocks” may also contain various other non-iron materials, generally referred to as “impurities.”

[0040] As used herein, the term “impurity” refers to an element or compound other than a desired final product material (e.g., iron). In various aspects, depending on the intended end-use of a product material, a given element or compound may or may not be considered an “impurity.” In some cases, one or more elements or compounds that may be impurities to one process or sub-process may be isolated or purified, collected, and sold as a secondary product material.

[0041] In various aspects herein, various compositions, compounds, or solutions may be substantially “isolated” or “purified” to a degree sufficient for the purposes described herein. In various aspects, a substantially purified composition, compound or formulation (e.g., ferrous iron solutions, ferric iron solutions, or plated metallic iron) may have a chemical purity of 90% (e.g., by molarity of ionic concentrations or by weight), optionally for some applications 95%, optionally for some applications 99%, optionally for some applications 99.9%, optionally for some applications 99.99%, and optionally for some applications 99.999% pure.

[0042] Reference made herein to a “tank” is intended to include any vessel suitable for containing liquids, such as highly acidic or caustic aqueous solutions if needed. In some aspects, such a vessel may include additional features or components to assist or improve mixing of solid and/or liquid contents of the vessel. For example, a dissolution tank may include passive or actively operated structures or features for agitating a solution or solid/liquid mixture. A dissolution tank or other tank useful in the systems and methods herein may also include features to allow for sparging a gas into or through solid and/or liquid contents of the tank to increase gas contact with solid and/or liquid materials within the tank. Various tanks may also include baskets, sieves, pans, filters, or other structures to collect and separate solids from liquids. In some aspects, a tank may be configured to direct liquid or gas flow through the tank in such a way as to agitate the mixture therein (e.g., flow-directing structures, pumps, impellers, baffles, impellers, stir-bars, stir blades, vibrators, cyclonic flow channels, etc.).

[0043] In some aspects described herein, a system for converting iron ore into iron metal (i.e., an “iron conversion system”) may comprise two or more subsystems. Some aspects include a “dissolution subsystem” in which components of an iron-containing feedstock are dissolved into an aqueous solution. Some aspects further include an “iron plating subsystem” in which dissolved iron is electrochemically reduced to iron metal in an “electroplating” (or simply “plating”) process. The iron metal may subsequently be removed from the iron plating subsystem.

[0044] The term “iron electroplating” (or “iron plating” as used synonymously herein) refers to a process by which dissolved iron is electrochemically reduced to metallic iron on a cathodic surface. Equivalent terms “electrodeposition,” “electroforming,” and “electrowinning” are also used herein synonymously with “iron electroplating.” The shape or form-factor of the electroplated iron need not be a “plate” by any definition of that term. For example, electroplated iron may take any shape or form and may be deposited on any suitable cathodic surface as described in various aspects herein.

[0045] The term “dissolution step” includes processes occurring in the dissolution subsystem, including but not limited to dissolution of iron oxide materials and electrochemical process(es) occurring in or via an “acid regeneration cell,” including but not limited to the claimed step of electrochemically reducing Fe^{3+} ions to Fe^{2+} ions in the acid regeneration cell. Dissolution step processes may also include oxidizing water or hydrogen gas in the first electrochemical cell, for example, to generate protons, which may allow for regeneration of the acid (in the form of protons) that is used to facilitate dissolution of an iron-containing feedstock.

[0046] The term “acid regenerator” and “acid regeneration cell” refers to an electrochemical cell according to embodiments and aspects herein, such as according to any of aspects 1-56 below. Optionally, the “acid regenerator” and “acid regeneration cell” may correspond to and/or further comprise any embodiment or aspect disclosed in PCT’732 and in Provis’092, which are incorporated herein as part of this disclosure.

[0047] The term “iron plating step” includes process(es) occurring in the iron plating subsystem, including but not limited to the electrochemical process(es) occurring in or via the claimed “plating cell,” including but not limited to the step of “electrochemically reducing” Fe^{2+} ions to Fe metal in the “plating cell” also referred to herein as the “plating cell.” The iron plating process may also include oxidizing a second portion of Fe^{2+} ions to form Fe^{3+} ions. In some aspects, such Fe^{2+} ions may be provided from the first electrochemical cell or from another part of the system.

[0048] As used herein, unless otherwise specified, the terms “ferrous iron solution” or “ferrous solution” may refer to an aqueous solution that contains dissolved iron that is at least predominantly (i.e., between 50% and 100%) in the Fe^{2+} (i.e., “ferrous”) ionic state with the balance of dissolved iron being in the “ferric” Fe^{3+} state. Similarly the term “ferrous ion” refers to one or more ions in the ferrous (Fe^{2+}) state.

[0049] As used herein, unless otherwise specified, the terms “ferric iron solution” or “ferric solution” may refer to an aqueous solution that contains dissolved iron that is at least predominantly (i.e., between 50% and 100%) in the Fe^{3+} (i.e., “ferric”) ionic state with the balance of dissolved iron being in the “ferrous” Fe^{2+} state. Similarly the term “ferric ion” refers to one or more ions in the ferric (Fe^{3+}) state. Either “ferric solutions” or “ferrous solutions” may also contain other dissolved ions or colloidal or particulate materials, including impurities.

[0050] As used herein, any reference to a “PEM” or “proton exchange membrane” may be interpreted as also including a “CEM” or “cation exchange membrane”, both terms may include any available membrane material that selectively allows passing positively charged cations and/or protons. The abbreviation “AEM” is used to refer to anion exchange membranes selective to negatively-charged aqueous ions and includes any available anion-selective membrane.

[0051] As used herein, aqueous protons and electrochemically generated protons are intended to be inclusive of aqueous protons and aqueous hydronium ions.

[0052] As used herein, the term “unprocessed ore” refers to an iron-containing ore that has been neither thermally reduced nor air roasted according to aspects disclosed herein. Unprocessed ore is optionally a raw iron-containing ore.

[0053] As used herein, electrochemically generated ions, such as electrochemically generated protons and electrochemically generated iron ions (e.g., Fe^{2+}, Fe^{3+}), refer to ions that are generated or produced in an electrochemical reaction. For example, electrochemical oxidation of water at an anode may electrochemically generated protons and electrochemically generated oxygen.

[0054] As used herein, the term “air roasting” refers to a thermal treatment performed at an elevated temperature in the presence of air. Air roasting of ore, such as iron-containing ore, can break down or decrease average particle size of an ore. Optionally, air roasting is performed at temperature selected from the range 300 °C and 500 °C. Additional description and potentially useful aspects of air roasting may be found in the following reference, which is incorporated herein in its entirety: “Study of the calcination process of two limonitic iron ores between 250°C and 950°C”, Revista de la Facultad de Ingeneria, p. 33 (2017).

[0055] As used herein, the term “redox couple” refers to two chemical species, such as ions and/or molecules, that correspond to a reduced species and an oxidized species of an electrochemical reaction or a half-cell reaction. For example, in the electrochemical reduction of Fe^{3+} ions to Fe^{2+} ions, the corresponding redox couple is Fe^{3+}/Fe^{2+}, where Fe^{3+} is the oxidized species and Fe^{2+} is the reduced species. As used herein, the order in which a redox couple is described (e.g., Fe^{3+}/Fe^{2+} vs. Fe^{2+}/Fe^{3+}) is not intended to denote which species is the reduced species and which is the oxidized species. Additional description and potentially useful aspects of redox couples may be found in the following reference, which is incorporated herein in its entirety: “Redox – Principles and Advanced Applications”: Book by Mohammed Khalid, Chapter 5: Redox Flow Battery Fundamental and Applications.

[0056] As used herein, the terms “steady state” and “steady-state” generally refer to a condition or a set of conditions characterizing a process, a method step, a reaction or reactions, a solution, a (sub)system, etc., that are true longer than they are not true during operation or performance of the process, method step, reaction or reactions, solution, (sub)system, etc. For example, dissolution of an ore or feedstock may be characterized by a steady state condition, wherein the steady state condition is true during at least 50%, optionally at least 60%, optionally at least 70%, optionally at least 80%, optionally at least 90%, optionally at least 95% of a time during which the dissolution is occurring. For example, a steady state condition may be exclusive of conditions characterizing the transient start-up and shut-down phases of a process such as dissolution of a feedstock.

[0057] The term “cathodic chamber” refers to a region, compartment, vessel, etc. comprising a cathode, or at least a portion or surface thereof, and a catholyte. The term “anodic chamber” refers to a region, compartment, vessel, etc. comprising an anode, or at least a portion or surface thereof, and an anolyte.

[0058] As used herein, the term “iron-rich solution” may be also referred to as an “iron iron-rich solution” or a “ferrous product solution”, corresponding to the iron ion-rich solution formed in the ore dissolution subsystem.

[0059] As used herein, the term “precipitation pH” refers to a pH at which the referenced one or more ions or salts are thermodynamically favored or expected to precipitate out of the host aqueous solution. Generally, the solubility of ions and salts dissolved in an aqueous solution may depend on the pH of the aqueous solution. As pH increases, many metallic ions form metal hydroxides which tend to precipitate out of the host solution due to decreasing solubility. The precipitation pH is defined herein as the pH corresponding to a point where solubility of a given ion or salt is below a concentration threshold. The precipitation pH may be an upper boundary beyond which the solubility of a given ion or salt is less than 1 mM, optionally less than 0.1 mM.

[0060] As used herein, the term “metallic iron” refers to a material comprising metallic iron, such as but not limited to scrap iron, electroplated iron, iron powder, etc.

[0061] As used herein, the term “supporting salt” and “supporting ion” refers to a salt and ion, respectively, corresponding to or serve as a supporting electrolyte or which form, at least partially, a supporting electrolyte when dissolved in order to increase a conductivity of a host solution. In some aspects, for example, the electrolytes and solutions in either the dissolution subsystem and the plating subsystem may contain dissolved iron species, acid, and additionally inert salts serving as supporting electrolyte to enhance the electrolyte conductivity, which may be particularly beneficial at low ferrous concentrations, wherein the inert salts serving as supporting electrolyte to enhance conductivity may be referred to as supporting salts. Supporting salts may include any electrochemically inert salt such as sodium chloride, potassium chloride, ammonium chloride, sodium sulfate, potassium sulfate, ammonium sulfate, sodium chloride, potassium chloride, ammonium chloride or others, or combinations of salts. The concentration of the supporting salts in the solution, if used, may range from about 0.1 to about 1 M, for example.

[0062] As used herein, the terms “dissolved iron,” “dissolved iron ions,” “aqueous iron,” and “aqueous iron ions” are used interchangeably to refer to aqueous or dissolved iron ions, including ferrous ions, ferric ions, and combinations thereof, present in a solution.

[0063] As used herein, the term “wt.%” or “wt%” refers to a weight percent, or a mass fraction represented as a percentage by mass. The term “at.%” or “at%” refers to an atomic percent, or an atomic ratio represented as a percentage of a type of atom with respect to total atoms in a given matter, such as a molecule, compound, material, nanoparticle, polymer, dispersion, etc. The term “mol.%” refers to molar percent or percent by moles. The term “vol.%” refers to volume percent.

[0064] The terms “substantially” and “approximately” interchangeably refer to a property, condition, or value that is within 20%, 10%, within 5%, within 1%, optionally within 0.1%, or is equivalent to a reference property, condition, or value. The term “substantially equal”, “substantially equivalent”, or “substantially unchanged”, when used in conjunction with a reference value describing a property or condition, refers to a value that is within 20%, within 10%, optionally within 5%, optionally within 1%, optionally within 0.1%, or optionally is equivalent to the provided reference value. For example, a diameter is substantially equal or approximately equal to 100 nm (or, is “substantially 100 nm” or “approximately 100 nm”) if the value of the diameter is within 20%, optionally within 10%, optionally within 5%, optionally within 1%, within 0.1%, or optionally equal to 100 nm. The term “substantially greater”, when used in conjunction with a reference value describing a property or condition, refers to a value that is at least 1%, optionally at least 5%, optionally at least 10%, or optionally at least 20% greater than the provided reference value. The term “substantially less”, when used in conjunction with a reference value describing a property or condition, refers to a value that is at least 1%, optionally at least 5%, optionally at least 10%, or optionally at least 20% less than the provided reference value. As used herein, the term “about” means a range of values including the specified value, which a person of ordinary skill in the art would consider reasonably similar to the specified value. In aspects, about means within a standard deviation using measurements generally acceptable in the art. In aspects, about means a range extending to +/−10% of the specified value. In aspects, about means the specified value. In aspects, the terms “about”, “approximately”, and “substantially” are interchangeable and have identical means. For example, a particle having a size of about 1 μm may have a size is within 20%, optionally within 10%, optionally within 5%, optionally within 1%, optionally within 0.1%, or optionally equal to 1 μm.

[0065] As used herein, the term “and/or” is used herein, in the description and in the claims, to refer to a single element alone or any combination of elements from the list in which the term and/or appears. In other words, a listing of two or more elements having the term “and/or” is intended to cover aspects having any of the individual elements alone or having any combination of the listed elements. For example, the phrase “element A and/or element B” is intended to cover aspects having element A alone, having element B alone, or having both elements A and B taken together. For example, the phrase “element A, element B, and/or element C” is intended to cover aspects having element A alone, having element B alone, having element C alone, having elements A and B taken together, having elements A and C taken together, having elements B and C taken together, or having elements A, B, and C taken together.

[0066] As used herein, the term “±” refers to an inclusive range of values, such that “X±Y,” wherein each of X and Y is independently a number, refers to an inclusive range of values selected from the range of X-Y to X+Y. In the cases of “X±Y” wherein Y is a percentage (e.g., 1.0±20%), the inclusive range of values is selected from the range of X-Z to X+Z, wherein Z is equal to X•(Y/100). For example, 1.0±20% refers to the inclusive range of values selected from the range of 0.8 to 1.2.

DETAILED DESCRIPTION OF THE INVENTION

[0067] In the following description, numerous specific details of the devices, device components and methods of the present invention are set forth in order to provide a thorough explanation of the precise nature of the invention. It will be apparent, however, to those of skill in the art that the invention can be practiced without these specific details.

[0068] In aspects, the present disclosure provides processes, systems, and methods for stabilizing a lead anode against shedding, dissolution, and/or other degrading processes, such as in the context of the lead anode being used for an oxygen evolution reaction (OER). In various aspects, the present disclosure provides processes, systems, and methods for reducing or eliminating solid manganese oxide sludge or contamination, which may detrimentally accumulate in the anodic chamber or anolyte or may poison or coat the anode, such as by dissolving the manganese oxide in the anolyte. In various aspects, the present disclosure further includes processes, systems, and methods for enabling efficient, low-temperature aqueous hydrometallurgical processes for producing pure iron from various iron source materials including relatively low-purity iron feedstock materials.

[0069] Various additional useful aspects, aspects, and definitions, of the present systems and methods are further set forth and exemplified in PCT'732 and in Provis'092.

[0070] Electrodes containing lead and/or a lead oxide (typically, lead dioxide) have been used as oxygen-evolution anodes in various electrochemical systems for many years. However, persistent issues have complicated the use of lead electrodes in many processes. Two major problems include shedding and sludge formation:

[0071] "Shedding" or mechanical delamination of lead oxide material, and in some aspects lead sulfate, from the electrode, causing dimensional instability, loss of catalyst material, and loss of electrode conductivity, ultimately limiting electrode lifetime. As a prelude to lead shedding, large crystals of $PbSO_4$ typically form (e.g., see top right SEM image in FIG. 14 labeled "PbO_2 in H_2SO_4") and facilitate mechanical delamination, particularly upon (re)starting OER.

[0072] Manganese oxide deposits, or "sludge," collecting on and around the electrode, requiring regular clean-up to prevent (a) occlusion of PbO_2, (b) permanganate formation, and (c) uneven current distributions which cause impeded cell operation. For example, manganese ion is typically included in zinc electrowinning anolyte to minimize dissolution and incorporation of lead into the plated zinc. Manganese may also be present due it being an impurity in the original process feedstock, such as an iron ore.

[0073] Unexpected discoveries, disclosed and contemplated herein, include that the operation of lead dioxide anodes in the presence of a finite concentration of dissolved iron facilitates the use of lead as a viable electrode material in iron electrowinning systems and/or other electrowinning systems. Further contemplated are several system configurations, electrode constructions, and operating methods that may advantageously leverage the discovered operations.

[0074] First, for example, it is discovered that, in the presence of ferric sulfate, the surface of a lead dioxide electrode appears to behave very differently compared to an electrode in acid without ferric sulfate. When a lead electrode is cycled between OER and open-circuit rest in the presence of substantial ferric sulfate concentrations, the electrode surface remains denser and does not exhibit the highly crystalline, fractured, and broken surface seen on identically-cycled electrodes in sulfuric acid with no ferric ions. In the absence of iron ions (e.g., ferric ions), the surface of the lead electrode can self-discharge to form $PbSO_4$, in the presence of sulfate ions in the anolyte, at transient or non-operating conditions such as the lead anode being at open circuit voltage (OCV), a potential too low for OER, and/or if/when potential on the anode is decreased too rapidly. Without wishing to be held to a particular theory, in the presence of iron ions (e.g., ferric ions) and sulfate ions in the anolyte, it is contemplated that an iron-lead compound (e.g., $Fe_xPb_ySO_4$) may be formed which protects the lead electrode surface from the formation of large lead sulfate ($PbSO_4$) crystals, which tend to cause the shedding commonly seen in lead electrodes. A lead/lead dioxide electrode in OER operation in electrolyte containing iron sulfate is found to be far more mechanically stable with less shedding than similar electrodes operating in electrolyte without iron sulfate. The iron-lead compound may also be smooth, which may further facilitate stability of the lead electrode surface.

[0075] For example, FIG. 14 shows a series of SEM images of Pb and PbO_2 surfaces soaked after having been soaked H_2SO_4, $PbSO_4$, or $Pb_2(SO_4)_3$, as labeled, for 12 hours followed by air drying (no liquid rinse). It is clear that PbO_2 exposed to sulfuric acid, in absence of iron sulfate, even without current-voltage cycling, has a significantly rougher surface with large boulders or crystals of $PbSO_4$, compared to the other shown surfaces. FIGs. 12B-C show similar results after a lead oxide surface is electrochemical cycled, where electrochemical cycling in the presence of sulfuric acid without dissolved iron ions (FIG. 12A) leads to formation of the large $PbSO_4$ crystals whereas the presence of dissolved iron ions with the sulfuric acid (FIG. 12B) suppresses formation of $PbSO_4$ such any $PbSO_4$ crystals present are much smaller and less destabilizing. FIG. 15 likewise shows images of lead electrode surfaces exposed to ferric sulfate or sulfuric acid, demonstrating that surfaces of lead electrodes exposed to sulfuric acid in absence of iron sulfate become rougher, corresponding to poorer dimensional stability, compared to lead electrodes in the presence of iron sulfate. FIG. 13 illustrates, according to some aspects without being held to any particular theory, that presence of iron sulfate protects a PbO_2 electrode surface from formation of large destabilizing $PbSO_4$ crystals, or at least slows the formation of said $PbSO_4$ crystals. When oxygen bubbles evolve from a PbO_2 electrode, the bubbles can aggressively disrupt surface roughness features and composition that are weakly adhered to the surface, thereby causing shedding of Pb from the PbO_2 electrode exposed to sulfuric acid. The reduction, slowing, or prevention of $PbSO_4$ crystal formation, achieved via presence of iron sulfate in the electrolyte, therefore stabilizing the PbO_2 electrode.

[0076] It is contemplated, therefore, that lead may be advantageously used as an oxygen evolution anode in contact with an electrolyte (e.g., acidic, alkaline, or neutral pH) containing at least 0.01 M total dissolved iron (optionally at least 0.05 M) in various electrochemical cells, including electrowinning cells (e.g., iron electrowinning cells with OER anodes), acid regeneration cells (e.g., cells with OER anodes and ferric-reducing cathodes), water electrolysis cells (e.g., PEM electrolyzers for hydrogen production). It is further contemplated that lead may be used as anode and/or cathode in a decoupled iron plating cell, defined as an iron electroplating cell, such as an “iron-plating subsystem” or “second electrochemical cell” thereof as described in PCT’732 and in Provis’092, in which ferrous iron is oxidized at the anode. It is further contemplated that in a two-step (or “decoupled”) iron electrowinning system, such as an “iron-plating subsystem” as described in PCT’732 and in Provis’092, at least a portion of “spent” plating anolyte or catholyte may be directed as anolyte to an oxygen-evolving anode of an acid regeneration cell, such as a “dissolution subsystem” or “first electrochemical cell” thereof as described in PCT’732 and in Provis’092.

[0077] Using lead anodes in an iron electrowinning cell may cause incorporation of some quantity of lead into the plated iron. It is found that a ferrous sulfate plating electrolyte saturated with lead ions (optionally having ~30 to 40 micro-molar or about 5 to 10 ppm lead ions) may yield plated iron containing a quantity of Pb from 0.014% to 0.022% by weight. Therefore, plated iron containing a measurable amount (e.g., more than about 3 ppm) of lead may be suggestive of an iron electrowinning process using a lead anode.

[0078] Another challenge conventionally encountered when using lead dioxide electrodes as OER anodes in standard electrowinning processes is the formation of manganese dioxide (MnO_2) in the anolyte during oxygen evolution if dissolved manganese is present in the electrolyte. This MnO_2 does not tend to adhere to the lead dioxide anode and instead precipitates as a solid sludge in the electrolyte and on the electrode surface. While Zn electrowinning processes frequently use the Mn impurities in the ore to "protect" the PbO_2 from the shedding challenges described above, those processes require a very frequent cleaning schedule to remove the excess MnO_2 sludge from the anolyte. Cu electrowinning processes tend to make efforts to minimize Mn concentrations present in the electrolyte to avoid the need for costly or disruptive MnO_2 removal methods. In aspects herein, if, for example, salt solution produced by ore dissolution, such as in a “dissolution subsystem” described in PCT’732 and in Provis’092, is used to provide dissolved iron to the anolyte (“first anolyte”) as described above, that electrolyte may contain some concentration of dissolved Mn, which may concentrate over time.

[0079] It is discovered that because ferrous sulfate very rapidly reacts with and dissolves any solid MnO_2, forming aqueous $MnSO_4$ as a product via electrochemical reduction, ferrous sulfate may be used in-situ in an electrochemical cell to decrease or eliminate solid MnO_2 without reducing cell performance. For example, it is contemplated that if/when MnO_2 is formed in the OER anolyte, then a maintenance procedure may be performed by introducing or producing a quantity of ferrous sulfate adequate to dissolve the MnO_2.

[0080] For example, the (first) anolyte, or (first) anodic chamber, may be flushed or rinsed with a solution having aqueous ferrous salt, such as aqueous ferrous sulfate, to dissolve any solid manganese oxide. As another example, some quantity of solution having aqueous ferrous salt, such as aqueous ferrous sulfate, may be added to the (first) anolyte. For example, ferrous sulfate may be introduced to the anolyte (first anolyte) by directing a quantity of a ferrous-containing solution from a decoupled electrowinning system, such as an “iron-plating subsystem” described in PCT’732 and in Provis’092, into the anode chamber (first anodic chamber) of the acid regenerator, or an electrochemical cell according to aspects disclosed herein. For example, ferrous-containing solutions may include acid-regenerator catholyte and “spent” plating cell anolyte or catholyte, such as an electrolyte, optionally spent electrolyte, from an “iron-plating subsystem” described in PCT’732 and in Provis’092. For example, ferrous sulfate may be introduced periodically or occasionally in the (first) anode chamber using a ferrous sulfate solution that is stored in a separate tank for the sole purpose of cleaning the manganese sludges from the anode chamber. In such approach, the manganese compounds are not put back in the main electrolyte circuit thereby enabling natural separation of manganese impurities from the main circuit.

[0081] Alternatively, or in addition, ferrous sulfate may be produced in-situ in an acid regenerator anode chamber (first anodic chamber) by briefly allowing the cell to self-discharge or by applying a reverse-polarity current to the cell or stack, causing ferric iron in the anolyte to be reduced to ferrous. Such production may be performed with or without flowing anolyte and/or catholyte through the acid regeneration cell/stack.

[0082] Lead electrodes may be made and structured in various ways. In some aspects, a lead electrode may comprise a substantially solid or porous bulk lead structure. The diminished shedding caused by operating a lead electrode in a ferrous (and/or ferric) sulfate electrolyte allows for use of lead anode structures not usable in other systems. For example, in some aspects, a lead electrode may comprise a non-lead substrate supporting one or more layers of lead, including thin and porous layers. The lead may provide a protective layer over a substrate material that may otherwise be susceptible to chemical attack by a liquid electrolyte.

[0083] With reference to FIG. 1, a lead electrode 100 may comprise a porous substrate 102 coated with either a single layer of lead on one face 104, lead coatings on both faces 104 and 106, or a coating covering interior surfaces of a three-dimensional substrate. Such lead coatings may be applied to the substrate surface(s) by electroplating, spray pyrolysis (e.g., spraying the substrate with a liquid containing dissolved lead and heating the substrate to evaporate and/or combust the liquid and/or binder materials, leaving the lead adhered to the substrate surface), dipping the substrate in molten lead and cooling, spraying or painting molten lead on one or both substrate faces, or other processes. Alternatively or in addition, lead may be applied to a solid substrate in a manner selected to impart a microstructured and/or nanostructured surface. For example, lead may be applied by chemical vapor deposition (CVD), physical vapor deposition (PVD), atomic layer deposition (ALD), sol-gel deposition, or any other method. In some cases, a method of applying a lead coating layer may be selected based on a layer thickness to be applied. For example, techniques such as electroplating, spray pyrolysis, PVD, CVD, and ALD may be useful for applying relatively thin layers, while techniques involving dipping, brushing, or spraying molten lead onto a substrate may be useful for thicker layers. In other aspects, thin layer techniques may be used to apply multiple layers to build up a thicker total lead coating.

[0084] The porous substrate 102 may be made of a conductive material such as titanium, graphite, carbon, stainless steel, nickel, or other conductive material suitable for use in the electrolyte of choice (e.g., acidic, alkaline, or neutral). In various aspects, a porous substrate may comprise a foam, woven mesh, nonwoven mesh, expanded metal (e.g., “EXMET"), felt, perforated sheet, or other two-dimensional or three-dimensional structure made of a metal, carbon, graphite, or other material or combination of materials. In some aspects, the substrate may beneficially have sufficient mechanical strength to resist bending, warping, compression, etc. For example, a substrate material may have a compressive yield strength of between about 10 and about 200 MPa, and/or a Young’s modulus of between about 600 and about 1,500 MPa.

[0085] A lead layer may have a thickness of about 50 microns up to about 5 millimeters. In some particular aspects, a lead layer on a porous or three dimensional substrate may have an average or minimum thickness of about 50 microns, about 100 microns, about 500 microns, about 1 mm, about 1.5 mm, about 2 mm, about 2.5 mm, about 3 mm, about 3.5 mm, about 4 mm, about 4.5 mm, or about 5 mm.

[0086] With reference to FIG. 2, a bipolar lead electrode 200 may be made by coating a solid (non-porous and electrolyte-impermeable) substrate with layers of lead 204, 206 on each face of the substrate. The use of lead protective layers may allow for use of lower-cost materials that may be more susceptible to chemical attack from the electrolyte. Optionally, the edge surfaces of the substrate may also be coated with lead, thereby fully encapsulating the substrate in lead. The lead layers 204, 206 are preferably of sufficient thickness and density that liquid electrolyte and dissolved ions are unable to reach the substrate 202.

[0087] The bipolar electrode 200 may further comprise a carbon cathode layer 208 on one face, and a lead anode layer 210 on the opposite face.

[0088] In some aspects, each face of a porous or non-porous substrate 102 or 202 may be coated with lead layers of equal thickness or of different thicknesses. For example, one face 204 may have a thinner or thicker lead layer than the opposite face 206. In some aspects, the lead layers 204, 206 may have thicknesses of between about 0.1 mm and about 2mm.

[0089] In some aspects, a protective layer 204 underlying a carbon cathode 208 may comprise a material other than lead, such as graphite, conductive polymers, conductive graphitized polymers, polymers impregnated with carbon nanotubes, carbon glues, carbon adhesives, or other carbon-based materials of sufficient thickness and density to protect the substrate 202 while providing through-plane and in-plane electrical conductivity.

[0090] The carbon cathode layer 208 may comprise a high surface area structure of carbon, graphite, graphene, or other conductive carbon material. The cathode layer may be provided in a form-factor of a felt, a foam, a papers, a machined or cast graphite sheet, or other structure with a high surface-area face.

[0091] The carbon cathode layer 208 may be conductively adhered to the protective layer 204 (whether lead or other material(s)) by any suitable method that maintains electrical conductivity between the cathode layer 208, the protective layer 204, and the substrate 202. Such techniques may include conductive adhesives, welding, soldering, mechanical compression, or combinations of these or other techniques.

[0092] In some aspects, the lead anode layer 210 may be a portion of the lead layer 206, or may be an additional layer on top of the lead layer 206. For example, the lead layer 206 may have a very low surface area in the interest of forming a dense protective layer. Such a dense low-surface-area layer may provide insufficient electrochemical surface area to catalyze efficient electrochemical oxidation reactions (e.g., oxygen evolution). Therefore, a lead anode layer 210 may be made with a higher surface area than the underlying protective lead layer 206. In various aspects, a high-surface area lead anode layer may be made by producing porous or “spongy” lead on top of the protective layer 206. In some aspects, such porous or spongy lead may be made directly on the protective layer 206, or may be formed separately and adhered to the protective lead layer 206 by welding, adhesives, soldering, mechanical compression, or combinations of these or other techniques. US Patent 778,894 (granted in 1905) describes a process for making spongy lead which may be used to form a high surface area lead anode layer 210.

[0093] In other aspects, a high surface area lead anode layer 210 may be made by laminating a lead electrode 100 of the type described in FIG. 1 onto the protective lead layer 206. Such lamination may be performed by heating the protective lead layer sufficiently to soften it and then mechanically pressing the lead electrode 100 into the protective lead layer. Alternatively, conductive adhesives, welding, or other techniques may be used to attach a lead electrode 100 to a protective lead layer while maintaining electrical conductivity between the lead layer 206 and the lead electrode 100.

[0094] The solid substrate 202 may comprise a solid single-sheet, a plate, or a laminated structure configured to provide electrical conductivity and mechanical support for the lead layers 204, 206 while also providing mechanical strength when the bipolar electrode is compressed in a cell-stack. Alternatively, in some aspects a solid substrate may comprise a solid lead sheet or plate. The term “solid” as used herein refers to a non-porous material or a material impermeable to anolyte, catholyte, or both.

[0095] In various aspects, the material composition and properties of the substrate 202, lead deposition techniques, and lead layer thicknesses may include those described above for use with porous substrates. The solid substrate 202 may be made of a conductive material such as titanium, graphite, carbon, stainless steel, nickel, or other conductive material suitable for use in the electrolyte of choice (e.g., acidic, alkaline, or neutral). In some aspects, the substrate may beneficially have sufficient mechanical strength to resist bending, warping, compression, etc. For example, a substrate material may have a compressive yield strength of between about 10 and about 200 MPa, and/or a Young’s modulus of between about 600 and about 1,500 MPa.

[0096] With reference to FIG. 3, in some aspects a series of bipolar electrodes 200 may be combined in electrical series in a bipolar cell-stack 300. As shown, an impermeable non-porous, conductive substrate (e.g., 202 of FIG. 2) may form a bipolar plate 302 when stacked in a bipolar cell. The bipolar plate 302 is so-named because it has different or opposite polarity charge on opposing faces, such as a positive charge on its anode-adjacent face and a negative charge on its cathode-adjacent face.

[0097] In FIG. 3, each bipolar plate 302 may be a substrate 202 of the type described with reference to FIG. 2. Similarly, each bipolar plate 302 may be coated with a cathode-side protective layer 304 and an anode-side protective layer 306. Furthermore, each cathode-side protective layer 304 may be overlayed by a cathode layer 308 and each anode-side protective layer may be overlayed by an anode layer 310.

[0098] Each anode layer 310 is separated from an adjacent cathode layer 308 by a separator membrane 316 (which may be a PEM, AEM, or microporous separator). In a bipolar stack 300, end plates 320 and 321 may be provided to apply mechanical compression and electrical conductivity. An anode-side end-plate 320 may be overlayed (coated or simply mechanically covered) with a protective layer 326 (e.g., of lead), which may be overlayed by an end-anode 326. A cathode-side end-plate 321 may be overlayed with a protective layer 324 (e.g., of lead or other material as described above), which may be overlayed (coated or simply mechanically covered) with an end-cathode layer 308.

[0099] In some aspects, a bipolar stack 300 may also include electrically-conductive spacer layers or flow field layers (not shown in FIG. 3) through which fluid(s) may flow. Such fluids may include liquid electrolyte, gaseous reactants, gaseous electrolysis products, etc. Alternatively, flow fields, spacers, or other fluid flow channels may be provided as features of the anode layers 310 and cathode layers 308 themselves. Anolyte and catholyte (and any other reactant) may be flowed through each electrode chamber in a common direction or in opposite (or orthogonal) directions as desired.

[0100] In some aspects, a bipolar stack 300 such as that shown in FIG. 3 may be configured as an acid regeneration cell as described in PCT’732 and in Provis’092. In such aspects, an iron sulfate anolyte solution may be flowed through the anode chambers. The anolyte which may contain predominantly ferric sulfate as any ferrous ions present in the anolyte will tend to be oxidized to the ferric state. As described in PCT’732 and in Provis’092, the catholyte may contain a mix of ferric and ferrous sulfate, depending on the stage of dissolution and reduction.

[0101] FIG. 4 is a schematic diagram illustrating a cross-sectional view of an exemplary bipolar electrode structure incorporating lead structures according to some aspects herein. As shown in FIG. 4, the substrate (e.g., 202) may be formed of stainless steel. Protective lead sheets (e.g., examples of layers 204 and 206) may be used on each of the anode-facing and cathode-facing sides of the substrate. A cathode, such as a carbon electrode, may be deposited on the lead sheet on the cathode-facing side of the substrate. A lead anode may be deposited on the lead sheet on the anode-facing side of the substrate. When used as an “acid regenerator” cell, ferric-to-ferrous reduction may be performed on the carbon cathode and water oxidation may be performed on the lead anode. In other aspects, different reactions may be performed at the anode and/or cathode.

[0102] In various aspects, a lead coating, layer, or bulk structure as described in the various examples above may also comprise additives or dopants or alloying elements such as silver, tin, calcium, cobalt, cadmium, antimony, copper, strontium, barium, titanium, or other metal or nonmetal elements or compounds.

[0103] In some aspects, lead anodes in contact with an anolyte solution containing iron sulfate may be configured as a monopolar cell-stack.

[0104] In various aspects, lead anodes in contact with an anolyte solution containing iron sulfate may be used in iron electroplating cells such as those described in PCT’732 and in Provis’092 with reference to FIG. 1A, FIG. 1B, FIG. 3, FIG. 4, and others therein.

[0105] In various aspects, the first anode (lead anode) is a high surface area lead anode. A high surface area lead anode may be microstructured and/or nanostructured. The high surface area lead anode, or lead microstructures and/or nanostructures thereof, may be electroplated. For example, electroplating high surface area lead anode may include high current density (e.g., greater than about 50 mA/cm^2 in some aspects) electroplating of lead on the lead protective layer or another substrate and low amounts or removal of any leveler additives present in an electroplating electrolyte used to electroplate a high surface area lead anode. Microstructures and/or nanostructures may be introduced onto a lead surface (e.g., on a lead protective layer or on an additional lead anode layer) via surface roughening such as electrochemical cycling and/or mechanical techniques such as by cutting grooves, sandblasting, laser etching, chemical etching, and others. In some aspects, the lead anode may be or comprise a catalyst coated membrane (CCM) comprising a lead catalyst layer coated onto a membrane surface.

[0106] In various aspects, the bipolar stack may comprise zero-gap bipolar stack. For example, in at least some of the electrochemical cells, a first anode and a first cathode may be directly in contact with a separator membrane having a thickness of less than 2 mm, less than 1 mm, less than 0.5mm, less than 0.3mm, or less than 0.2 mm.

[0107] In other aspects, lead anodes in contact with an anolyte solution containing iron sulfate may be used in copper electrowinning cells in which oxygen is evolved at an anode and copper metal is plated at a cathode. Some copper electrowinning cells use a single electrolyte with no separator between anode and cathode. Therefore, in such cases, “anolyte” and “catholyte” are the same solution.

[0108] Aspects explicitly contemplated include an electrochemical cell with a lead oxide electrode in contact with an electrolyte with at least 0.01 mol/l or at least 0.05 mol/l concentration of iron (ferric or ferrous or total Fe) salt, such as iron sulfate or iron chloride, the lead electrode operating:

(1) As anode performing OER;

(2) As anode performing Fe^{2+} to Fe^{3+} oxidation (e.g., in an acid regenerator); and/or

(3) As cathode performing Fe^{3+} to Fe^{2+} reduction (e.g., in an acid regenerator)

[0109] Aspects explicitly contemplated include operating an electrochemical cell with an oxygen-evolving lead (or lead dioxide) anode in contact with an anolyte solution containing at least 0.01 mol/l total dissolved iron, then prior to shutdown reversing polarity of the cell and converting at least a portion of Fe^{3+} to Fe^{2+} prior to shutting off power to the cell.

[0110] Aspects explicitly contemplated include, in a two-step iron conversion system, such as systems described in PCT’732 and in Provis’092, directing a spent electrolyte (e.g., plating anolyte and/or plating catholyte) from a metal electroplating cell to the acid-regenerator anode chamber (first anodic chamber), and operating the acid-regenerator (electrochemical cell according to embodiments and aspects herein) to generate O_2 in the anode.

[0111] Aspects explicitly contemplated include periodically directing a solution containing at least 0.01 mol/l ferrous iron into an OER anode chamber (first anodic chamber) containing solid MnO_2 sludge to dissolve the MnO_2. For example, preferably for some applications, there is a 1:1, or greater, molar ratio of aqueous ferrous ions in the anolyte (first anolyte) to MnO_2 in the anodic chamber or MnO_2 exposed to the anolyte (first anolyte). For example, preferably for some applications, there is a 2:1, or greater, molar ratio of aqueous ferrous ions in the anolyte (first anolyte) to MnO_2 in the anodic chamber or MnO_2 exposed to the anolyte (first anolyte). For example, preferably for some applications, there is a 3:1, or greater, molar ratio of aqueous ferrous ions in the anolyte (first anolyte) to MnO_2 in the anodic chamber or MnO_2 exposed to the anolyte (first anolyte).

[0112] Aspects explicitly contemplated include producing ferrous iron in an OER anode chamber (first anodic chamber) containing a quantity of solid MnO_2 sludge by electrochemically reducing a quantity of dissolved ferric iron.

Stabilized Lead Anodes in Acid Regeneration

[0113] FIG. 5 is a schematic diagram illustrating an exemplary system 500, according to aspects herein, having electrochemical cell 580. The cell 580 may be substantially similar to the “acid regeneration” cell as described in further detail in PCT’732 and below herein. The cathode of cell 580 performs an electrochemical reduction of Fe^{3+} ions to Fe^{2+} ions in the catholyte. The anode of cell 580 performs an electrochemical oxidation of water to oxygen, otherwise referred to as the oxygen evolution reaction (OER). A proton exchange membrane (PEM), according to some aspects, separates the catholyte and anolyte compartments.

[0114] The catholyte is shown fluidically connected to a catholyte circulation tank 570, and may contain an aqueous acidic solution containing a mixture of dissolved ferric (Fe^{3+}) and ferrous (Fe^{2+}) ions. In various embodiments and aspects, the ferric and ferrous ions may be supplied to the catholyte as an aqueous solution or as a soluble solid contacted by the catholyte so as to dissolve the iron-bearing materials into the solution as described in various examples in PCT’732 and herein.

[0115] The anolyte (or anode electrolyte) is shown fluidically connected to an anolyte circulation tank 560. In some aspects, the anolyte may be an aqueous acid solution containing a concentration of iron cations within the ranges described herein.

[0116] In various aspects or aspects, electrolytes may be recirculated between their respective half-cells and storage tanks. In some aspects, reactants (e.g., dissolved or soluble iron and water) may be added to the electrolyte streams via the tanks or directly into the respective half-cell compartments.

[0117] In some circumstances, iron cations (ferric or ferrous) from the anolyte may cross or become lodged in the separator membrane separating the anolyte from the catholyte, decreasing the availability of iron cations for the lead anode stabilization function as described herein. As a result, the concentration of iron in the anolyte may fall too low to provide the stabilization function as described herein. In various embodiments and aspects, iron cations lost from the anolyte may be replenished by periodically or continuously "dosing" additional iron into the anolyte by one or more mechanisms.

[0118] Optionally, the anolyte may be dosed with iron cations to replenish, maintain, or establish a target or PbO_2-electrode stabilizing concentration of iron cation, or in aspects of iron (ferric and/or ferrous) sulfate. Inputs 501, 502, and 503 and solid iron source 505 represent optional sources or methods for dosing the catholyte with iron cations. For example, optionally, in some aspects, an aqueous dosing-solution and/or one or more solid iron-containing materials may be provided via input 503. For example, optionally, in some aspects, the anolyte may be dosed by providing an anolyte from an iron-electroplating cell via input 501. For example, optionally, in some aspects, the anolyte may be dosed by providing a catholyte from an iron-electroplating cell via input 502. For example, optionally, in some aspects, the anolyte may be dosed by providing a solid iron source 505 which may dissolve, rapidly or slowly, as may be appropriate for an application, into the anolyte.

[0119] System 500 optionally includes tap 510 for providing liquid and/or solid to the anolyte and/or for extracting anolyte. Optionally, for example, inputs 501, 502, and 503 may be provided to/via tap 510 rather than directly into tank 560. System 5 includes an "iron extraction" mechanism. Optionally, iron extraction mechanism may include extraction of a ferrous-containing solution and providing said ferrous-containing solution to an iron electroplating cell in order to extract metallic iron. Optionally, iron extraction mechanism may include extraction of a ferrous-containing solution and precipitating an iron-containing material, such as an iron-containing salt, from said extracted solution, thereby extracting iron from system 500.

[0120] In some embodiments and aspects, iron may be extracted from the catholyte as a solid. In some aspects, iron may be extracted from the catholyte by precipitating or crystallizing an iron salt, an iron oxide, or an iron hydroxide from the solution. Alternatively, the ferrous-rich catholyte iron may be directed to an electroplating cell in which iron may be electroplated from the solution.

Single Step Iron Conversion Using Lead Anodes

[0121] FIG. 6 is a schematic diagram illustrating an exemplary system 600 for electroplating metallic iron from an aqueous solution containing dissolved iron. According to aspects herein, the system 600 includes an electrochemical cell 680. The cathode 634 of cell 680 performs an iron electroplating reaction, or an electrochemical reduction of aqueous Fe^{2+} ions and/or Fe^{3+} in the catholyte to metallic iron (Fe^0). The cathode 634 may be made of any conductive material suitable for acting as a substrate or support onto which metallic iron may be electroplated.

[0122] In some aspects, any Fe^{3+} “ferric” ions present in the catholyte solution may be advantageously reduced to the Fe^{2+} “ferrous” oxidation state prior to electroplating. In some aspects, ferric ions may be reduced to ferrous ions using an acid regeneration cell such as that described above with reference to FIG. 5. In other aspects or aspects, aqueous ferric ions may be reduced to aqueous ferrous ions by contacting the solution with a reducing gas such as hydrogen sulfide or sulfur dioxide. In still other aspects, ferric ions may be reduced to ferrous ions by contacting the solution with metallic iron.

[0123] The anode 636 of cell 680 performs an electrochemical oxidation of water to produce oxygen and acid in the anode electrolyte (anolyte). The anode 363 may be a lead dioxide anode for catalyzing the oxygen evolution reaction (OER). The anolyte may be an aqueous acid solution containing dissolved iron cations in concentrations described herein as suitable for stabilizing the lead dioxide electrode. The anolyte is shown fluidically connected to an anolyte tank 660 and the catholyte is shown fluidically connected to a catholyte tank 670.

[0124] In various aspects, acid produced in the anolyte may be removed or consumed such as in a dissolution reaction for converting an iron-containing feedstock material into an aqueous iron-containing solution.

[0125] According to some aspects, an anion exchange membrane (AEM), may separate the catholyte and anolyte. Some anion exchange membranes may tend to “leak” cations such as aqueous iron cations from the anolyte to the catholyte, causing a decrease in the concentration of iron in the anolyte over time. As a result, the concentration of iron in the anolyte may fall too low to provide the stabilization function as described herein. In various embodiments and aspects, iron ions lost from the anolyte may be replenished by periodically or continuously “dosing” additional iron into the anolyte by one or more mechanisms.

[0126] Optionally, the anolyte may be dosed with iron cations to replenish, maintain, or establish a target or PbO_2-electrode stabilizing concentration of iron cation, or in aspects of iron (ferric and/or ferrous) sulfate. Input 604 and solid iron source 605 represent optional sources or methods for dosing the catholyte with iron cations. For example, optionally, in some aspects, an aqueous dosing-solution and/or one or more solid iron-containing materials may be provided via input 604. For example, optionally, in some aspects, the anolyte may be dosed by providing a solid iron source 605 which may dissolve, rapidly or slowly, as may be appropriate for an application, into the anolyte. System 500 optionally includes tap 610 for providing liquid and/or solid to the anolyte and/or for extracting anolyte. Optionally, for example, input 604 may be provided to/via tap 610 rather than directly into tank 660. Tap 612 is optional and likewise may be used to provide liquid and/or solid to the catholyte and/or for extracting catholyte.

Two-Step Iron Conversion Using Lead Anodes

[0127] With reference to FIG. 7-11, in some aspects, an iron conversion system 700, 800, 900, 1000, or 1100 may be separated into two main subsystems: a dissolution subsystem 102 and a plating subsystem 130. The dissolution subsystem 102 may generally be configured to dissolve iron feedstock materials 152 efficiently and relatively quickly at low temperatures to form a dissolved-iron solution 122. The dissolution subsystem 102 may be further configured to convert ferric (Fe^{3+}) ions in the dissolved-iron solution 122 to ferrous (Fe^{2+}) ions in an “acid regeneration” cell 104 prior to the dissolved-iron solution 122 being transferred to a plating cell 132 in the plating subsystem 130. The plating subsystem 130 may generally be configured to electrolytically plate the dissolved ferrous iron into a solid form that may be removed at 148 and sold as relatively pure iron and preparing the plating subsystem 130 for further plating. Once the dissolved-iron solution 122 is sufficiently depleted of ferrous iron by the plating cell 132, it may be returned to the dissolution subsystem 102 for use in subsequent dissolutions coupled with the acid regeneration cell 104.

[0128] As shown, the acid regeneration cell 104 may be configured to reduce ferric ions (produced during dissolution of feedstocks 120) to ferrous ions in a cathode chamber 106 (first cathode chamber) while oxidizing a consumable reactant, supplied from a reactant source 116, at the anode 112 (first anode). In some aspects, the anodic reactant may be water and the anode 112 (first anode) may evolve oxygen 111 from an anode chamber 110 (first anode chamber). In some aspects, water 154 is added to anode chamber 110 to replenish water consumed by the OER.

[0129] In various aspects, one or more treatment steps 124, 126, 128, 127 may be performed to adjust the dissolved-iron solution 122 to remove materials or to increase or decrease concentrations of one or more components of the solution. For example, a treatment step 124 may comprise directing the dissolved-iron solution 122 exiting a dissolution tank 118 through a treatment vessel configured to remove solid particulates and/or colloidal dispersions of materials released during dissolution. In some cases, silica from iron feedstocks may enter the dissolved-iron solution 122 as a gel-like mass in a colloidal dispersion, which may interfere with operations within an acid regeneration cell 104. A treatment step 124 may comprise contacting the solution with a flocculant such as polyethylene glycol, polyethylene oxide, or other flocculant known to be effective at removing colloidal silica from a solution. The treatment step 124 may further comprise any other solid-liquid separation techniques, devices, or additives as needed to remove materials that may be detrimental to operations in the acid regeneration cell 104.

[0130] The plating subsystem 130 may comprise a plating cell 132 with a cathode electrode 136 (second cathode) in a cathode chamber 134 (second cathode chamber) that is fluidically coupled to a catholyte tank 142 (second catholyte tank) and an anode electrode 140 (second anode) in an anode chamber 138 (second anode chamber) that is fluidically coupled to an anolyte tank 144 (second anolyte tank). Ferrous ions may be reduced to plated metallic iron in the cathode chamber 134 (second cathode chamber) of the plating cell 132. An oxidation reaction, such as OER or ferrous ions to ferric ions, is performed in the anode chamber 138 (second anode chamber) of the plating cell 132.

[0131] In some aspects the plating reaction is performed against an Fe^{2+} to Fe^{3+} oxidation reaction, such as shown in systems 700 and 900 of FIGs. 7 and 9, respectively. In such aspects, such as in systems 700 or 900, the dissolved iron solution 122 may be divided into a plating anolyte and a plating catholyte. The plating anolyte may be recirculated between a plating anolyte tank 144 and the anode chamber 138 of the plating cell 132 within which species in the plating anolyte will be oxidized at the anode electrode 140. The plating catholyte may be recirculated between a plating catholyte tank 142 and the cathode chamber 134 of the plating cell 132 where iron will be electroplated onto the cathode electrode 108. Iron may be removed at 148 from the plating cell 132 by various methods, examples of which are described below. In some cases, hydrogen gas may be evolved 146 from the plating cell cathode chamber 134. Such hydrogen gas may be captured and stored for use in other sub-processes described herein.

[0132] In some aspects the plating reaction is performed against an oxygen evolution reaction (OER), such as shown in systems 800 and 1000 of FIGs. 8 and 10, respectively.

[0133] In some aspects, the anolyte of the acid regeneration cell (first anolyte) of the dissolution subsystem comprises a concentration of aqueous iron cations. In some aspects, the electrochemical oxidation reaction performed in the anolyte of the plating cell (second anolyte) of the plating subsystem is an oxygen evolution reaction, such as shown in FIGs. 8 (system 800) and 10 (system 1000), wherein the second anolyte comprises a concentration of aqueous iron cations. In some aspects, aqueous iron cations may be depleted from the first anolyte over time via one or more processes, such as, but not limited to: leakage of aqueous iron cations through the membrane into the respective catholyte; entrapment of aqueous iron cations via chemical and/or physical mechanisms in or at components of the cell, such as in the membrane or in pores of a porous lead electrode whereby optionally the iron cations are lost when the porous electrode or anodic chamber is flushed or rinsed; side or parasitic reactions; or other(s). In aspects, therefore, the concentration of aqueous iron cations in the first anolyte, in the second anolyte (such as in systems 800 and 1000, for example), or both the first anolyte and the second anolyte (such as in systems 800 and 1000, for example) may be maintained within a stabilizing-concentration range during one or more temporary periods of operation the acid regeneration cell, whereby operation refers to the cell operating under an operating voltage such that an intended electrochemical reduction occurs at the cathode and an intended electrochemical oxidation, such as OER, occurs at the cathode. Generally, in aspects herein, a cell under open circuit voltage is not in a state of operation. In aspects, the concentration of aqueous iron cations in the first anolyte, in the second anolyte (such as in systems 800 and 1000, for example), or both the first anolyte and the second anolyte (such as in systems 800 and 1000, for example) may be maintained within a stabilizing-concentration range an entirety or at least a majority of the operation of the acid regeneration cell.

[0134] Establishing and/or maintaining the aqueous iron cation concentration within the stabilizing-concentration in the first anolyte and/or in the second anolyte may comprise dosing the first anolyte and/or the second anolyte with a liquid iron source and/or a solid iron source. The dosing may be performed continuously and/or via one or more discrete events. The dosing may be performed directly, such as by providing a liquid and/or solid iron source directly to the anodic chamber or anolyte thereof, and/or indirectly, such as by providing a liquid and/or solid iron source to a circulation tank fluidically connected to the anodic chamber or anolyte thereof. In some aspects, a liquid iron source is an aqueous solution (also referred to herein as a dosing-solution) comprising aqueous iron cations. The dosing-solution, as described throughout herein, may comprise a spent or used electrolyte from a different cell and/or leachate from a metal and/or ore processing system, an aqueous solution formed by dissolving one or more iron-containing materials therein, such as by dissolving an iron-containing salt or oxide in said solution and/or flowing the solution over an iron-containing substrate, or any combination of these.

[0135] Optionally, the first anolyte may be dosed directly and/or indirectly with an aqueous dosing-solution and/or a solid iron source via input 703, 803, 903, 1003, or 1103. Optionally, in aspects wherein an OER is performed in the second anolyte, the second anolyte may be dosed directly and/or indirectly with an aqueous dosing-solution and/or a solid iron source via input 804 or 1004. For example, optionally, a solid iron containing material, such as an iron salt or oxide, may be provided via input 703, 803, 903, 1003, 804, or 1004. For example, optionally, an aqueous dosing-solution may be provided via input 703, 803, 903, 1003, 804, or 1004. In some aspects, directly dosing corresponds to providing a liquid and/or solid iron source directly into the anodic chamber or anolyte thereof. In some aspects, indirectly dosing corresponds to providing a liquid and/or solid iron source to a circulation tank fluidically connected to the anodic chamber or anolyte thereof.

[0136] Optionally, the first anolyte may be dosed by including a solid iron source 705, 805, 905, or 1005 in contact with the first anolyte. Optionally, conditions of the first anolyte (such as but not limited to temperature) and the solid iron source (such as but not limited to its composition) 705, 805, 905, 1005, or 1105 are selected or controlled such that said solid iron source dissolves slowly or at a selected rate during cell operation in order to maintain the stabilizing concentration of aqueous iron cations. Solid iron source 705, 805, 905, or 1005 may be provided in the first anodic chamber, in a circulation tank fluidically connected to first anodic chamber or first anolyte thereof, or both.

[0137] Optionally, in aspects wherein an OER is performed in the second anolyte, the second anolyte may be dosed by including a solid iron source 805 or 1005 in contact with the second anolyte. Optionally, conditions of the second anolyte (such as but not limited to temperature) and the solid iron source (such as but not limited to its composition) 805 or 1005 are selected or controlled such that said solid iron source dissolves slowly or at a selected rate during cell operation in order to maintain the stabilizing concentration of aqueous iron cations. Solid iron source 805 or 1005 may be provided in the second anodic chamber, in a circulation tank 810 or 1010 fluidically connected to second anodic chamber or first anolyte thereof, or both.

[0138] Optionally, in aspects wherein the iron reduction/plating reaction is performed against an iron cation oxidation (Fe^{2+} to Fe^{3+}) reaction, the first anolyte may be dosed with an aqueous dosing-solution comprising a used or spent anolyte of the plating cell (second anolyte), such as depicted in FIGs. 7 and 9, such as via input 701 or 901.

[0139] Optionally, the first anolyte may be dosed with an aqueous dosing-solution comprising a used or spent catholyte of the plating cell (second catholyte), such as depicted in FIGs. 7-10, such as via input 702, 802, 902, 1002, or 1102.

[0140] Optionally, in some aspects, metallic iron may be provided to the first catholyte or the first catholyte may be exposed to metallic iron to consume protons (acid) that leak through the AEM from the first anolyte. Optionally, in some aspects, metallic iron may be provided to the second catholyte or the second catholyte may be exposed to metallic iron to consume protons (acid) that leak through the separator from the second anolyte.

Various additional aspects:

[0141] Various aspects are contemplated herein, several of which are set forth in the paragraphs below. It is explicitly contemplated that any aspect or portion thereof can be combined to form an aspect. In addition, it is explicitly contemplated that: any reference to aspect 1 includes reference to aspects 1a, 1b, 1c, and/or 1d, any reference to aspect 5 includes reference to aspects 5a and 5b, and so on (any reference to an aspect includes reference to that aspects lettered versions). Moreover, the terms “any preceding aspect” and “any one of the preceding aspects” means any aspect that appears prior to the aspect that contains such phrase (in other words, the sentence “Aspect 32: The method or system of any preceding aspect…” means that any aspect prior to aspect 32 is referenced, including aspects 1a through 31). For example, it is contemplated that, optionally, any system or method of any the below aspects may be useful with or combined with any other aspect provided below. Further, for example, it is contemplated that any aspect described above may, optionally, be combined with any of the below listed aspects.

[0142] Aspect 1a: A method for stabilizing a lead anode, the method comprising:

operating an electrochemical cell comprising performing electrochemical reduction at a first cathode and electrochemical oxidation at a first anode;

wherein:

the electrochemical cell comprises a first anodic chamber having a first anolyte in contact with the first anode, a first cathodic chamber having a first catholyte in contact with the first cathode, and a first separator separating the first anolyte from the first catholyte;

the first anode is a lead electrode;

each of the first anolyte and the first catholyte independently comprises aqueous iron cations and aqueous anions; and

the first anolyte comprises the aqueous iron cations at a concentration of at least approximately 0.01 M or a concentration selected from the range of approximately 0.01 M (optionally approximately 0.02 M, optionally approximately 0.03 M, optionally approximately 0.04 M, optionally approximately 0.05 M, optionally approximately 0.06 M, optionally approximately 0.07 M, optionally approximately 0.08 M, optionally approximately 0.09 M, optionally approximately 0.095 M, optionally approximately 0.099 M, optionally approximately 0.1 M) to 0.5 M (optionally approximately 0.49 M, optionally approximately 0.48 M, optionally approximately 0.47 M, optionally approximately 0.46 M, optionally approximately 0.45 M, optionally approximately 0.44 M, optionally approximately 0.43 M, optionally approximately 0.42 M, optionally approximately 0.41 M, optionally approximately 0.40 M, optionally approximately 0.39 M, optionally approximately 0.38 M), such as optionally a concentration selected from the range of approximately 0.01 M to approximately 0.45 M, optionally a concentration selected from the range of approximately 0.01 M to approximately 0.4 M, optionally a concentration selected from the range of approximately 0.01 M to approximately 0.44 M, optionally a concentration selected from the range of approximately 0.01 M to approximately 0.445 M, optionally a concentration selected from the range of approximately 0.01 M to approximately 0.440 M, optionally selected from the range of approximately 0.02 M to approximately 0.08 M.

[0143] Aspect 1b: A system for stabilizing a lead anode, the system comprising:

an electrochemical cell comprising:

a first anodic chamber having a first anolyte in contact with the first anode, a first cathodic chamber having a first catholyte in contact with the first cathode, and a first separator separating the first anolyte from the first catholyte;

wherein:

the first anode is a lead electrode;

each of the first anolyte and the first catholyte independently comprises aqueous iron cations and aqueous anions; and

the first anolyte comprises the aqueous iron cations at a concentration of at least approximately 0.01 M or a concentration selected from the range of approximately 0.01 M (optionally approximately 0.02 M, optionally approximately 0.03 M, optionally approximately 0.04 M, optionally approximately 0.05 M, optionally approximately 0.06 M, optionally approximately 0.07 M, optionally approximately 0.08 M, optionally approximately 0.09 M, optionally approximately 0.095 M, optionally approximately 0.099 M, optionally approximately 0.1 M) to approximately 0.5 M (optionally approximately 0.49 M, optionally approximately 0.48 M, optionally approximately 0.47 M, optionally approximately 0.46 M, optionally approximately 0.45 M, optionally approximately 0.44 M, optionally approximately 0.43 M, optionally approximately 0.42 M, optionally approximately 0.41 M, optionally approximately 0.40 M, optionally approximately 0.39 M, optionally approximately 0.38 M), such as optionally a concentration selected from the range of approximately 0.01 M to approximately 0.45 M, optionally a concentration selected from the range of approximately 0.01 M to approximately 0.4 M, optionally a concentration selected from the range of approximately 0.01 M to approximately 0.44 M, optionally a concentration selected from the range of approximately 0.01 M to approximately 0.445 M, optionally a concentration selected from the range of approximately 0.01 M to approximately 0.440 M, optionally selected from the range of approximately 0.02 M to approximately 0.08 M.

[0144] Aspect 1c: A method for stabilizing a lead anode, the method comprising:

operating an electrochemical cell comprising performing electrochemical reduction at a first cathode and electrochemical oxidation at a first anode; and

recycling a second electrolyte from a metal electroplating cell to the first anolyte, the second electrolyte having aqueous iron cations;

wherein:

the electrochemical cell comprises a first anodic chamber having a first anolyte in contact with the first anode, a first cathodic chamber having a first catholyte in contact with the first cathode, and a first separator separating the first anolyte from the first catholyte;

the first anode is a lead electrode;

each of the first anolyte and the first catholyte independently comprises aqueous iron cations and aqueous anions; and

the first anolyte comprises the aqueous iron cations at a concentration of at least approximately 0.01 M or a concentration selected from the range of approximately 0.01 M (optionally approximately 0.02 M, optionally approximately 0.03 M, optionally approximately 0.04 M, optionally approximately 0.05 M, optionally approximately 0.06 M, optionally approximately 0.07 M, optionally approximately 0.08 M, optionally approximately 0.09 M, optionally approximately 0.095 M, optionally approximately 0.099 M, optionally approximately 0.1 M) to approximately 0.5 M (optionally approximately 0.49 M, optionally approximately 0.48 M, optionally approximately 0.47 M, optionally approximately 0.46 M, optionally approximately 0.45 M, optionally approximately 0.44 M, optionally approximately 0.43 M, optionally approximately 0.42 M, optionally approximately 0.41 M, optionally approximately 0.40 M, optionally approximately 0.39 M, optionally approximately 0.38 M), such as optionally a concentration selected from the range of approximately 0.01 M to approximately 0.45 M, optionally a concentration selected from the range of approximately 0.01 M to approximately 0.4 M, optionally a concentration selected from the range of approximately 0.01 M to approximately 0.44 M, optionally a concentration selected from the range of approximately 0.01 M to approximately 0.445 M, optionally a concentration selected from the range of approximately 0.01 M to approximately 0.440 M, optionally selected from the range of approximately 0.02 M to approximately 0.08 M.

[0145] Aspect 1d: A system for stabilizing a lead anode, the system comprising:

an electrochemical cell comprising:

a first anodic chamber having a first anolyte in contact with the first anode, a first cathodic chamber having a first catholyte in contact with the first cathode, and a first separator separating the first anolyte from the first catholyte; and

a metal electroplating cell; and

an electrolyte-recycling subsystem for recycling an electrolyte from the metal electroplating cell to the first anolyte;

wherein:

the first anode is a lead electrode;

each of the first anolyte and the first catholyte independently comprises aqueous iron cations and aqueous anions; and

the first anolyte comprises the aqueous iron cations at a concentration of at least approximately 0.01 M or a concentration selected from the range of approximately 0.01 M (optionally approximately 0.02 M, optionally approximately 0.03 M, optionally approximately 0.02 M, optionally approximately 0.03 M, optionally approximately 0.04 M, optionally approximately 0.05 M, optionally approximately 0.06 M, optionally approximately 0.07 M, optionally approximately 0.08 M, optionally approximately 0.09 M, optionally approximately 0.095 M, optionally approximately 0.099 M, optionally approximately 0.1 M) to approximately 0.5 M (optionally approximately 0.49 M, optionally approximately 0.48 M, optionally approximately 0.47 M, optionally approximately 0.46 M, optionally approximately 0.45 M, optionally approximately 0.44 M, optionally approximately 0.43 M, optionally approximately 0.42 M, optionally approximately 0.41 M, optionally approximately 0.40 M, optionally approximately 0.39 M, optionally approximately 0.38 M), such as optionally a concentration selected from the range of approximately 0.01 M to approximately 0.45 M, optionally a concentration selected from the range of approximately 0.01 M to approximately 0.4 M, optionally a concentration selected from the range of approximately 0.01 M to approximately 0.44 M, optionally a concentration selected from the range of approximately 0.01 M to approximately 0.445 M, optionally a concentration selected from the range of approximately 0.01 M to approximately 0.440 M, optionally selected from the range of approximately 0.02 M to approximately 0.08 M.

[0146] Aspect 1e: The method or system of Aspect 1, such as of any one of Aspects 1a-1d, wherein the concentration of aqueous iron cations in the first anolyte is selected from the range of approximately 0.01 M to approximately 0.1 M, wherein any value and range therebetween is explicitly contemplated and disclosed herein, such as optionally approximately 0.02 M to approximately 0.09 M or optionally approximately 0.03 M to approximately 0.08 M or optionally approximately 0.04 M to approximately 0.07 M or optionally approximately 0.03 M to approximately 0.08 M or optionally approximately 0.05 M..

[0147] Aspect 2a: The method or system of Aspect 1, wherein the second electrolyte comprises a catholyte and/or an anolyte from an iron electroplating cell, wherein the second electrolyte comprises aqueous iron ions. Aspect 2b: The method or system of Aspect 1 or 2a, wherein the second electrolyte comprises a spent catholyte and/or spent anolyte from an iron electroplating cell.

[0148] Aspect 3: The method or system of any preceding aspect, wherein performing electrochemical oxidation comprises an oxygen evolution reaction (OER) at the first anode.

[0149] Aspect 4: The method or system of any preceding aspect, wherein the first anolyte comprises aqueous sulfate anions.

[0150] Aspect 5a: A method for stabilizing a lead anode, the method comprising:

operating an electrochemical cell comprising performing electrochemical reduction at a first cathode and an oxygen evolution reaction (OER) at a first anode;

wherein:

the electrochemical cell comprises a first anodic chamber having a first anolyte in contact with the first anode, a first cathodic chamber having a first catholyte in contact with the first cathode, and a first separator separating the first anolyte from the first catholyte;

the first anode is a lead electrode;

each of the first anolyte and the first catholyte independently comprises aqueous iron cations and aqueous anions; and

the first anolyte comprises aqueous iron sulfate at a concentration of at least approximately 0.01 M or a concentration selected from the range of approximately 0.01 M (optionally approximately 0.02 M, optionally approximately 0.03 M, optionally approximately 0.04 M, optionally approximately 0.05 M, optionally approximately 0.06 M, optionally approximately 0.07 M, optionally approximately 0.08 M, optionally approximately 0.09 M, optionally approximately 0.095 M, optionally approximately 0.099 M, optionally approximately 0.1 M) to approximately 0.5 M (optionally approximately 0.49 M, optionally approximately 0.48 M, optionally approximately 0.47 M, optionally approximately 0.46 M, optionally approximately 0.45 M, optionally approximately 0.44 M, optionally approximately 0.43 M, optionally approximately 0.42 M, optionally approximately 0.41 M, optionally approximately 0.40 M, optionally approximately 0.39 M, optionally approximately 0.38 M), such as optionally a concentration selected from the range of approximately 0.01 M to approximately 0.45 M, optionally a concentration selected from the range of approximately 0.01 M to approximately 0.4 M, optionally a concentration selected from the range of approximately 0.01 M to approximately 0.44 M, optionally a concentration selected from the range of approximately 0.01 M to approximately 0.445 M, optionally a concentration selected from the range of approximately 0.01 M to approximately 0.440 M, optionally selected from the range of approximately 0.02 M to approximately 0.08 M.

[0151] Aspect 5b: A system for stabilizing a lead anode, the system comprising:

an electrochemical cell comprising:

a first anodic chamber having a first anolyte in contact with the first anode, a first cathodic chamber having a first catholyte in contact with the first cathode, and a first separator separating the first anolyte from the first catholyte;

wherein:

an oxygen evolution reaction (OER) occurs at the first anode;

the first anode is a lead electrode;

each of the first anolyte and the first catholyte independently comprises aqueous iron cations and aqueous anions; and

the first anolyte comprises the aqueous iron sulfate at a concentration of at least approximately 0.01 M or a concentration selected from the range of approximately 0.01 M (optionally approximately 0.02 M, optionally approximately 0.03 M, optionally approximately 0.04 M, optionally approximately 0.05 M, optionally approximately 0.06 M, optionally approximately 0.07 M, optionally approximately 0.08 M, optionally approximately 0.09 M, optionally approximately 0.095 M, optionally approximately 0.099 M, optionally approximately 0.1 M) to approximately 0.5 M (optionally approximately 0.49 M, optionally approximately 0.48 M, optionally approximately 0.47 M, optionally approximately 0.46 M, optionally approximately 0.45 M, optionally approximately 0.44 M, optionally approximately 0.43 M, optionally approximately 0.42 M, optionally approximately 0.41 M, optionally approximately 0.40 M, optionally approximately 0.39 M, optionally approximately 0.38 M), such as optionally a concentration selected from the range of approximately 0.01 M to approximately 0.45 M, optionally a concentration selected from the range of approximately 0.01 M to approximately 0.4 M, optionally a concentration selected from the range of approximately 0.01 M to approximately 0.44 M, optionally a concentration selected from the range of approximately 0.01 M to approximately 0.445 M, optionally a concentration selected from the range of approximately 0.01 M to approximately 0.440 M, optionally selected from the range of approximately 0.02 M to approximately 0.08 M.

[0152] Aspect 6a: The method or system of any preceding aspect, wherein the concentration of the aqueous iron cations in the first anolyte is at least approximately 0.05 M or selected from the range of approximately 0.05 M to approximately 0.5 M.

[0153] Aspect 7a: The method or system of any preceding aspect, wherein the concentration of the aqueous iron cations in the first anolyte is less than the concentration of the aqueous iron cations in the first catholyte. Aspect 7b: The method or system of any preceding aspect, wherein the concentration of the aqueous iron cations in the first anolyte is equal, greater, or less than the concentration of the aqueous iron cations in the first catholyte. Aspect 7c: The method or system of any preceding aspect, wherein the concentration of the aqueous iron cations in the first anolyte is greater than the concentration of the aqueous iron cations in the first catholyte. Aspect 7d: The method or system of any preceding aspect, wherein the concentration of the aqueous iron cations in the first anolyte is equal to the concentration of the aqueous iron cations in the first catholyte.

[0154] Aspect 8a: The method or system of any preceding aspect, wherein a steady state concentration of the aqueous iron cations in the first anolyte is at least approximately 0.01 M or is a concentration selected from the range of approximately 0.01 M (optionally approximately 0.02 M, optionally approximately 0.03 M, optionally approximately 0.04 M, optionally approximately 0.05 M, optionally approximately 0.06 M, optionally approximately 0.07 M, optionally approximately 0.08 M, optionally approximately 0.09 M, optionally approximately 0.095 M, optionally approximately 0.099 M, optionally approximately 0.1 M) to approximately 0.5 M (optionally approximately 0.49 M, optionally approximately 0.48 M, optionally approximately 0.47 M, optionally approximately 0.46 M, optionally approximately 0.45 M, optionally approximately 0.44 M, optionally approximately 0.43 M, optionally approximately 0.42 M, optionally approximately 0.41 M, optionally approximately 0.40 M, optionally approximately 0.39 M, optionally approximately 0.38 M), such as optionally a concentration selected from the range of approximately 0.01 M to approximately 0.45 M, optionally a concentration selected from the range of approximately 0.01 M to approximately 0.4 M, optionally a concentration selected from the range of approximately 0.01 M to approximately 0.44 M, optionally a concentration selected from the range of approximately 0.01 M to approximately 0.445 M, optionally a concentration selected from the range of approximately 0.01 M to approximately 0.440 M, optionally selected from the range of approximately 0.02 M to approximately 0.08 M. Aspect b8: The method or system of any preceding aspect, wherein a steady state concentration of the aqueous iron cations in the first anolyte is at least approximately 0.01 M [or is a concentration selected from the range of approximately 0.01 M (optionally approximately 0.02 M, optionally approximately 0.03 M, optionally approximately 0.04 M, optionally approximately 0.05 M, optionally approximately 0.06 M, optionally approximately 0.07 M, optionally approximately 0.08 M, optionally approximately 0.09 M, optionally approximately 0.095 M, optionally approximately 0.099 M, optionally approximately 0.1 M) to approximately 0.5 M (optionally approximately 0.49 M, optionally approximately 0.48 M, optionally approximately 0.47 M, optionally approximately 0.46 M, optionally approximately 0.45 M, optionally approximately 0.44 M, optionally approximately 0.43 M, optionally approximately 0.42 M, optionally approximately 0.41 M, optionally approximately 0.40 M, optionally approximately 0.39 M, optionally approximately 0.38 M), such as optionally a concentration selected from the range of approximately 0.01 M to approximately 0.5 M or optionally a concentration selected from the range of approximately 0.01 M to approximately 0.45 M or optionally a concentration selected from the range of approximately 0.01 M to approximately 0.4 M] and a steady state concentration of aqueous sulfate anions in the first anolyte is at least approximately 0.01 M [or is a concentration selected from the range of approximately 0.01 M (optionally approximately 0.02 M, optionally approximately 0.03 M, optionally approximately 0.04 M, optionally approximately 0.05 M, optionally approximately 0.06 M, optionally approximately 0.07 M, optionally approximately 0.08 M, optionally approximately 0.09 M, optionally approximately 0.095 M, optionally approximately 0.099 M, optionally approximately 0.1 M) to 0.5 M (optionally approximately 0.49 M, optionally approximately 0.48 M, optionally approximately 0.47 M, optionally approximately 0.46 M, optionally approximately 0.45 M, optionally approximately 0.44 M, optionally approximately 0.43 M, optionally approximately 0.42 M, optionally approximately 0.41 M, optionally approximately 0.40 M, optionally approximately 0.39 M, optionally approximately 0.38 M), such as optionally a concentration selected from the range of approximately 0.01 M to approximately 0.5 M or optionally a concentration selected from the range of approximately 0.01 M to approximately 0.45 M or optionally a concentration selected from the range of approximately 0.01 M to approximately 0.445 M or optionally a concentration selected from the range of approximately 0.01 M to approximately 0.44 M or optionally a concentration selected from the range of approximately 0.01 M to approximately 0.4 M].

[0155] Aspect 9a: The method or system of any preceding aspect, wherein the steady state concentration of the aqueous iron cations in the first anolyte is at least approximately 0.05 M or is selected from the range of approximately 0.05 M to 0.5 M. Aspect 9b: The method or system of any preceding aspect, wherein the steady state concentration of the aqueous iron cations in the first anolyte is at least approximately

0.05 M or is selected from the range of approximately 0.05 M to 0.5 M and a steady state concentration of the aqueous sulfate anions in the first anolyte is at least approximately 0.05 M or is selected from the range of approximately 0.05 M to 0.5 M.

[0156] Aspect 10a: The method or system of any preceding aspect, wherein the steady state concentration of the aqueous iron cations in the first anolyte is less than a steady state concentration of the aqueous iron cations in the first catholyte. Aspect 10b: The method or system of any preceding aspect, wherein the steady state concentration of the aqueous iron cations in the first anolyte is greater, equal to, or lower than a steady state concentration of the aqueous iron cations in the first catholyte. Aspect 10c: The method or system of any preceding aspect, wherein the steady state concentration of the aqueous iron cations in the first anolyte is greater than a steady state concentration of the aqueous iron cations in the first catholyte. Aspect 10d: The method or system of any preceding aspect, wherein the steady state concentration of the aqueous iron cations in the first anolyte is equal to a steady state concentration of the aqueous iron cations in the first catholyte.

[0157] Aspect 11: The method or system of any preceding aspect, wherein the aqueous iron cations in the first anolyte comprise aqueous ferric ions.

[0158] Aspect 12a: A method comprising:

operating an electrochemical cell comprising performing electrochemical reduction at a first cathode and electrochemical oxidation at a first anode;
wherein:
the electrochemical cell comprises a first anodic chamber having a first anolyte in contact with a first anode, a first cathodic chamber having a first catholyte in contact with a first cathode, and a first separator separating the first anolyte from the first catholyte;
the first anode is a lead electrode; and
each of the first anolyte and the first catholyte independently comprises aqueous iron cations and aqueous anions; and
wherein the method further comprises:
dissolving solid manganese oxide in the first anolyte in the presence of aqueous ferrous ions.

[0159] Aspect 12b: A system comprising:

an electrochemical cell comprising:

a first anodic chamber having a first anolyte in contact with the first anode, a first cathodic chamber having a first catholyte in contact with the first cathode, and a first separator separating the first anolyte from the first catholyte;

wherein:

the first anode is a lead electrode;

each of the first anolyte and the first catholyte independently comprises aqueous iron cations and aqueous anions; and

the first anolyte comprises aqueous ferrous ions that facilitate dissolution, in the first anolyte, of solid manganese oxide present in the first anodic chamber.

[0160] Aspect 13: The method or system of aspect 12, wherein the step of dissolving comprises converting the solid manganese oxide to one or more aqueous manganese salts in the presence of the aqueous ferrous ions.

[0161] Aspect 14: The method or system of aspect 13, wherein the step of converting comprises (i) reacting the solid manganese oxide with the aqueous ferrous ions and/or (ii) electrochemically reducing the solid manganese oxide to one or more aqueous manganese salts in the presence of the aqueous ferrous ions.

[0162] Aspect 15: The method or system of aspect 13 or 14, wherein a ratio of moles of aqueous ferrous ions in the first anolyte to moles of solid manganese oxide in the first anodic chamber is at least 0.9 (optionally at least 0.95, optionally at least 0.99, optionally at least 1, optionally at least 1.2, optionally at least 1.5, optionally at least 1.7, optionally at least 2, optionally at least 2.2, optionally at least 2.5, optionally at least 2.7, optionally at least 3) during at least a portion of the step of dissolving (optionally at an onset of the step of dissolving, optionally during the entirety of the step of dissolving).

[0163] Aspect 16: The method or system of aspect 15, wherein a ratio of moles of aqueous ferrous ions in the first anolyte to moles of solid manganese oxide in the first anodic chamber is at least 2 during at least a portion of the step of dissolving.

[0164] Aspect 17a: The method of any one of claims 12-16, wherein the first anolyte comprises at least 5 mM aqueous ferrous ions during at least a portion of the step of dissolving (optionally at an onset of the step of dissolving, optionally during the entirety of the step of dissolving). Aspect 17b: The method of any one of claims 12-16, wherein the first anolyte comprises at least 5 mM aqueous iron cations during at least a portion of the step of dissolving (optionally at an onset of the step of dissolving, optionally during the entirety of the step of dissolving). Aspect 17c: The method of any one of claims 12-16, wherein the first anolyte comprises at least 10 mM aqueous ferrous ions during at least a portion of the step of dissolving (optionally at an onset of the step of dissolving, optionally during the entirety of the step of dissolving). Aspect 17d: The method of any one of claims 12-16, wherein the first anolyte comprises at least 10 mM aqueous iron cations during at least a portion of the step of dissolving (optionally at an onset of the step of dissolving, optionally during the entirety of the step of dissolving).

[0165] Aspect 18: The method or system of aspect 12-17 comprising a step of providing aqueous ferrous ions to the first anolyte prior to and/or during the step of dissolving.

[0166] Aspect 19a: The method or system of aspect 18, wherein the step of providing comprises flushing the first anodic chamber with a solution comprising aqueous ferrous ions. Aspect 19b: The method or system of aspect 18, wherein the step of providing comprises adding a solution comprising aqueous ferrous ions to the first anodic chamber.

[0167] Aspect 20: The method or system of aspect 18 or 19, wherein the step of providing comprises recycling ferrous-containing electrolyte from an electroplating cell directly or indirectly to the first anolyte.

[0168] Aspect 21: The method or system of aspect 18-20, wherein the step of providing comprises electrochemically producing aqueous ferrous ions in the first anolyte.

[0169] Aspect 22: The method or system of aspect 12-21, wherein the first anolyte comprises aqueous Mn ions.

[0170] Aspect 23a: A method comprising:

operating an electrochemical cell comprising performing electrochemical reduction at a first cathode and electrochemical oxidation at a first anode;

wherein:

the electrochemical cell comprises a first anodic chamber having a first anolyte in contact with a first anode, a first cathodic chamber having a first catholyte in contact with a first cathode, and a first separator separating the first anolyte from the first catholyte;

the first anode is a lead electrode; and

each of the first anolyte and the first catholyte independently comprises aqueous iron cations and aqueous anions; and

wherein the method further comprises:

reverse-biasing the first anode for a finite time comprising electrochemically reducing aqueous ferric ions to aqueous ferrous ions at the first anode in the presence of the first anolyte.

[0171] Aspect 23b: A system comprising:

an electrochemical cell comprising:

a first anodic chamber having a first anolyte in contact with the first anode, a first cathodic chamber having a first catholyte in contact with the first cathode, and a first separator separating the first anolyte from the first catholyte;

wherein:

the first anode is a lead electrode;

each of the first anolyte and the first catholyte independently comprises aqueous iron cations and aqueous anions; and

the electrochemical cell is configured to reverse-bias the first anode for a finite time to electrochemically reduce aqueous ferric ions to aqueous ferrous ions at the first anode in the presence of the first anolyte.

[0172] Aspect 24a: A method comprising:

operating an electrochemical cell comprising performing electrochemical reduction at a first cathode and electrochemical oxidation at a first anode;

wherein:

the electrochemical cell comprises a first anodic chamber having a first anolyte in contact with a first anode, a first cathodic chamber having a first catholyte in contact with a first cathode, and a first separator separating the first anolyte from the first catholyte;

each of the first anode and the first cathode comprises lead and

each of the first anolyte and the first catholyte independently comprises aqueous iron cations and aqueous anions.

[0173] In embodiments and aspects herein, an electrode comprising lead may comprise a lead layer as an underlying or supporting layer. For example, a cathode comprising lead may comprise a lead layer as an underlying or supporting layer, however the surface or electrocatalyst material that is exposed to the catholyte does not necessarily comprise lead, such that a cathode comprising lead does not necessarily have lead contacting the catholyte because the lead is optionally part of the cathode only as a supporting or underlying layer. For example, a cathode comprising lead may be a carbon electrode on a lead supporting or underlying layer.

[0174] Aspect 25a: The method or system of any preceding aspect, comprising operating two or more of the electrochemical cells; wherein adjacent electrochemical cells share a bipolar plate between them; and wherein each bipolar plate comprises a first lead electrode being the first anode of an electrochemical cell and a second electrode comprising lead being the first cathode of an adjacent electrochemical cell. embodiments and aspects herein, an electrode comprising lead may comprise a lead layer as an underlying or supporting layer. For example, a cathode comprising lead may comprise a lead layer as an underlying or supporting layer, however the surface or electrocatalyst material that is exposed to the catholyte does not necessarily comprise lead, such that a cathode comprising lead does not necessarily have lead contacting the catholyte because the lead is optionally part of the cathode only as a supporting or underlying layer. For example, a cathode comprising lead may be a carbon electrode on a lead supporting or underlying layer. Aspect 25b: The method or system of any preceding aspect, comprising operating two or more of the electrochemical cells; wherein adjacent electrochemical cells share a bipolar plate between them; and wherein each bipolar plate comprises a first electrode being the first anode of an electrochemical cell and a second electrode being the first cathode of an adjacent electrochemical cell.

[0175] Aspect 26: The method or system of any preceding aspect, comprising operating a bipolar stack of electrochemical cells, each electrochemical cell of the stack independently being the electrochemical cell according to any one of the preceding claims.

[0176] Aspect 27a: The method or system of aspect 26, wherein:

the bipolar stack comprises one or more bipolar plates;

adjacent electrochemical cells share a bipolar plate between them; and

each bipolar plate comprises a first lead electrode being the first anode of an electrochemical cell and a second electrode comprising lead being the first cathode of an adjacent electrochemical cell. In embodiments and aspects herein, an electrode comprising lead may comprise a lead layer as an underlying or supporting layer. For example, a cathode comprising lead may comprise a lead layer as an underlying or supporting layer, however the surface or electrocatalyst material that is exposed to the catholyte does not necessarily comprise lead, such that a cathode comprising lead does not necessarily have lead contacting the catholyte because the lead is optionally part of the cathode only as a supporting or underlying layer. For example, a cathode comprising lead may be a carbon electrode on a lead supporting or underlying layer.

[0177] Aspect 27b: The method or system of aspect 26, wherein:

the bipolar stack comprises one or more bipolar plates;

adjacent electrochemical cells share a bipolar plate between them; and

each bipolar plate comprises a first electrode being the first anode of an electrochemical cell and a second electrode being the first cathode of an adjacent electrochemical cell.

[0178] Aspect 28a: A method comprising:

operating two or more electrochemical cells comprising performing electrochemical reduction at a first cathode and electrochemical oxidation at a first anode;

wherein:

each electrochemical cell comprises a first anodic chamber having a first anolyte in contact with a first anode, a first cathodic chamber having a first catholyte in contact with a first cathode, and a first separator separating the first anolyte from the first catholyte;

the first anode is a lead electrode;

each of the first anolyte and the first catholyte independently comprises aqueous iron cations and aqueous anions;

adjacent electrochemical cells share a bipolar plate between them; and

each bipolar plate comprises a first lead electrode being the first anode of an electrochemical cell and a second electrode comprising lead being the first cathode of an adjacent electrochemical cell. In embodiments and aspects herein, an electrode comprising lead may comprise a lead layer as an underlying or supporting layer. For example, a cathode comprising lead may comprise a lead layer as an underlying or supporting layer, however the surface or electrocatalyst material that is exposed to the catholyte does not necessarily comprise lead, such that a cathode comprising lead does not necessarily have lead contacting the catholyte because the lead is optionally part of the cathode only as a supporting or underlying layer. For example, a cathode comprising lead may be a carbon electrode on a lead supporting or underlying layer.

[0179] Aspect 28b: A method comprising:

operating two or more electrochemical cells comprising performing electrochemical reduction at a first cathode and electrochemical oxidation at a first anode;

wherein:

each electrochemical cell comprises a first anodic chamber having a first anolyte in contact with a first anode, a first cathodic chamber having a first catholyte in contact with a first cathode, and a first separator separating the first anolyte from the first catholyte;

the first anode is a lead electrode;

each of the first anolyte and the first catholyte independently comprises aqueous iron cations and aqueous anions;

adjacent electrochemical cells share a bipolar plate between them; and

each bipolar plate comprises a first lead electrode being the first anode of an electrochemical cell and a second electrode being the first cathode of an adjacent electrochemical cell.

[0180] Aspect 28c: A method comprising:

operating a bipolar stack of electrochemical cells, each electrochemical cell of the stack independently having a first cathode performing electrochemical reduction and a first anode performing electrochemical oxidation;

wherein:

each electrochemical cell comprises a first anodic chamber having a first anolyte in contact with a first anode, a first cathodic chamber having a first catholyte in contact with a first cathode, and a first separator separating the first anolyte from the first catholyte;

the first anode is a lead electrode;

each of the first anolyte and the first catholyte independently comprises aqueous iron cations and aqueous anions;

the bipolar stack comprises one or more bipolar plates;

adjacent electrochemical cells share a bipolar plate between them; and

each bipolar plate comprises a first lead electrode being the first anode of an electrochemical cell and a second electrode comprising lead being the first cathode of an adjacent electrochemical cell. In embodiments and aspects herein, an electrode comprising lead may comprise a lead layer as an underlying or supporting layer. For example, a cathode comprising lead may comprise a lead layer as an underlying or supporting layer, however the surface or electrocatalyst material that is exposed to the catholyte does not necessarily comprise lead, such that a cathode comprising lead does not necessarily have lead contacting the catholyte because the lead is optionally part of the cathode only as a supporting or underlying layer. For example, a cathode comprising lead may be a carbon electrode on a lead supporting or underlying layer.

[0181] Aspect 28d: A method comprising:

operating a bipolar stack of electrochemical cells, each electrochemical cell of the stack independently having a first cathode performing electrochemical reduction and a first anode performing electrochemical oxidation;

wherein:

each electrochemical cell comprises a first anodic chamber having a first anolyte in contact with a first anode, a first cathodic chamber having a first catholyte in contact with a first cathode, and a first separator separating the first anolyte from the first catholyte;

the first anode is a lead electrode;

each of the first anolyte and the first catholyte independently comprises aqueous iron cations and aqueous anions;

the bipolar stack comprises one or more bipolar plates;

adjacent electrochemical cells share a bipolar plate between them; and

each bipolar plate comprises a first lead electrode being the first anode of an electrochemical cell and a second electrode being the first cathode of an adjacent electrochemical cell.

[0182] Aspect 28e: A system comprising:

two or more electrochemical cells, each cell comprising:

a first anodic chamber having a first anolyte in contact with the first anode, a first cathodic chamber having a first catholyte in contact with the first cathode, and a first separator separating the first anolyte from the first catholyte; and

a bipolar plate between two adjacent electrochemical cells, such that adjacent electrochemical cells share a bipolar plate between them;

wherein:

the first anode is a lead electrode;

each of the first anolyte and the first catholyte independently comprises aqueous iron cations and aqueous anions; and

each bipolar plate comprises a first lead electrode being the first anode of an electrochemical cell and a second electrode comprising lead being the first cathode of an adjacent electrochemical cell. In embodiments and aspects herein, an electrode comprising lead may comprise a lead layer as an underlying or supporting layer. For example, a cathode comprising lead may comprise a lead layer as an underlying or supporting layer, however the surface or electrocatalyst material that is exposed to the catholyte does not necessarily comprise lead, such that a cathode comprising lead does not necessarily have lead contacting the catholyte because the lead is optionally part of the cathode only as a supporting or underlying layer. For example, a cathode comprising lead may be a carbon electrode on a lead supporting or underlying layer.

[0183] Aspect 28f: A system comprising:

two or more electrochemical cells, each cell comprising:

a first anodic chamber having a first anolyte in contact with the first anode, a first cathodic chamber having a first catholyte in contact with the first cathode, and a first separator separating the first anolyte from the first catholyte; and

a bipolar plate between two adjacent electrochemical cells, such that adjacent electrochemical cells share a bipolar plate between them;

wherein:

the first anode is a lead electrode;

each of the first anolyte and the first catholyte independently comprises aqueous iron cations and aqueous anions; and

each bipolar plate comprises a first lead electrode being the first anode of an electrochemical cell and a second electrode being the first cathode of an adjacent electrochemical cell.

[0184] Aspect 28g: A system comprising:

a bipolar stack of two or more electrochemical cells, each cell comprising:

a first anodic chamber having a first anolyte in contact with the first anode, a first cathodic chamber having a first catholyte in contact with the first cathode, and a first separator separating the first anolyte from the first catholyte;

wherein:

the first anode is a lead electrode;

each of the first anolyte and the first catholyte independently comprises aqueous iron cations and aqueous anions;

the bipolar stack comprises one or more bipolar plates;

adjacent electrochemical cells share a bipolar plate between them; and

each bipolar plate comprises a first lead electrode being the first anode of an electrochemical cell and a second electrode comprising lead being the first cathode of an adjacent electrochemical cell. In embodiments and aspects herein, an electrode comprising lead may comprise a lead layer as an underlying or supporting layer. For example, a cathode comprising lead may comprise a lead layer as an underlying or supporting layer, however the surface or electrocatalyst material that is exposed to the catholyte does not necessarily comprise lead, such that a cathode comprising lead does not necessarily have lead contacting the catholyte because the lead is optionally part of the cathode only as a supporting or underlying layer. For example, a cathode comprising lead may be a carbon electrode on a lead supporting or underlying layer.

[0185] Aspect 25h: A system comprising:

a bipolar stack of two or more electrochemical cells, each cell comprising:

a first anodic chamber having a first anolyte in contact with the first anode, a first cathodic chamber having a first catholyte in contact with the first cathode, and a first separator separating the first anolyte from the first catholyte;

wherein:

the first anode is a lead electrode;

each of the first anolyte and the first catholyte independently comprises aqueous iron cations and aqueous anions;

the bipolar stack comprises one or more bipolar plates;

adjacent electrochemical cells share a bipolar plate between them; and

each bipolar plate comprises a first lead electrode being the first anode of an electrochemical cell and a second electrode being the first cathode of an adjacent electrochemical cell.

[0186] Aspect 29: The method or system of any one of aspects 25-28, wherein each bipolar plate comprises an electrically conductive substrate, an anode-facing side, and a cathode-facing side.

[0187] Aspect 30: The method or system of aspect 29, wherein the electrically conductive substrate is porous or permeable to electrolyte and dissolved ions.

[0188] Aspect 31: The method or system of aspect 30, wherein each bipolar plate comprises a coating of lead on at least a portion of internal or pore surfaces of the porous substrate.

[0189] Aspect 32: The method or system of aspect 31, wherein the coating has a thickness selected from the range of 50 μm to 5 mm.

[0190] Aspect 33: The method or system of aspect 29, wherein the electrically conductive substrate is non-porous or impermeable to electrolyte and dissolved ions.

[0191] Aspect 34: The method or system of any one of aspects 29-33, wherein each bipolar plate comprises a first layer of lead on the anode-facing side, a second layer of lead on the cathode-facing side, or a layer of lead independently on each of the anode-facing side and the cathode-facing side.

[0192] Aspect 35: The method or system of aspect 34, wherein each layer of lead is a layer on the substrate.

[0193] Aspect 36: The method or system of aspect 34 or 35, wherein each layer of lead is non-porous or non-permeable to electrolyte and dissolved ions.

[0194] Aspect 37: The method or system of any one of aspects 34-36, wherein each layer of lead protects the substrate from exposure to nearest electrolyte.

[0195] Aspect 38: The method or system of any one of aspects 34-37, wherein each layer of lead independently has a thickness selected from the range of 50 μm to 5 mm.

[0196] Aspect 39: The method or system of any one of aspects 29-38, wherein the electrically conductive substrate is characterized by a compressive yield strength selected from the range of 10 MPa to 200 MPa and/or a Young's modulus selected from the range of 600 MPa to 1500 MPa.

[0197] Aspect 40: The method or system of any one of aspects 25-39, wherein the first cathode of each bipolar plate is a carbon cathode or a carbon-comprising cathode.

[0198] Aspect 41: The method or system of any one of aspects 34-40, wherein each bipolar plate comprises a first layer of lead on the anode-facing side; and wherein the first layer of lead is the first anode of the respective bipolar plate.

[0199] Aspect 42: The method or system of any one of aspects 34-40, wherein each bipolar plate comprises a layer of lead on the anode-facing side; and wherein each bipolar plate further comprises the first anode on, adhered-to, coated on, or otherwise adjacent to the first layer of lead.

[0200] Aspect 43: The method or system of any one of aspects 28-42, wherein the bipolar stack comprises electrically-conductive spacer layers or flow field layers through which a fluid may flow.

[0201] Aspect 44a: The method or system of any preceding aspect, wherein the first anode is a lead electrode comprising a microstructured and/or nanostructured lead-containing surface in contact with the anolyte. Aspect 44b: The method or system of any preceding Aspect, wherein the lead electrode is porous and at least partially permeable to the first anolyte. Aspect 44c: The method or system of any preceding Aspect, wherein the lead electrode is a lead-containing and/or lead-coated wool or foam.

[0202] Aspect 45: The method or system of any preceding aspect, wherein the first anode is free of lead shedding or is characterized by a rate of lead shedding being less than that in an equivalent electrochemical cell under equivalent conditions where the first anolyte is free of aqueous iron cations.

[0203] Aspect 46: The method or system of any preceding aspect, wherein the aqueous anions comprise aqueous sulfur-containing anions, aqueous chloride anions, or both.

[0204] Aspect 47a: The method or system of Aspect 46, wherein the aqueous sulfur-containing anions comprise aqueous sulfate ions. Aspect 47b: The method or system of Aspect 46, wherein the aqueous sulfur-containing anions are aqueous sulfate ions. Aspect 47c: The method or system of Aspect 46, wherein the aqueous sulfur-containing anions are aqueous sulfate ions having a concentration stoichiometric with the concentration of aqueous iron cations in the respective electrolyte. Aspect 47d: The method or system of Aspect 46, wherein the aqueous sulfur-containing anions comprise aqueous sulfate ions and the first anolyte is free of aqueous chloride anions.

[0205] Aspect 48a: The method or system of any preceding aspect, wherein the first anolyte comprises aqueous lead ions having a concentration of at least 5 ppm. Aspect 48b: The method or system of any preceding aspect, wherein the first anolyte comprises aqueous lead ions having a concentration of at least 10 ppm or is selected from the range of 10 ppm to 0.5 M.

[0206] Aspect 49: The method or system of any preceding aspect, wherein the first anolyte comprises aqueous lead ions having a concentration being greater than 10 ppm and equal to or less than a lead ion saturation concentration in the first anolyte at its temperature (e.g., lead ion saturation concentration in H_2SO_4 and/or HCl at ~50 ^oC to 80 ^oC).

[0207] Aspect 50: The method or system of any preceding aspect, wherein the electrochemical cell further comprises a secondary or sacrificial source of lead ions (other than the first anode itself) in contact with the first anolyte to slow or prevent dissolution of Pb from the first anode into the first anolyte.

[0208] Aspect 51: The method or system of any preceding aspect, wherein the step of operating the electrochemical cell comprises:

electrochemically reducing first Fe^{3+} ions at the first cathode to form Fe^{2+} ions in the first catholyte.

[0209] Aspect 52: The method or system of any preceding aspect, wherein the step of operating the electrochemical cell further comprises:

electrochemically oxidizing water at the first anode to generate O_2 and aqueous protons in the first anolyte.

[0210] Aspect 53a: The method or system of any preceding aspect, wherein: the step of operating comprises the first anode being characterized by a steady state anode potential selected from the range of 1.2 to 3.0 V vs. NHE; and/or the step of operating comprises each electrochemical cell being characterized by a current density selected from the range of 5 to 200 mA/cm^2(optionally about 30 to 100 mA/cm^2); and/or the step of operating comprises each electrochemical cell being characterized by a bias current density is between 5 to 50 mA/cm^2. Aspect 53b: The method or system of any preceding aspect, wherein the step of operating comprises the first anode being characterized by a steady state anode potential of at least 1 V vs. NHE (optionally at least 1.1, optionally at least 1.2, optionally at least 1.3 V, optionally at least 1.4 V, optionally at least 1.5 V, optionally at least 1.6 V vs. NHE) and optionally less than or equal to 2.5 V vs. NHE (optionally 2.7 V, optionally 2.9 V, optionally 3.0 V, optionally 3.2 V, optionally 3.5 V vs. NHE). Aspect 53c: The method or system of any preceding aspect, wherein: the step of operating comprises each electrochemical cell being characterized by a current density selected from the range of 5 to 200 mA/cm^2 (optionally about 30 to 100 mA/cm^2); and/or the step of operating comprises each electrochemical cell being characterized by a bias current density is between 5 to 50 mA/cm^2.

[0211] Aspect 54a: The method or system of any preceding aspect, wherein the electrochemical cell is characterized by a steady state current density selected from the range of 1 to 500 mA/cm^2. Aspect 54b: The method or system of any preceding aspect, wherein the electrochemical cell is characterized by a steady state current density of at least 1 mA/cm^2 (optionally at least 5 mA/cm^2, optionally at least 10 mA/cm^2, optionally at least 20 mA/cm^2, optionally at least 50 mA/cm^2, optionally at least 75 mA/cm^2, optionally at least 100 mA/cm^2) and optionally less than or equal to 2 A/cm^2 (optionally 1.5 A/cm^2, optionally 1 A/cm^2, optionally 900 mA/cm^2, optionally 800 mA/cm^2, optionally 700 mA/cm^2, optionally 600 mA/cm^2, optionally 500 mA/cm^2, optionally 400 mA/cm^2).

[0212] Aspect 55a: The method or system of any preceding aspect comprising adding a dosing-solution having aqueous iron cations to the first anodic chamber and/or to the first anolyte. Aspect 55b: The method or system of any preceding aspect comprising rinsing or flushing the anodic chamber with a solution having aqueous iron cations.

[0213] Aspect 56a: The method or system of aspect 55, wherein the dosing-solution comprises aqueous ferrous. Aspect 56b: The method or system of aspect 55, wherein the aqueous iron cations in the solution are majority or substantially aqueous ferrous ions.

[0214] Aspect 57: The method or system of aspect 55 or 56, wherein the dosing-solution is an electrolyte from a different electrochemical cell or system.

[0215] Aspect 58: The method or system of any one of aspects 55-57, wherein the dosing-solution comprises electrolyte from a metal electroplating cell or system.

[0216] Aspect 59: The method or system of any one of aspects 55-58, wherein the dosing-solution is provided from a separate solution-storage tank.

[0217] Aspect 60: The method or system of any preceding aspect comprising recycling a second electrolyte from a metal electroplating cell to the first anolyte, the second electrolyte having aqueous iron cations.

[0218] Aspect 61a: The method or system of aspect 60, wherein the second electrolyte comprises a concentration of aqueous iron cations being at least approximately 0.01 M or a concentration selected from the range of approximately 0.01 M (optionally approximately 0.02 M, optionally approximately 0.03 M, optionally approximately 0.04 M, optionally approximately 0.05 M, optionally approximately 0.06 M, optionally approximately 0.07 M, optionally approximately 0.08 M, optionally approximately 0.09 M, optionally approximately 0.095 M, optionally approximately 0.099 M, optionally approximately 0.1 M) to 0.5 M (optionally approximately 0.49 M, optionally approximately 0.48 M, optionally approximately 0.47 M, optionally approximately 0.46 M, optionally approximately 0.45 M, optionally approximately 0.44 M, optionally approximately 0.43 M, optionally approximately 0.42 M, optionally approximately 0.41 M, optionally approximately 0.40 M, optionally approximately 0.39 M, optionally approximately 0.38 M), such as optionally a concentration selected from the range of approximately 0.01 M to 0.5 M or optionally a concentration selected from the range of approximately 0.01 M to 0.45 M or optionally a concentration selected from the range of approximately 0.01 M to 0.445 M or optionally a concentration selected from the range of approximately 0.01 M to 0.44 M or optionally a concentration selected from the range of approximately 0.01 M to 0.4 M or optionally a concentration selected from the range of approximately 0.05 M to 0.5 M. Aspect 61b: The method or system of aspect 60, wherein the second electrolyte comprises a concentration of aqueous ferrous or ferric cations being at least approximately 0.01 M or is selected from the range of approximately 0.01 M to approximately 0.5 M, optionally selected from the range of approximately 0.05 M to approximately 0.5 M.

[0219] Aspect 62: The method or system of aspect 60 or 61, wherein the second comprises a catholyte and/or anolyte from an iron electroplating cell.

[0220] Aspect 63: The method or system of aspect 62, wherein the catholyte and/or anolyte from the iron electroplating cell is a spent catholyte and/or spent anolyte, respectively.

[0221] Aspect 64: The method or system of any preceding aspect further comprising:

dissolving an iron-containing ore in an acid to form an acidic iron-salt solution; and

providing the acidic iron-salt solution to the cathodic chamber of the electrochemical cell.

[0222] Aspect 65: The method or system of any preceding aspect further comprising:

second electrochemically reducing Fe^{2+} ions to Fe metal at a second cathode in the presence of a second catholyte;

wherein an iron electroplating cell comprises the second cathode and the second catholyte.

[0223] Aspect 66: The method or system of any preceding, comprising a step of switching the first electrochemical cell to a first temporary intermediate condition; wherein the first temporary intermediate condition comprises the first anode being in contact with the first anolyte and being characterized by an open circuit voltage.

[0224] Aspect 67: The method or system of aspect 66, wherein the surface of the first anode is free of lead sulfate during the step of electrochemically oxidizing and/or during the step of switching.

[0225] Aspect 68: The method or system of aspect 67, wherein the surface of the first anode is free of lead sulfate while being in contact with the first anolyte and being characterized by an open circuit voltage.

[0226] Aspect 69: The method or system of any of aspects 66-68, wherein the first temporary intermediate condition further comprises the surface of the first anode having a lead-iron alloy comprising Pb, Fe, S, and O.

[0227] Aspect 70: The method or system of aspect 69, wherein the lead-iron alloy is characterized by formula **FX1**: $Fe_xPb_{2-x}SO_4$, wherein x is greater than 0 and less than 2.

[0228] Aspect 71: The method or system of aspect 69 or 70, wherein the surface of the first anode is free of the lead-iron alloy during steady state operation of the step of electrochemically oxidizing.

[0229] Aspect 72: The method or system of any of aspects 69-71 comprising a step of forming the lead-iron alloy during the step of switching or when the surface of the first anode is in contact with the first anolyte and characterized by an open circuit voltage.

[0230] Aspect 73: The method or system of aspect 72, wherein the lead-iron alloy forms in the presence of aqueous ferric sulfate in the first anolyte.

[0231] Aspect 74: The method or system of any preceding aspect, wherein the electrochemical cell is according to any embodiment or aspect of “first electrochemical cell” disclosed in PCT’732 and in Provis’092 and/or further comprises any embodiment or aspect of “first electrochemical cell” disclosed in PCT’732 and in Provis’092, which are incorporated herein in their entirety.

[0232] Aspect 75: The method or system of any preceding aspect, wherein the metal electroplating cell or iron electroplating cell is according to any embodiment or aspect of “second electrochemical cell” disclosed in PCT’732 and in Provis’092.

[0233] Aspect 76: The method or system of any preceding aspect further comprising any feature, step, embodiment, or aspect disclosed in PCT’732 and in Provis’092.

[0234] Aspect 77: The method or system of any preceding aspect wherein the first separator is the first separator according to any embodiment or aspect described in PCT’732 and in Provis’092.

[0235] Aspect 78: The method or system of any preceding aspect wherein the first cathode comprises lead as an underlying or supportive layer.

[0236] Aspect 79: The method or system of any preceding aspect wherein the first cathode does not comprise lead in contact with the first catholyte.

[0237] Aspect 80: The method or system of any preceding aspect wherein the first cathode comprises a carbon electrode in contact with the first catholyte.

[0238] Aspect 81: A method for making one or more electrochemical cells according to any preceding aspect and/or any embodiment disclosed herein, such as any embodiments, features, aspects, processes, techniques, and steps described at paragraphs [0064] to [0093] and shown in FIGs. 1-4.

[0239] Aspect 82: A method for making a bipolar stack according to any preceding aspect and/or any embodiment disclosed herein, such as any embodiments, features, aspects, processes, techniques, and steps described at paragraphs [0064] to [0093] and shown in FIGs. 1-4.

[0240] Aspect 83a: The method or system of any preceding Aspect, wherein the step of operating comprises one or more steps of establishing and/or the step of operating comprises a step of maintaining the concentration of the aqueous iron cations in said first anolyte within a stabilizing-concentration range; wherein the stabilizing-concentration range is selected from the range of approximately 0.01 M (optionally approximately 0.02 M, optionally approximately 0.03 M, optionally approximately 0.04 M, optionally approximately 0.05 M, optionally approximately 0.06 M, optionally approximately 0.07 M, optionally approximately 0.08 M, optionally approximately 0.09 M, optionally approximately 0.095 M, optionally approximately 0.099 M, optionally approximately 0.1 M) to approximately 0.5 M (optionally approximately 0.49 M, optionally approximately 0.48 M, optionally approximately 0.47 M, optionally approximately 0.46 M, optionally approximately 0.45 M, optionally approximately 0.44 M, optionally approximately 0.43 M, optionally approximately 0.42 M, optionally approximately 0.41 M, optionally approximately 0.40 M, optionally approximately 0.39 M, optionally approximately 0.38 M). Optionally, in any Aspect herein, the stabilizing-concentration range is selected from the range of approximately 0.01 M to approximately 0.1 M, wherein any value and range therebetween is explicitly contemplated and disclosed herein, such as optionally approximately 0.02 M to approximately 0.09 M or optionally approximately 0.03 M to approximately 0.08 M or optionally approximately 0.04 M to approximately 0.07 M or optionally approximately 0.03 M to approximately 0.08 M or optionally approximately 0.05 M. Aspect 83b: The method or system of any preceding Aspect, wherein the step of operating comprises said one or more steps of establishing. Aspect 83c: The method or system of any preceding Aspect, wherein the step of operating comprises the step of maintaining.

[0241] Aspect 84: The method or system of Aspect 83, wherein each step of establishing provides the stabilizing concentration range temporarily.

[0242] Aspect 85: The method or system of Aspect 83 or 84, wherein the step of establishing is performed prior to startup of the electrochemical cell and/or prior to shutdown of the electrochemical cell. Optionally, startup of the cell comprises a cell voltage, such as a voltage between the first anode and the first cathode, transitioning from open circuit voltage (OCV) to an operating voltage, wherein the operating voltage corresponds to a voltage that corresponds to the performance of said electrochemical reduction at the first cathode and said electrochemical oxidation at said first anode such as an oxygen evolution reaction. Optionally, shutdown of the cell comprises a cell voltage, such as a voltage between the first anode and the first cathode, transitioning from an operating voltage, wherein the operating voltage corresponds to a voltage that corresponds to the performance of said electrochemical reduction at the first cathode and said electrochemical oxidation at said first anode such as an oxygen evolution reaction, to an open circuit voltage (OCV). Said performance of said electrochemical reduction at the first cathode and said electrochemical oxidation at said first anode does not or cannot occur when the cell is at the OCV.

[0243] Aspect 86a: The method or system of any one of Aspects 83-85, wherein each step of establishing and the step of maintaining, if present, comprises dosing the first anolyte with said aqueous iron cations. Aspect 86b: The method or system of any one of Aspects 83-85, wherein each step of establishing comprises dosing the first anolyte with said aqueous iron cations. Aspect 86c: The method or system of any one of Aspects 83-85, wherein the step of maintaining comprises dosing the first anolyte with said aqueous iron cations. Aspect 86d: The method or system of any one of Aspects 83-85, wherein each step of establishing and the step of maintaining comprise dosing the first anolyte with said aqueous iron cations.

[0244] Aspect 87: The method or system of Aspect 86, wherein the step of dosing is performed as one or more discrete events during the step of operating the cell.

[0245] Aspect 88: The method or system of Aspect 86, wherein the step of dosing is performed continuously during the step of operating the cell.

[0246] Aspect 89: The method or system of any one of Aspects 86-88, wherein the step of dosing comprises providing a liquid iron source; the liquid iron source being an aqueous solution comprising a dosing-concentration of the aqueous iron cations.

[0247] Aspect 90: The method or system of Aspect 89, wherein the liquid iron source comprises a spent or used anolyte from a metal electroplating cell or system.

[0248] Aspect 91: The method or system of Aspect 89 or 90, wherein the liquid iron source comprises a spent or used catholyte from a metal electroplating cell or system.

[0249] Aspect 92: The method or system of any one of Aspects 89-91, wherein the liquid iron source is provided directly to the first anolyte or to a first anodic chamber having said first anolyte.

[0250] Aspect 93: The method or system of any one of Aspects 89-92, wherein the liquid iron source is provided indirectly to the first anolyte or to a first anodic chamber having said first anolyte.

[0251] Aspect 94: The method or system of any one of Aspects 89-93, wherein the liquid iron source is provided to a first anolyte-circulation tank which is fluid communication with the first anodic chamber having the first anolyte, to a fluid line entering the first anodic chamber, and/or to a fluid line exiting the first anodic chamber.

[0252] Aspect 95: The method or system of any one of Aspects 89-94, wherein the liquid iron source comprise aqueous ferrous ions.

[0253] Aspect 96: The method or system of any one of Aspects 89-95, wherein the liquid iron source is an iron-containing slag and/or iron-containing leachate from a metal and/or ore processing system.

[0254] Aspect 97: The method or system of any one of Aspects 89-96, wherein the dosing-concentration of aqueous iron cations in the liquid iron source is greater than 0 M and less than 0.5 M.

[0255] Aspect 98: The method or system of any one of Aspects 83-97 wherein the step of dosing comprises providing a solid iron source in the presence of the first anolyte; wherein the solid iron source is capable of being at least partially dissolved by the first anolyte.

[0256] Aspect 99: The method or system of Aspect 98, wherein the solid iron source is a raw ore and/or treated ore.

[0257] Aspect 100: The method or system of Aspect 98 or 99, wherein the solid iron source is a thermally treated ore.

[0258] Aspect 101: The method or system of any one of Aspects 98-100, wherein the solid iron source comprise solid ferrous ions.

[0259] Aspect 102: The method or system of any one of Aspects 86-101, wherein each the of dosing is performed in response to a trigger event; wherein the trigger event comprises:

the concentration of the aqueous iron cations in the first anolyte falling below the stabilizing-concentration range, and/or

a current density of the electrochemical cell falling below a normal operable current density.

[0260] Aspect 103: The method or system of any preceding Aspect, wherein the electrochemical reduction at the first cathode is an iron electroplating reaction; and wherein the electrochemical oxidation reaction is an oxygen evolution reaction (OER) at the first anode.

[0261] Aspect 104: The method or system of Aspect 103, wherein the separator is an anion exchange membrane.

[0262] Aspect 105: The method or system of any preceding Aspect, wherein the first anode is free of a mixed metal oxide (MMO) material.

[0263] Aspect 106: The method or system of any preceding Aspect, wherein the first anode is free of Ir, Ru, and Pt.

[0264] Aspect 107: The method or system of any preceding Aspect, wherein the first anode is an undoped or non-alloyed lead electrode.

STATEMENTS REGARDING INCORPORATION BY REFERENCE AND VARIATIONS

[0265] All references throughout this application, for example patent documents including issued or granted patents or equivalents; patent application publications; and non-patent literature documents or other source material; are hereby incorporated by reference herein in their entireties, as though individually incorporated by reference, to the extent each reference is at least partially not inconsistent with the disclosure in this application (for example, a reference that is partially inconsistent is incorporated by reference except for the partially inconsistent portion of the reference).

[0266] The terms and expressions which have been employed herein are used as terms of description and not of limitation, and there is no intention in the use of such terms and expressions of excluding any equivalents of the features shown and described or portions thereof, but it is recognized that various modifications are possible within the scope of any particular claimed invention. Thus, it should be understood that although inventions have been specifically disclosed by preferred embodiments, exemplary embodiments and optional features, modification and variation of the concepts herein disclosed may be resorted to by those skilled in the art, and that such modifications and variations are considered to be within the scope of inventions as defined by the appended claims. The specific embodiments provided herein are examples of useful embodiments of the inventions and it will be apparent to one skilled in the art that the inventions may be carried out using a large number of variations of the devices, device components, methods steps set forth in the present description. As will be obvious to one of skill in the art, methods and devices useful for the present methods can include a large number of optional composition and processing elements and steps.

[0267] As used herein and in the appended claims, the singular forms "a", "an", and "the" include plural reference unless the context clearly dictates otherwise. Thus, for example, reference to "a cell" includes a plurality of such cells and equivalents thereof known to those skilled in the art. As well, the terms "a" (or "an"), "one or more" and "at least one" can be used interchangeably herein. It is also to be noted that the terms "comprising", "including", and "having" can be used interchangeably. The expression “of any of claims XX-YY” (wherein XX and YY refer to claim numbers) is intended to provide a multiple dependent claim in the alternative form, and in some embodiments is interchangeable with the expression “as in any one of claims XX-YY.”

[0268] When a group of substituents is disclosed herein, it is understood that all individual members of that group and all subgroups, including iron oxide materials of an ore or structural and compositional polymorphs of the group members, are disclosed separately. When a Markush group or other grouping is used herein, all individual members of the group and all combinations and sub-combinations possible of the group are intended to be individually included in the disclosure. When a compound is described herein such that a particular isomer, enantiomer or diastereomer of the compound is not specified, for example, in a formula or in a chemical name, that description is intended to include each isomers and enantiomer of the compound described individual or in any combination. Additionally, unless otherwise specified, all isotopic variants of compounds disclosed herein are intended to be encompassed by the disclosure. For example, it will be understood that any one or more hydrogens in a molecule disclosed can be replaced with deuterium or tritium. Isotopic variants of a molecule are generally useful as standards in assays for the molecule and in chemical and biological research related to the molecule or its use. Methods for making such isotopic variants are known in the art. Specific names of compounds are intended to be exemplary, as it is known that one of ordinary skill in the art can name the same compounds differently.

[0269] With regard to salts of the compounds herein, one of ordinary skill in the art can select from among a wide variety of available counterions those that are appropriate for preparation of salts of this invention for a given application. In specific applications, the selection of a given anion or cation for preparation of a salt may result in increased or decreased solubility of that salt.

[0270] Every device, system, subsystem, method, process, component, and/or combination of components, described or exemplified herein can be used to practice any claimed invention(s), unless otherwise stated.

[0271] Whenever a range is given in the specification, for example, a temperature range, a time range, or a composition or concentration range, all intermediate ranges and subranges, as well as all individual values included in the ranges given are intended to be included in the disclosure. It will be understood that any subranges or individual values in a range or subrange that are included in the description herein can be excluded from the claims herein.

[0272] All patents and publications mentioned in the specification are indicative of the levels of skill of those skilled in the art to which the disclosed devices, systems, methods, and processes pertain. References cited herein are incorporated by reference herein in their entirety to indicate the state of the art as of their publication or filing date and it is intended that this information can be employed herein, if needed, to exclude specific embodiments that are in the prior art. For example, when composition of matter are claimed, it should be understood that compounds known and available in the art prior to Applicant's inventions, including compounds for which an enabling disclosure is provided in the references cited herein, are not intended to be included in the composition of matter claims herein.

[0273] As used herein, “comprising” is synonymous with "including," "containing," or "characterized by," and is inclusive or open-ended and does not exclude additional, unrecited elements or method steps. As used herein, "consisting of" excludes any element, step, or ingredient not specified in the claim element. As used herein, "consisting essentially of" does not exclude materials or steps that do not materially affect the basic and novel characteristics of the claim. In each instance herein any of the terms "comprising", "consisting essentially of" and "consisting of" may be replaced with either of the other two terms. The claimed inventions illustratively described herein suitably may be practiced in the absence of any element or elements, limitation or limitations which is not specifically disclosed herein.

[0274] One of ordinary skill in the art will appreciate that starting materials, reagents, synthetic methods, purification methods, analytical methods, and assay methods other than those specifically exemplified can be employed in the practice of the claimed inventions without resort to undue experimentation. All art-known functional equivalents, of any such materials and methods are intended to be included in these inventions.

We claim:

1. A method for stabilizing a lead anode, the method comprising:
   operating an electrochemical cell comprising performing electrochemical reduction at a first cathode and electrochemical oxidation at a first anode;
   wherein:
   the electrochemical cell comprises a first anodic chamber having a first anolyte in contact with the first anode, a first cathodic chamber having a first catholyte in contact with the first cathode, and a first separator separating the first anolyte from the first catholyte;
   the first anode is a lead electrode;
   each of the first anolyte and the first catholyte independently comprises aqueous iron cations and aqueous anions; and
   the first anolyte comprises the aqueous iron cations at a concentration selected from the range of 0.01 M to 0.5 M.

2. A method for stabilizing a lead anode, the method comprising:
   operating an electrochemical cell comprising performing electrochemical reduction at a first cathode and electrochemical oxidation at a first anode; and
   recycling a second electrolyte from a metal electroplating cell to the first anolyte, the second electrolyte having aqueous iron cations;
   wherein:
   the electrochemical cell comprises a first anodic chamber having a first anolyte in contact with the first anode, a first cathodic chamber having a first catholyte in contact with the first cathode, and a first separator separating the first anolyte from the first catholyte;
   the first anode is a lead electrode;
   each of the first anolyte and the first catholyte independently comprises aqueous iron cations and aqueous anions; and
   the first anolyte comprises the aqueous iron cations at a concentration selected from the range of 0.01 M to 0.5 M.

3. The method of claim 2, wherein the second electrolyte comprises a spent catholyte and/or spent anolyte from an iron electroplating cell.

4. The method of any one of the preceding claims, wherein performing electrochemical oxidation comprises an oxygen evolution reaction (OER) at the first anode.

5. The method of any one of the preceding claims, wherein the first anolyte comprises aqueous sulfate anions.

6. A method for stabilizing a lead anode, the method comprising:
operating an electrochemical cell comprising performing electrochemical reduction at a first cathode and an oxygen evolution reaction (OER) at a first anode;
wherein:
the electrochemical cell comprises a first anodic chamber having a first anolyte in contact with the first anode, a first cathodic chamber having a first catholyte in contact with the first cathode, and a first separator separating the first anolyte from the first catholyte;
the first anode is a lead electrode;
each of the first anolyte and the first catholyte independently comprises aqueous iron cations and aqueous anions; and
the first anolyte comprises aqueous iron sulfate at a concentration selected from the range of 0.01 M to 0.5 M.

7. The method of any one of the preceding claims, wherein the concentration of the aqueous iron cations in the first anolyte is selected from the range of 0.05 M to 0.5 M.

8. The method of any one of the preceding claims, wherein the concentration of the aqueous iron cations in the first anolyte is less than a concentration of the aqueous iron cations in the first catholyte.

9. The method of any one of the preceding claims, wherein a steady state concentration of the aqueous iron cations in the first anolyte is selected from the range of 0.01 M to 0.5 M.

10. The method of any one of the preceding claims, wherein the steady state concentration of the aqueous iron cations in the first anolyte is selected from the range of 0.05 M to 0.5 M.

11. The method of any one of the preceding claims, wherein the steady state concentration of the aqueous iron cations in the first anolyte is less than a steady state concentration of the aqueous iron cations in the first catholyte.

12. The method of any one of the preceding claims, wherein the aqueous iron cations in the first anolyte comprise aqueous ferric ions.

13. A method comprising:

operating an electrochemical cell comprising performing electrochemical reduction at a first cathode and electrochemical oxidation at a first anode;

wherein:

the electrochemical cell comprises a first anodic chamber having a first anolyte in contact with a first anode, a first cathodic chamber having a first catholyte in contact with a first cathode, and a first separator separating the first anolyte from the first catholyte;

the first anode is a lead electrode; and

each of the first anolyte and the first catholyte independently comprises aqueous iron cations and aqueous anions; and

wherein the method further comprises:

dissolving solid manganese oxide in the first anolyte in the presence of aqueous ferrous ions.

14. The method of claim 13, wherein the step of dissolving comprises converting the solid manganese oxide to one or more aqueous manganese salts in the presence of the aqueous ferrous ions.

15. The method of claim 14, wherein the step of converting comprises (i) reacting the solid manganese oxide with the aqueous ferrous ions and/or (ii) electrochemically reducing the solid manganese oxide to one or more aqueous manganese salts in the presence of the aqueous ferrous ions.

16. The method of any one of claims 13-15, wherein a ratio of moles of aqueous ferrous ions in the first anolyte to moles of solid manganese oxide in the first anodic chamber is at least 0.9 during at least a portion of the step of dissolving.

17. The method of claim 16, wherein a ratio of moles of aqueous ferrous ions in the first anolyte to moles of solid manganese oxide in the first anodic chamber is at least 2 during at least a portion of the step of dissolving.

18. The method of any one of claims 13-17, wherein the first anolyte comprises at least 5 mM aqueous ferrous ions during at least a portion of the step of dissolving.

19. The method of any one of claims 13-18 comprising a step of providing aqueous ferrous ions to the first anolyte prior to and/or during the step of dissolving.

20. The method of claim 19, wherein the step of providing comprises flushing the first anodic chamber with a solution comprising aqueous ferrous ions.

21. The method of claim 19 or 20, wherein the step of providing comprises recycling ferrous-containing electrolyte from an electroplating cell directly or indirectly to the first anolyte.

22. The method of any one of claims 19-21, wherein the step of providing comprises electrochemically producing aqueous ferrous ions in the first anolyte.

23. The method of any one of claims 13-22, wherein the first anolyte comprises aqueous Mn ions.

24. A method comprising:
operating an electrochemical cell comprising performing electrochemical reduction at a first cathode and electrochemical oxidation at a first anode;
wherein:
the electrochemical cell comprises a first anodic chamber having a first anolyte in contact with a first anode, a first cathodic chamber having a first catholyte in contact with a first cathode, and a first separator separating the first anolyte from the first catholyte;
the first anode is a lead electrode; and
each of the first anolyte and the first catholyte independently comprises aqueous iron cations and aqueous anions; and
wherein the method further comprises:
reverse-biasing the first anode for a finite time comprising electrochemically reducing aqueous ferric ions to aqueous ferrous ions at the first anode in the presence of the first anolyte.

25. The method of any one of the preceding claims comprising operating a bipolar stack of electrochemical cells, each electrochemical cell of the stack independently being the electrochemical cell according to any one of the preceding claims.

26. The method of claim 25, wherein:

the bipolar stack comprises one or more bipolar plates;

adjacent electrochemical cells share a bipolar plate between them;

each bipolar plate comprises a first lead electrode being the first anode of an electrochemical cell and a second electrode comprising lead being the first cathode of an adjacent electrochemical cell.

27. A method comprising:

operating two or more electrochemical cells comprising performing electrochemical reduction at a first cathode and electrochemical oxidation at a first anode;

wherein:

each electrochemical cell comprises a first anodic chamber having a first anolyte in contact with a first anode, a first cathodic chamber having a first catholyte in contact with a first cathode, and a first separator separating the first anolyte from the first catholyte;

the first anode is a lead electrode;

each of the first anolyte and the first catholyte independently comprises aqueous iron cations and aqueous anions;

adjacent electrochemical cells share a bipolar plate between them; and

each bipolar plate comprises a first lead electrode being the first anode of an electrochemical cell and a second electrode comprising lead being the first cathode of an adjacent electrochemical cell.

28. A method comprising:

operating a bipolar stack of electrochemical cells, each electrochemical cell of the stack independently having a first cathode performing electrochemical reduction and a first anode performing electrochemical oxidation;

wherein:

each electrochemical cell comprises a first anodic chamber having a first anolyte in contact with a first anode, a first cathodic chamber having a first catholyte in contact with a first cathode, and a first separator separating the first anolyte from the first catholyte;

the first anode is a lead electrode;

each of the first anolyte and the first catholyte independently comprises aqueous iron cations and aqueous anions;

the bipolar stack comprises one or more bipolar plates;

adjacent electrochemical cells share a bipolar plate between them; and

each bipolar plate comprises a first lead electrode being the first anode of an electrochemical cell and a second electrode comprising lead being the first cathode of an adjacent electrochemical cell.

29. The method of any one of claims 25-28, wherein each bipolar plate comprises an electrically conductive substrate, an anode-facing side, and a cathode-facing side.

30. The method of claim 29, wherein the electrically conductive substrate is porous or permeable to electrolyte and dissolved ions.

31. The method of claim 30, wherein each bipolar plate comprises a coating of lead on at least a portion of internal or pore surfaces of the porous substrate.

32. The method of claim 31, wherein the coating has a thickness selected from the range of 50 µm to 5 mm.

33. The method of claim 29, wherein the electrically conductive substrate is non-porous or impermeable to electrolyte and dissolved ions.

34. The method of any one of claims 29-33, wherein each bipolar plate comprises a first layer of lead on the anode-facing side, a second layer of lead on the cathode-facing side, or a layer of lead independently on each of the anode-facing side and the cathode-facing side.

35. The method of claim 34, wherein each layer of lead is a layer on the substrate.

36. The method of claim 34 or 35, wherein each layer of lead is non-porous or non-permeable to electrolyte and dissolved ions.

37. The method of any one of claim 34-36, wherein each layer of lead protects the substrate from exposure to nearest electrolyte.

38. The method of any one of claims 34-37, wherein each layer of lead independently has a thickness selected from the range of 50 µm to 5 mm.

39. The method of any one of claims 29-38, wherein the electrically conductive substrate is characterized by a compressive yield strength selected from the range of 10 MPa to 200 MPa and/or a Young’s modulus selected from the range of 600 MPa to 1500 MPa.

40. The method of any one of claims 25-39, wherein the first cathode of each bipolar plate is a carbon cathode or a carbon-comprising cathode.

41. The method of any one of claims 34-40, wherein each bipolar plate comprises a first layer of lead on the anode-facing side; and wherein the first layer of lead is the first anode of the respective bipolar plate.

42. The method of any one of claims 34-40, wherein each bipolar plate comprises a layer of lead on the anode-facing side; and wherein each bipolar plate further comprises the first anode on, adhered-to, coated on, or otherwise adjacent to the first layer of lead.

43. The method of any of claims 28-42, wherein the bipolar stack comprises electrically-conductive spacer layers or flow field layers through which a fluid may flow.

44. The method of any one of the preceding claims, wherein the first anode is a lead electrode comprising a microstructured and/or nanostructured lead-containing surface in contact with the anolyte.

45. The method of any one of the preceding claims, wherein the lead electrode is porous and at least partially permeable to the first anolyte.

46. The method of any one of the preceding claims, wherein the lead electrode is a lead-containing and/or lead-coated wool or foam.

47. The method of any one of the preceding claims, wherein the first anode is free of lead shedding or is characterized by a rate of lead shedding being less than that in an equivalent electrochemical cell under equivalent conditions where the first anolyte is free of aqueous iron cations.

48. The method of any one of the preceding claims, wherein the aqueous anions comprise aqueous sulfur-containing anions, aqueous chloride anions, or both.

49. The method of claim 48, wherein the aqueous sulfur-containing anions comprise aqueous sulfate ions.

50. The method of any one of the preceding claims, wherein the first anolyte comprises aqueous lead ions having a concentration of at least 10 ppm.

51. The method of any one of the preceding claims, wherein the first anolyte comprises aqueous lead ions having a concentration being greater than or equal

to 10 ppm and less than or equal to a lead ion saturation concentration in the first anolyte.

52. The method of any one of the preceding claims, wherein the electrochemical cell further comprises a secondary or sacrificial source of lead ions in contact with the first anolyte to slow or prevent dissolution of Pb from the first anode.

53. The method of any one of the preceding claims, wherein the step of operating the electrochemical cell comprises:
electrochemically reducing first Fe^{3+} ions at the first cathode to form Fe^{2+} ions in the first catholyte.

54. The method of any one of the preceding claims, wherein the step of operating the electrochemical cell further comprises:
electrochemically oxidizing water at the first anode to generate O_2 and aqueous protons in the first anolyte.

55. The method of any one of the preceding claims, wherein:
the step of operating comprises the first anode being characterized by a steady state anode potential selected from the range of 1.2 to 3.0 V,
the step of operating comprises each electrochemical cell being characterized by a current density selected from the range of 5 to 200 mA/cm^2, and/or
the step of operating comprises each electrochemical cell being characterized by a bias current density is between 5 to 50 mA/cm^2.

56. The method of any one of the preceding claims, wherein the electrochemical cell is characterized by a steady state current density selected from the range of 1 to 500 mA/cm^2.

57. The method of any one of the preceding claims comprising adding a dosing-solution having aqueous iron cations to the first anodic chamber and/or to the first anolyte.

58. The method of claim 57, wherein the dosing-solution comprises aqueous ferrous.

59. The method of claim 57 or 58, wherein the dosing-solution is an electrolyte from a different electrochemical cell or system.

60. The method of any one of claims 57-59, wherein the dosing-solution comprises electrolyte from a metal electroplating cell or system.

61. The method of any one of claims 57-60, wherein the dosing-solution is provided from a separate solution-storage tank.

62. The method of any one of the preceding claims comprising recycling a second electrolyte from a metal electroplating cell to the first anolyte, the second electrolyte having aqueous iron cations.

63. The method of claim 62, wherein the second electrolyte comprises a concentration of aqueous iron cations being selected from the range of 0.01 M to 0.5 M.

64. The method of claim 62 or 63, wherein the second electrolyte comprises a catholyte and/or an anolyte from an iron electroplating cell.

65. The method of claim 64, wherein the catholyte and/or anolyte from the iron electroplating cell is a spent catholyte and/or spent anolyte, respectively.

66. The method of any one of the preceding claims further comprising:
dissolving an iron-containing ore in an acid to form an acidic iron-salt solution; and
providing the acidic iron-salt solution to the cathodic chamber of the electrochemical cell.

67. The method of any one of the preceding claims further comprising:
second electrochemically reducing Fe^{2+} ions to Fe metal at a second cathode in the presence of a second catholyte;
wherein an iron electroplating cell comprises the second cathode and the second catholyte.

68. The method of any one of the preceding claims, wherein the step of operating comprises one or more steps of establishing and/or the step of operating comprises a step of maintaining the concentration of the aqueous iron cations in said first anolyte within a stabilizing-concentration range; wherein the stabilizing-concentration range is selected from the range of 0.01 M to 0.5 M.

69. The method of claim 68, wherein each step of establishing provides the stabilizing concentration range temporarily.

70. The method of claim 68 or 69, wherein the step of establishing is performed prior to startup of the electrochemical cell and/or prior to shutdown of the electrochemical cell.

71. The method of any one of claims 68-70, wherein each step of establishing and the step of maintaining, if present, comprises dosing the first anolyte with said aqueous iron cations.

72. The method of claim 71, wherein the step of dosing is performed as one or more discrete events during the step of operating the cell.

73. The method of claim 71, wherein the step of dosing is performed continuously during the step of operating the cell.

74. The method of any one of claims 71-74, wherein the step of dosing comprises providing a liquid iron source; the liquid iron source being an aqueous solution comprising a dosing-concentration of the aqueous iron cations.

75. The method of claim 74, wherein the liquid iron source comprises a spent or used anolyte from a metal electroplating cell or system.

76. The method of claims 74 or 75, wherein the liquid iron source comprises a spent or used catholyte from a metal electroplating cell or system.

77. The method of any one of claims 74-76, wherein the liquid iron source is provided directly to the first anolyte or to a first anodic chamber having said first anolyte.

78. The method of any one of claims 74-77, wherein the liquid iron source is provided indirectly to the first anolyte or to a first anodic chamber having said first anolyte.

79. The method of any one of claims 74-78, wherein the liquid iron source is provided to a first anolyte-circulation tank which is fluid communication with the first anodic chamber having the first anolyte, to a fluid line entering the first anodic chamber, and/or to a fluid line exiting the first anodic chamber.

80. The method of any one of claims 74-79, wherein the liquid iron source comprises aqueous ferrous ions.

81. The method of any one of claims 74-80, wherein the liquid iron source is an iron-containing slag and/or iron-containing leachate from a metal and/or ore processing system.

82. The method of any one of claims 74-81, wherein the dosing-concentration of aqueous iron cations in the liquid iron source is greater than 0 M and less than 0.5 M.

83. The method of any one of claims 71-82 wherein the step of dosing comprises providing a solid iron source in the presence of the first anolyte; wherein the solid iron source is capable of being at least partially dissolved by the first anolyte.

84. The method of 83, wherein the solid iron source is a raw ore and/or treated ore.

85. The method of 83 or 84, wherein the solid iron source is a thermally treated ore.

86. The method of any one of claims 84-85, wherein the solid iron source comprises solid ferrous ions.

87. The method of any one of claims 71-86, wherein each the of dosing is performed in response to a trigger event; wherein the trigger event comprises:

the concentration of the aqueous iron cations in the first anolyte falling below the stabilizing-concentration range, and/or

a current density of the electrochemical cell falling below a normal operable current density.

88. The method of any one of the preceding claims, wherein the electrochemical reduction at the first cathode is an iron electroplating reaction; and wherein the electrochemical oxidation reaction is an oxygen evolution reaction (OER) at the first anode.

89. The method of 88, wherein the separator is an anion exchange membrane.

90. The method of any one of the preceding claims, wherein the first anode is free of a mixed metal oxide (MMO) material.

91. The method of any one of the preceding claims, wherein the first anode is free of Ir, Ru, and Pt.

92. The method of any one of the preceding claims, wherein the first anode is an undoped or non-alloyed lead electrode.

93. A system for stabilizing a lead anode, the system comprising:

an electrochemical cell comprising:

a first anodic chamber having a first anolyte in contact with the first anode, a first cathodic chamber having a first catholyte in contact with the first cathode, and a first separator separating the first anolyte from the first catholyte;

wherein:

the first anode is a lead electrode;

each of the first anolyte and the first catholyte independently comprises aqueous iron cations and aqueous anions; and

the first anolyte comprises the aqueous iron cations at a concentration selected from the range of 0.01 M to 0.5 M.

94. A system for stabilizing a lead anode, the system comprising:

an electrochemical cell comprising:

a first anodic chamber having a first anolyte in contact with the first anode, a first cathodic chamber having a first catholyte in contact with the first cathode, and a first separator separating the first anolyte from the first catholyte; and

a metal electroplating cell; and

an electrolyte-recycling subsystem for recycling an electrolyte from the metal electroplating cell to the first anolyte;

wherein:

the first anode is a lead electrode;

each of the first anolyte and the first catholyte independently comprises aqueous iron cations and aqueous anions; and

the first anolyte comprises the aqueous iron cations at a concentration selected from the range of 0.01 M to 0.5 M.

95. A system for stabilizing a lead anode, the system comprising:

an electrochemical cell comprising:

a first anodic chamber having a first anolyte in contact with the first anode, a first cathodic chamber having a first catholyte in contact with the first cathode, and a first separator separating the first anolyte from the first catholyte;

wherein:

an oxygen evolution reaction (OER) occurs at the first anode;

the first anode is a lead electrode;

each of the first anolyte and the first catholyte independently comprises aqueous iron cations and aqueous anions; and

the first anolyte comprises the aqueous iron sulfate at a concentration selected from the range of 0.01 M to 0.5 M.

96. A system comprising:

an electrochemical cell comprising:

a first anodic chamber having a first anolyte in contact with the first anode, a first cathodic chamber having a first catholyte in contact with the first cathode, and a first separator separating the first anolyte from the first catholyte;

wherein:

the first anode is a lead electrode;

each of the first anolyte and the first catholyte independently comprises aqueous iron cations and aqueous anions; and

the first anolyte comprises aqueous ferrous ions that facilitate dissolution, in the first anolyte, of solid manganese oxide present in the first anodic chamber.

97. A system comprising:

an electrochemical cell comprising:

a first anodic chamber having a first anolyte in contact with the first anode, a first cathodic chamber having a first catholyte in contact with the first cathode, and a first separator separating the first anolyte from the first catholyte;

wherein:

the first anode is a lead electrode;

each of the first anolyte and the first catholyte independently comprises aqueous iron cations and aqueous anions; and

the electrochemical cell is configured to reverse-bias the first anode for a finite time to electrochemically reduce aqueous ferric ions to aqueous ferrous ions at the first anode in the presence of the first anolyte.

98. A system comprising:

two or more electrochemical cells, each cell comprising:

a first anodic chamber having a first anolyte in contact with the first anode, a first cathodic chamber having a first catholyte in contact with the first cathode, and a first separator separating the first anolyte from the first catholyte; and

a bipolar plate between two adjacent electrochemical cells, such that adjacent electrochemical cells share a bipolar plate between them;

wherein:

the first anode is a lead electrode;

each of the first anolyte and the first catholyte independently comprises aqueous iron cations and aqueous anions; and

each bipolar plate comprises a first lead electrode being the first anode of an electrochemical cell and a second electrode comprising lead being the first cathode of an adjacent electrochemical cell.

99. A system comprising:

a bipolar stack of two or more electrochemical cells, each cell comprising:

a first anodic chamber having a first anolyte in contact with the first anode, a first cathodic chamber having a first catholyte in contact with the first cathode, and a first separator separating the first anolyte from the first catholyte;

wherein:

the first anode is a lead electrode;

each of the first anolyte and the first catholyte independently comprises aqueous iron cations and aqueous anions;

the bipolar stack comprises one or more bipolar plates;

adjacent electrochemical cells share a bipolar plate between them; and

each bipolar plate comprises a first lead electrode being the first anode of an electrochemical cell and a second electrode comprising lead being the first cathode of an adjacent electrochemical cell.

100. The system of claim 98 or 99, wherein the first cathode comprises lead as an underlying or supportive layer.

101. The system of claim 100, wherein the first cathode does not comprise lead in contact with the first catholyte.

102. The system of claim 100 or 101, wherein the first cathode comprises a carbon electrode in contact with the first catholyte.

103. The method of claim 1, wherein the first anolyte comprises the aqueous iron cations at a concentration selected from the range of at least 0.01 M to 0.44 M.

104. The method of claim 2, wherein the first anolyte comprises the aqueous iron cations at a concentration selected from the range of at least 0.01 M to 0.44 M.

105. The method of claim 3, wherein the first anolyte comprises the aqueous iron cations at a concentration selected from the range of at least 0.01 M to 0.44 M.

106. The system of claim 93, wherein the first anolyte comprises the aqueous iron cations at a concentration selected from the range of at least 0.01 M to 0.44 M.

107. The system of claim 94, wherein the first anolyte comprises the aqueous iron cations at a concentration selected from the range of at least 0.01 M to 0.44 M.

108. The system of claim 95, wherein the first anolyte comprises the aqueous iron cations at a concentration selected from the range of at least 0.01 M to 0.44 M.

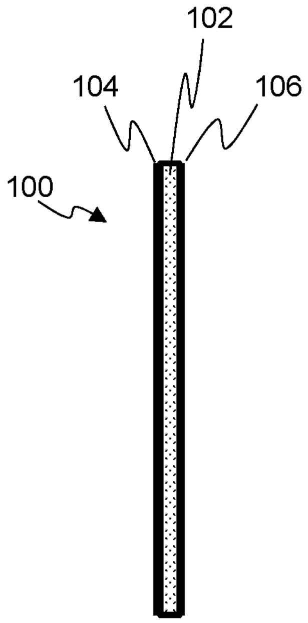


FIG. 1

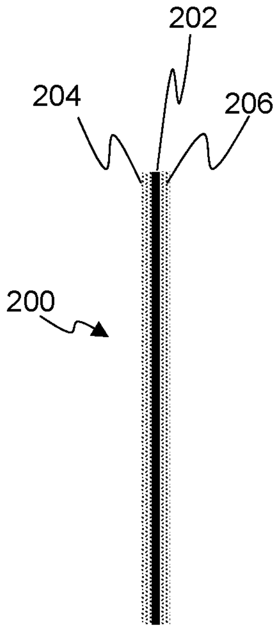


FIG. 2

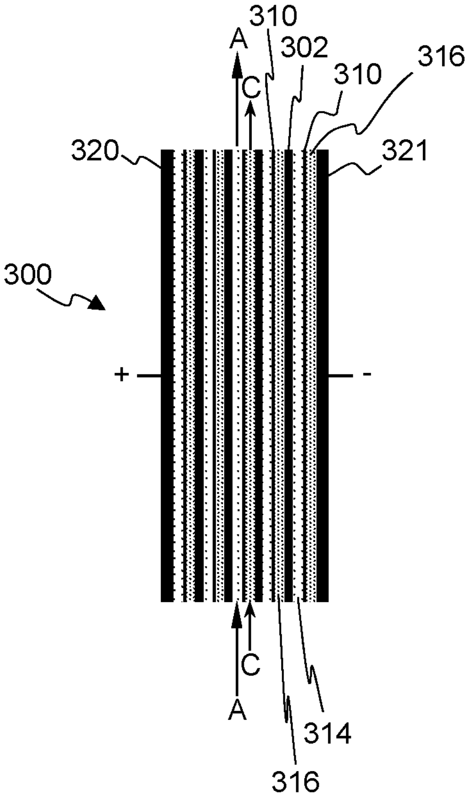


FIG. 3

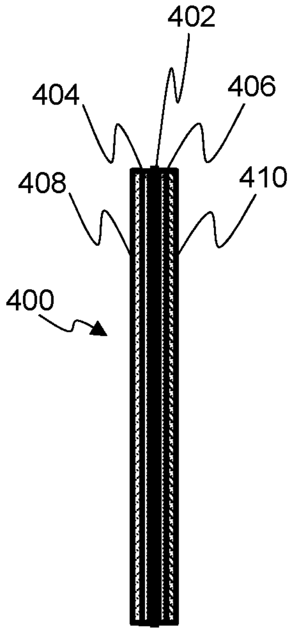


FIG. 4

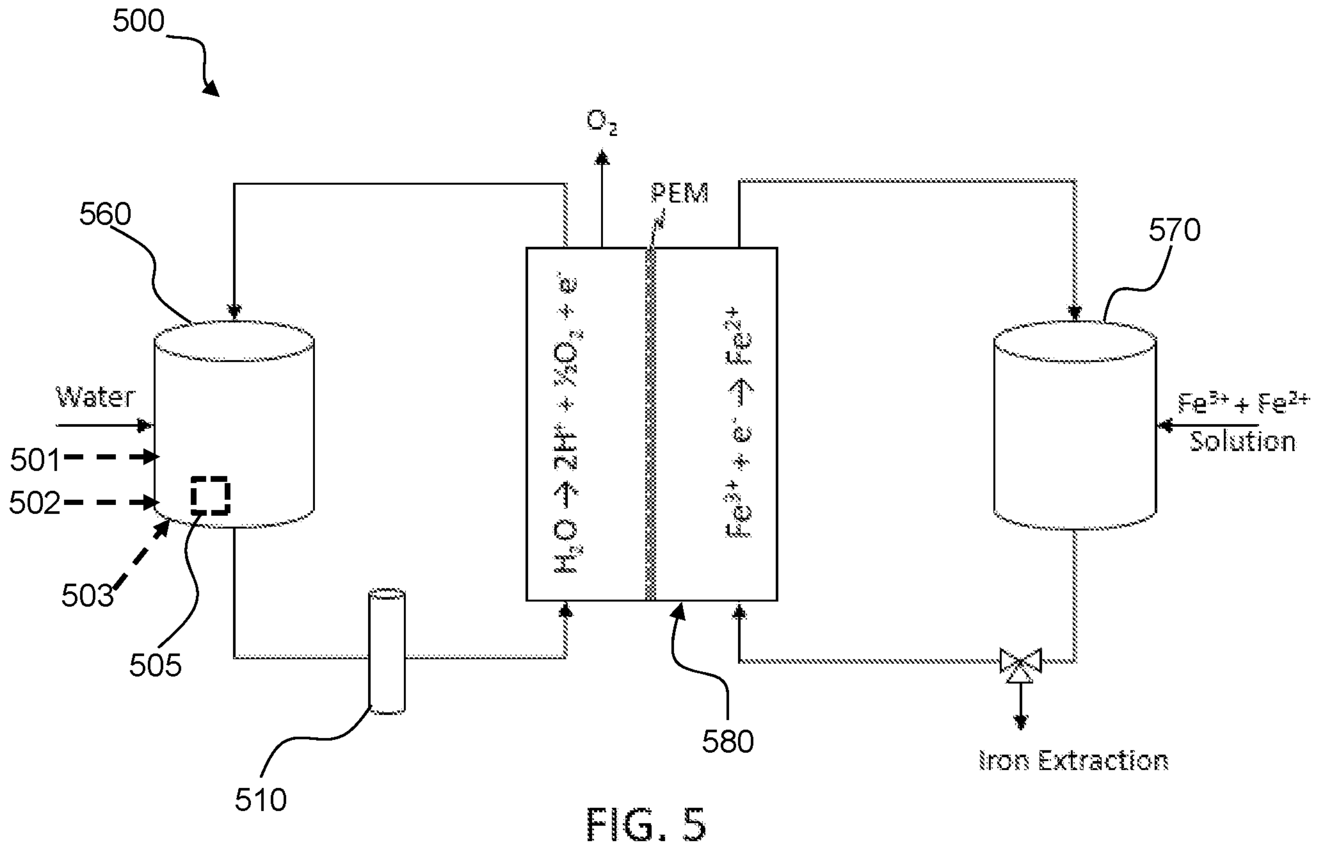

500
O_2
PEM
560
570
$H_2O \rightarrow 2H^+ + ½O_2 + e^-$
$Fe^{3+} + e^- \rightarrow Fe^{2+}$
Water
501
502
503
505
$Fe^{3+} + Fe^{2+}$ Solution
510
580
Iron Extraction

FIG. 5

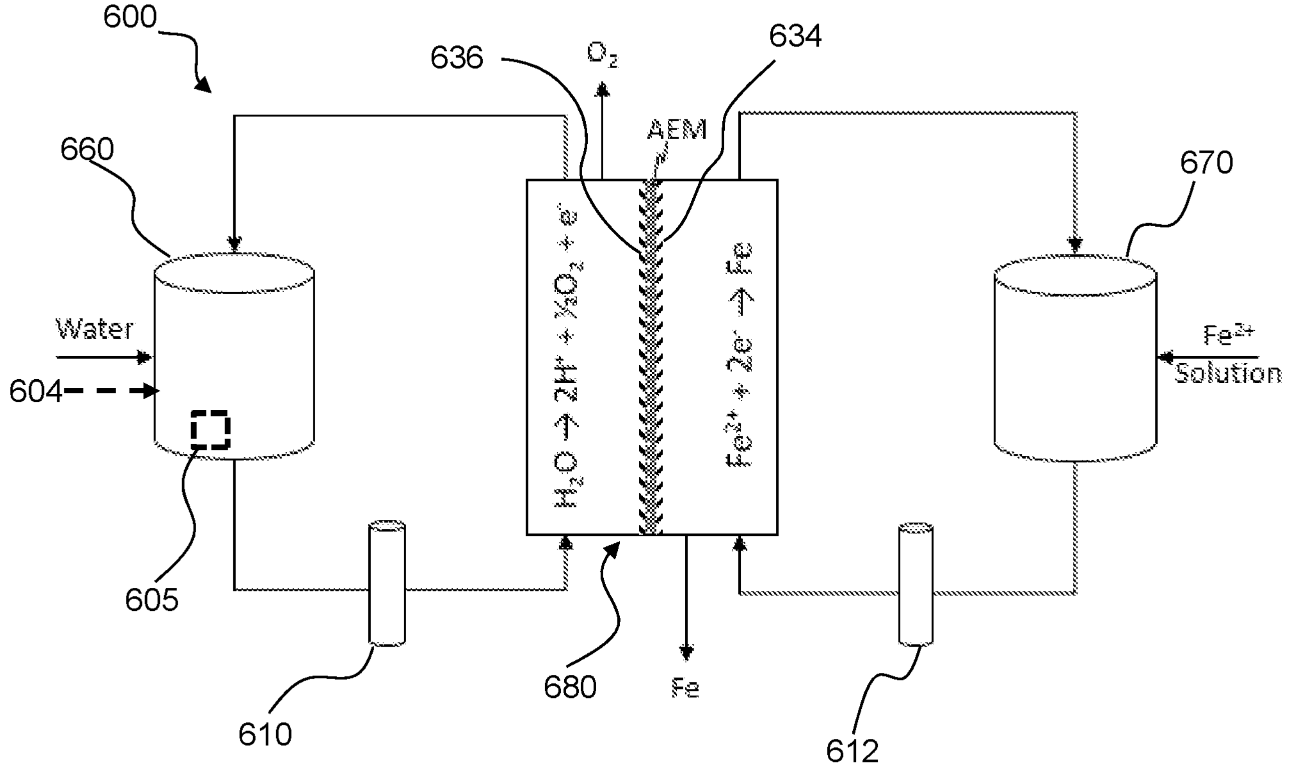

600
636
O_2
634
AEM
660
670
$H_2O \rightarrow 2H^+ + ½O_2 + e^-$
$Fe^{2+} + 2e^- \rightarrow Fe$
Water
604
605
Fe^{2+} Solution
610
680
Fe
612

FIG. 6

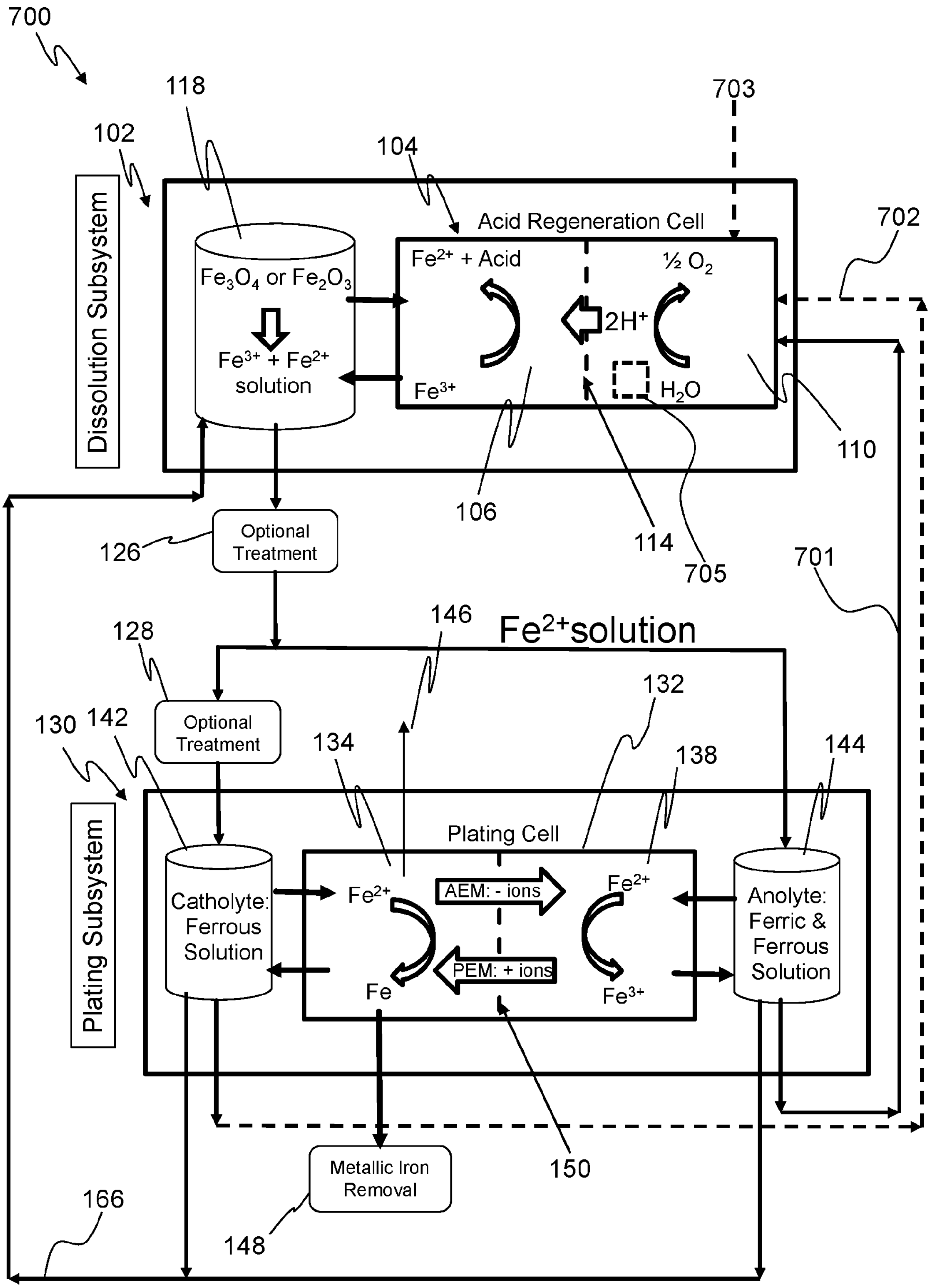

700
118
102
104
703
Dissolution Subsystem
Acid Regeneration Cell
702
Fe_3O_4 or Fe_2O_3
Fe^{2+} + Acid
½ O_2
$2H^+$
Fe^{3+} + Fe^{2+} solution
Fe^{3+}
H_2O
110
106
114
705
126
Optional Treatment
701
146
Fe^{2+}solution
128
132
130
142
Optional Treatment
134
138
144
Plating Subsystem
Plating Cell
Catholyte: Ferrous Solution
Fe^{2+}
AEM: - ions
Fe^{2+}
Anolyte: Ferric & Ferrous Solution
PEM: + ions
Fe
Fe^{3+}
150
Metallic Iron Removal
166
148

FIG. 7

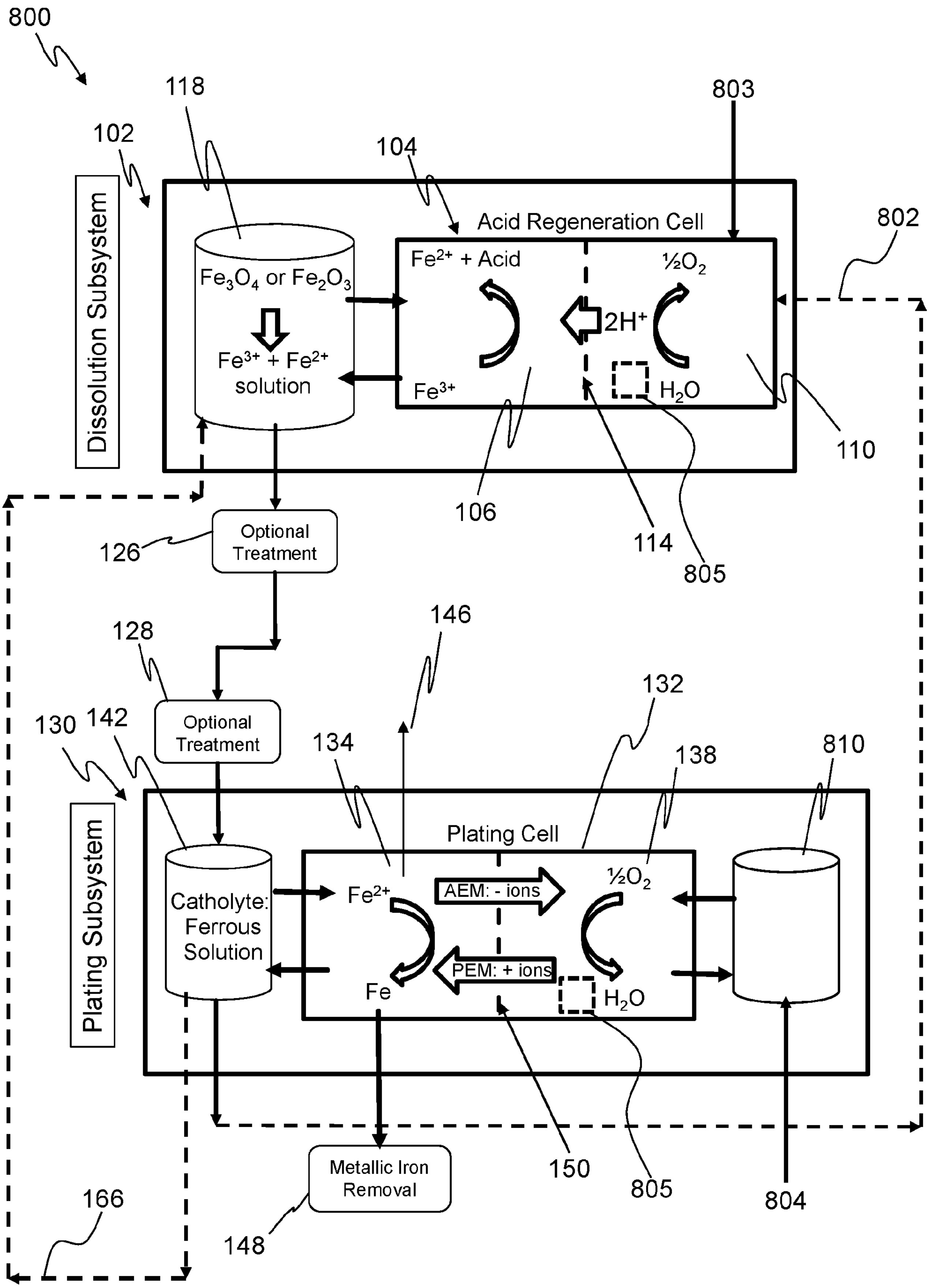

800
118
102
104
803
802
Dissolution Subsystem
Acid Regeneration Cell
Fe_3O_4 or Fe_2O_3
Fe^{3+} + Fe^{2+} solution
Fe^{2+} + Acid
$\frac{1}{2}O_2$
$2H^+$
Fe^{3+}
H_2O
110
106
114
805
126
Optional Treatment
146
128
Optional Treatment
132
130
142
134
138
810
Plating Subsystem
Plating Cell
Catholyte: Ferrous Solution
Fe^{2+}
AEM: - ions
PEM: + ions
$\frac{1}{2}O_2$
Fe
H_2O
Metallic Iron Removal
150
805
804
166
148

FIG. 8

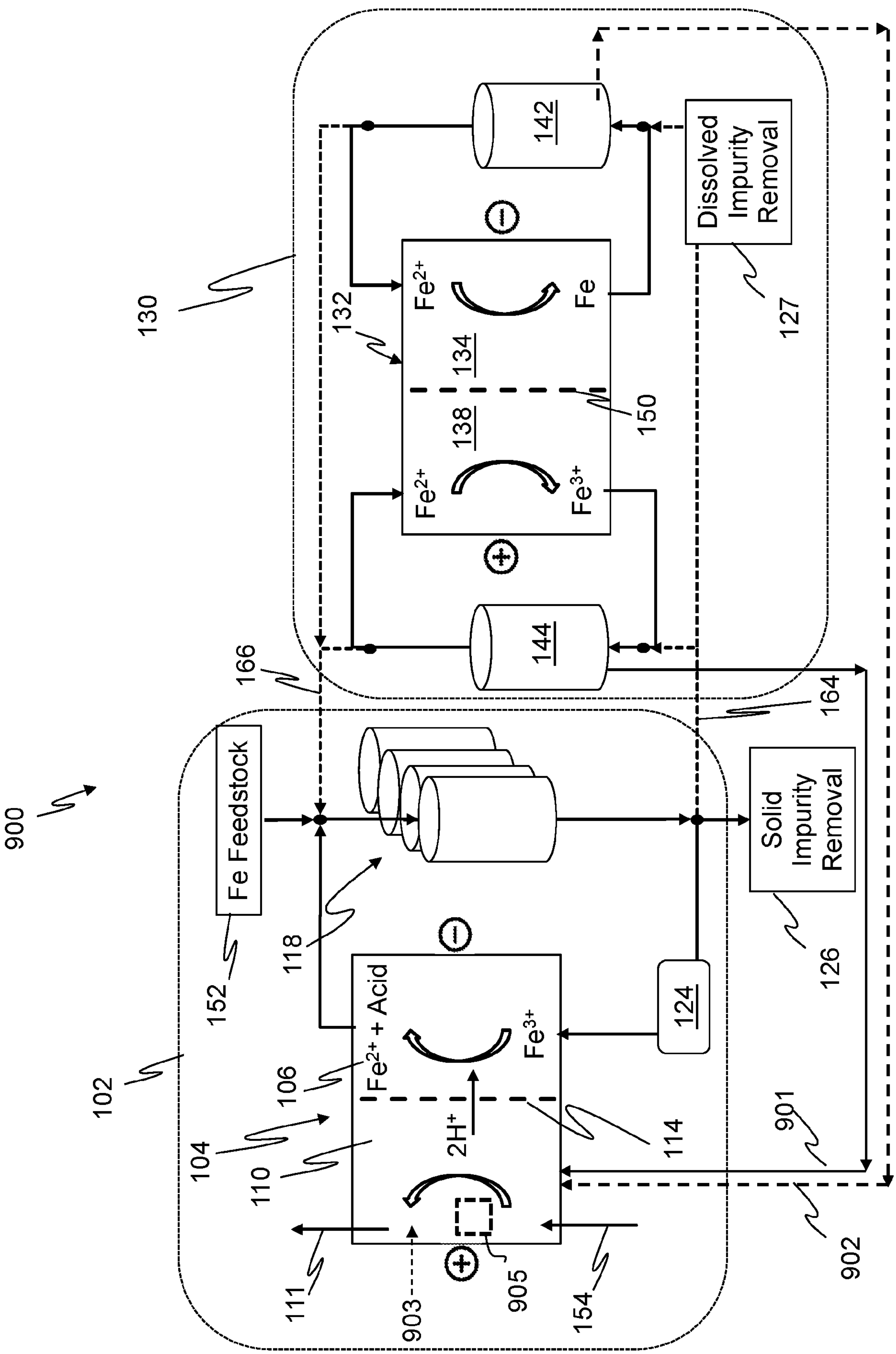

900
102
104
106
110
111
114
118
124
126
127
130
132
134
138
142
144
150
152
154
164
166
901
902
903
905
Fe Feedstock
Fe²⁺ + Acid
Fe³⁺
2H⁺
Fe²⁺
Fe
Fe²⁺
Fe³⁺
Solid Impurity Removal
Dissolved Impurity Removal
+
−

FIG. 9

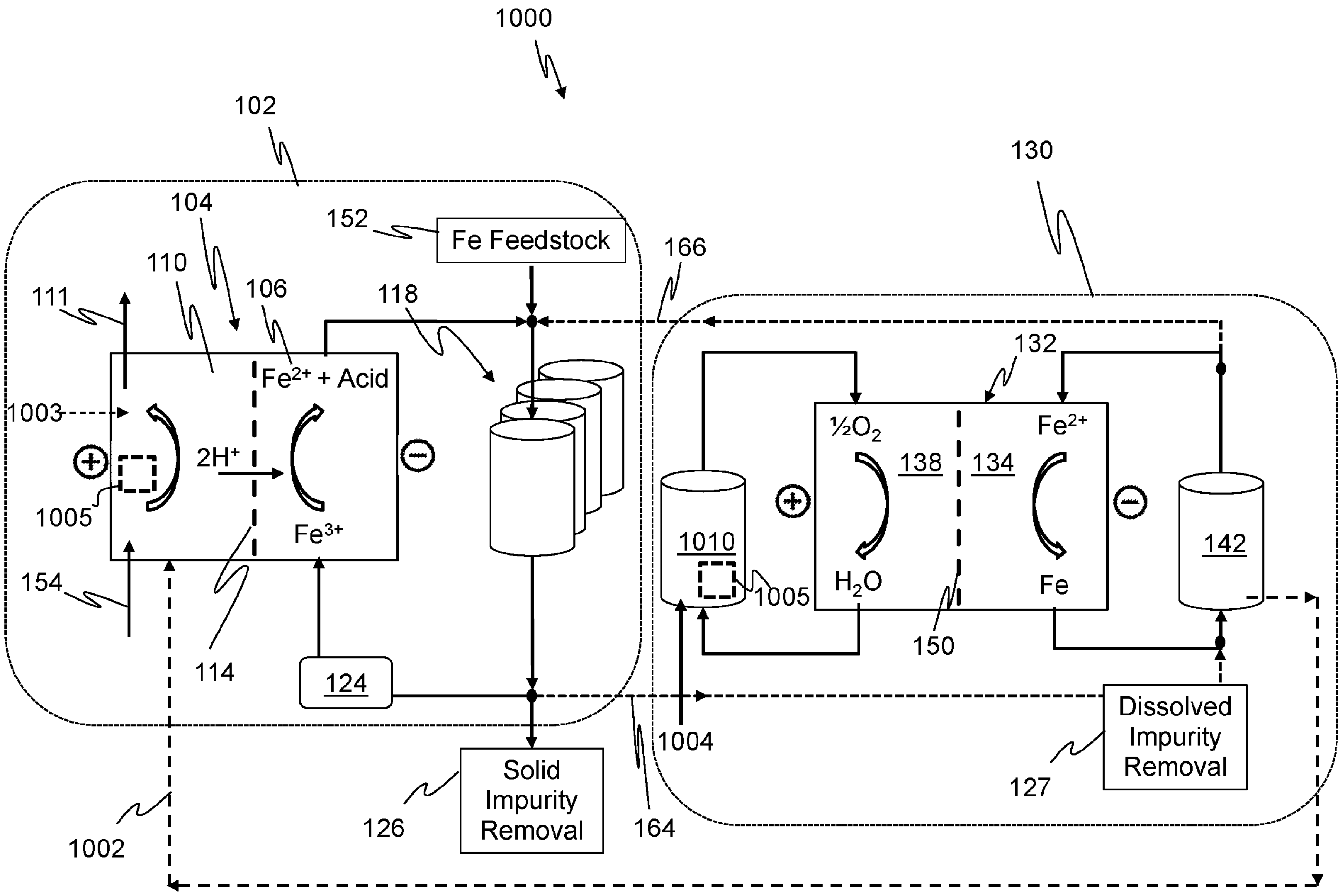

1000
102
104
110
111
106
118
152
Fe Feedstock
166
130
132
1003
2H+
Fe2+ + Acid
Fe3+
1005
114
154
124
½O2
138
134
Fe2+
H2O
Fe
1010
1005
142
150
Dissolved Impurity Removal
127
1004
Solid Impurity Removal
126
164
1002

FIG. 10

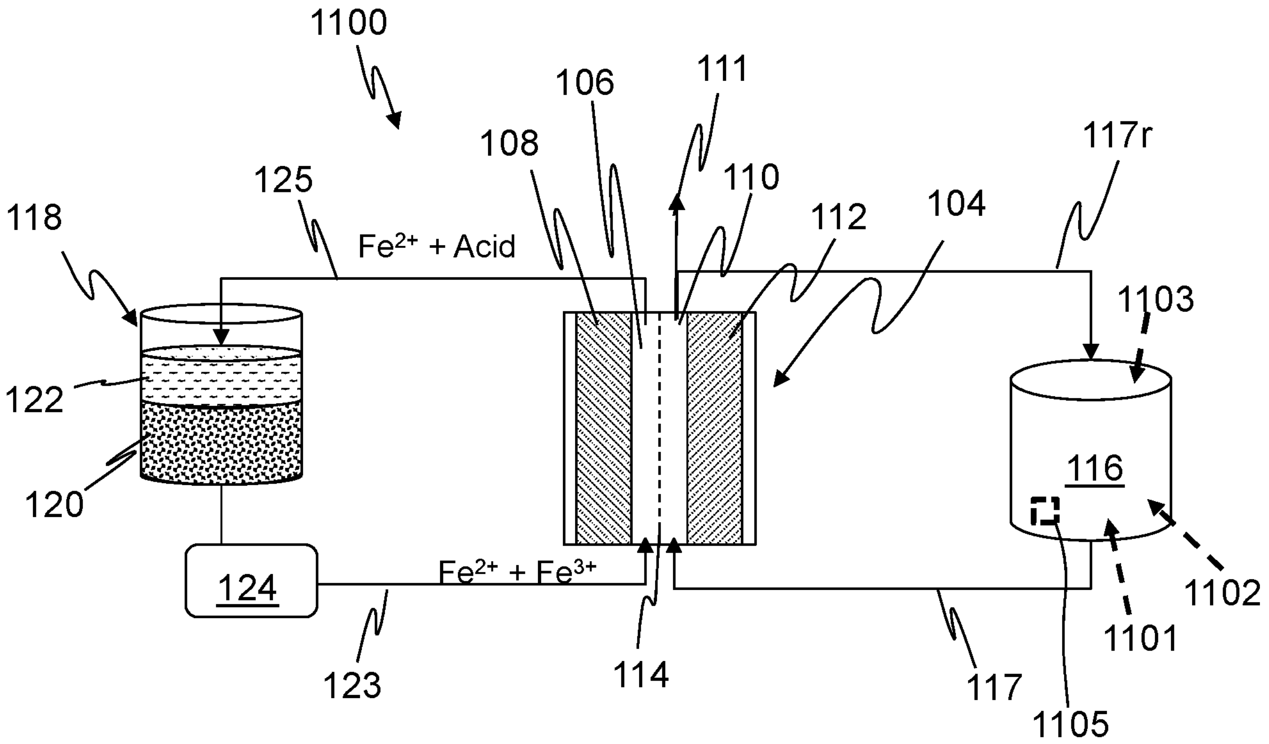

1100
106
111
108
110
117r
125
112
104
118
Fe²⁺ + Acid
1103
122
116
120
1102
124
Fe²⁺ + Fe³⁺
1101
123
114
117
1105

FIG. 11

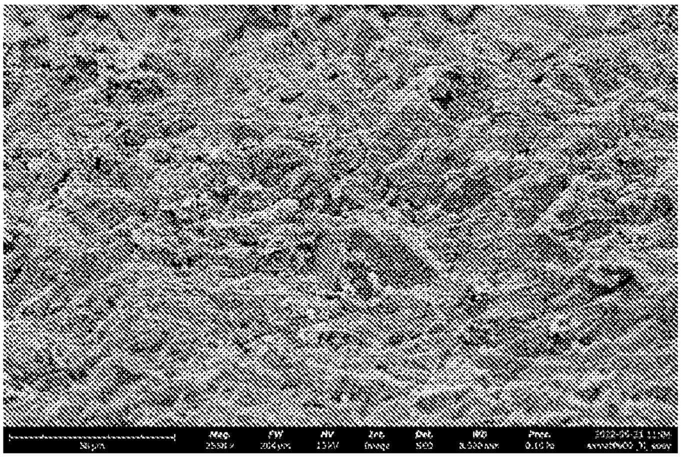


FIG. 12A

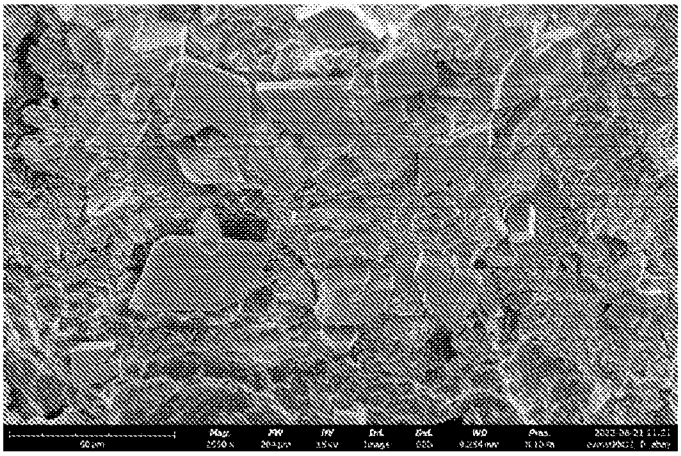


FIG. 12B

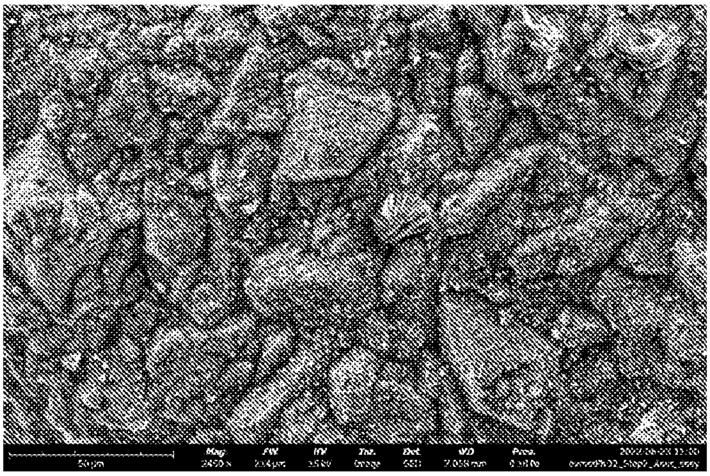


FIG. 12C

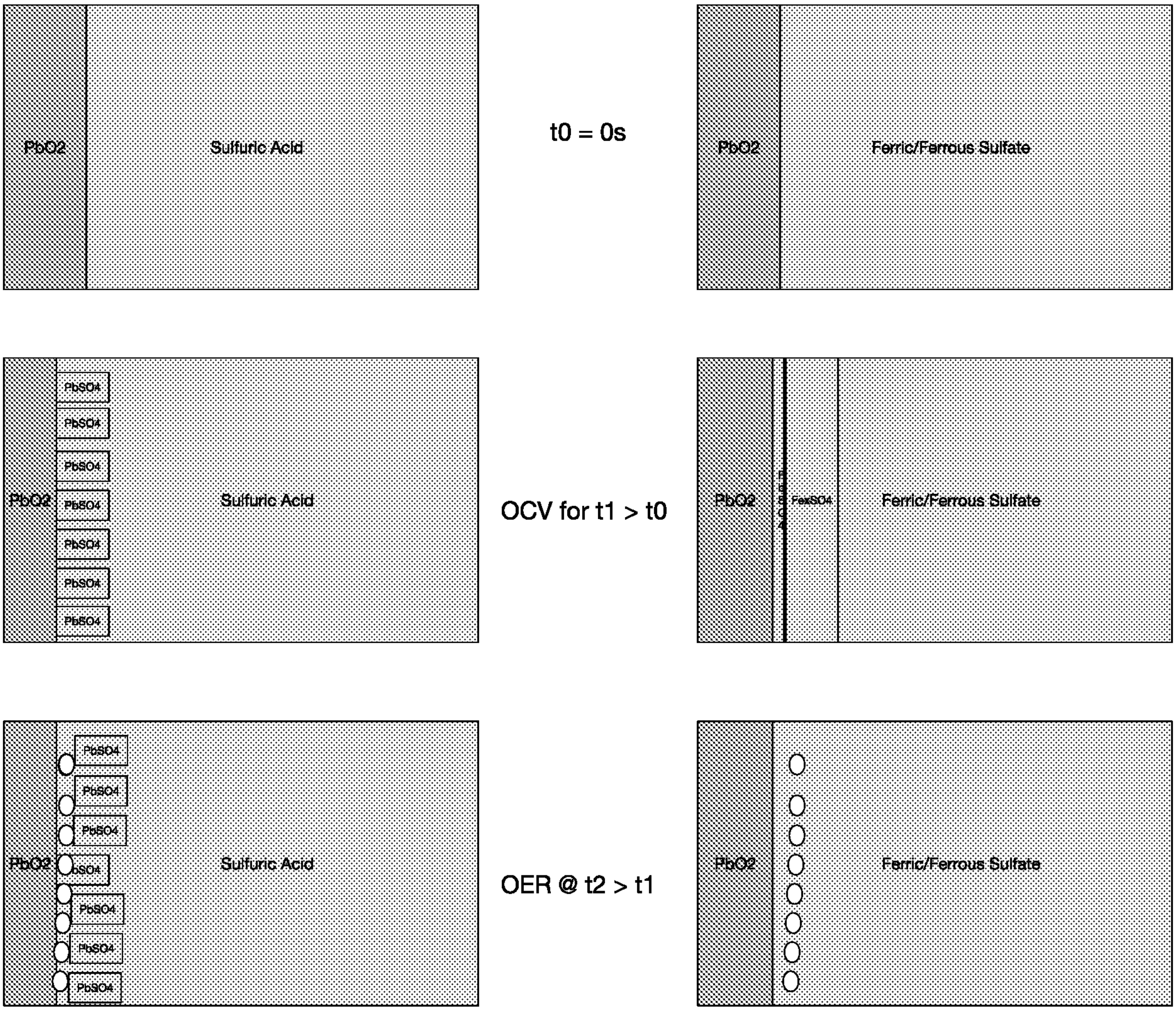

PbO2
Sulfuric Acid
t0 = 0s
PbO2
Ferric/Ferrous Sulfate
PbO2
PbSO4
PbSO4
PbSO4
PbSO4
PbSO4
PbSO4
PbSO4
Sulfuric Acid
OCV for t1 > t0
PbO2
PbSO4
FexSO4
Ferric/Ferrous Sulfate
PbO2
PbSO4
PbSO4
PbSO4
bSO4
PbSO4
PbSO4
PbSO4
Sulfuric Acid
OER @ t2 > t1
PbO2
Ferric/Ferrous Sulfate

FIG. 13

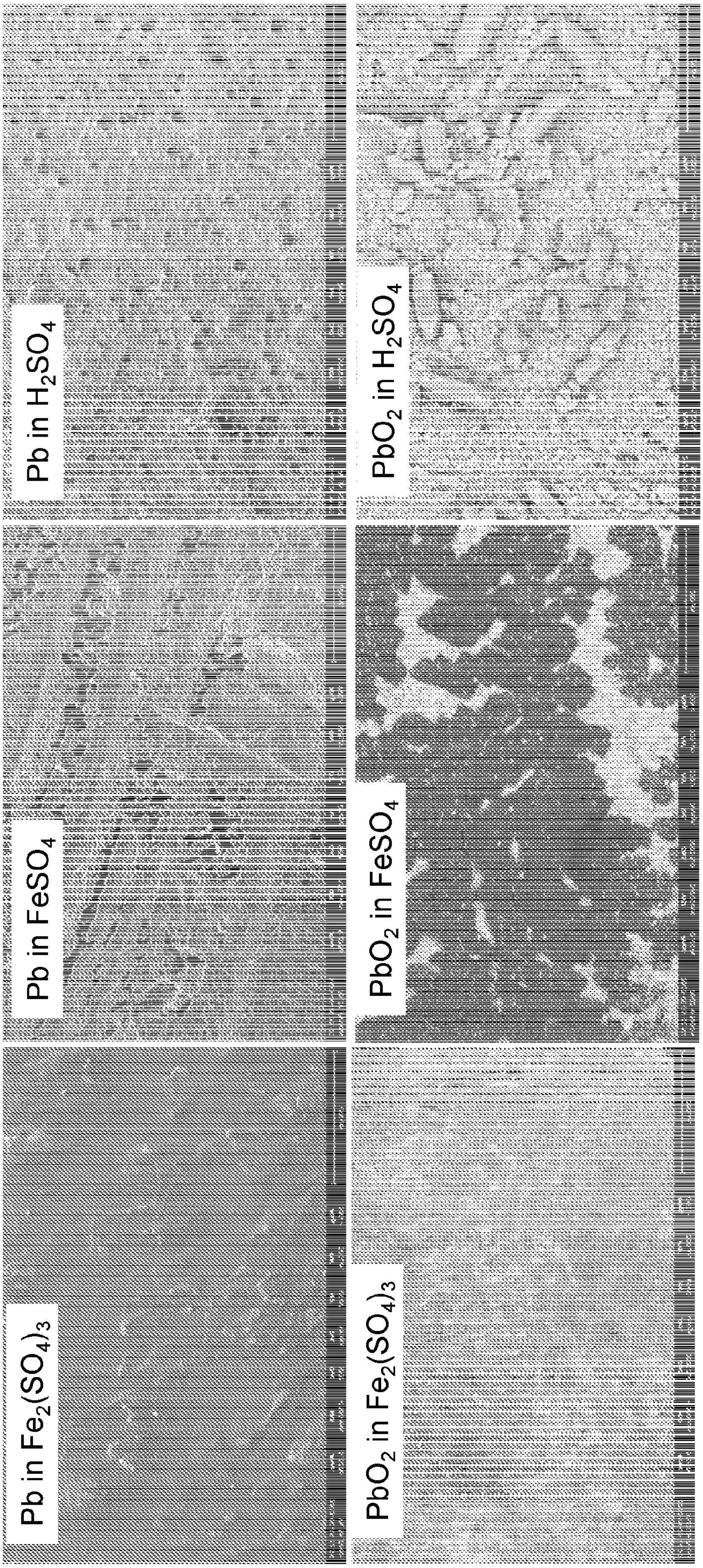
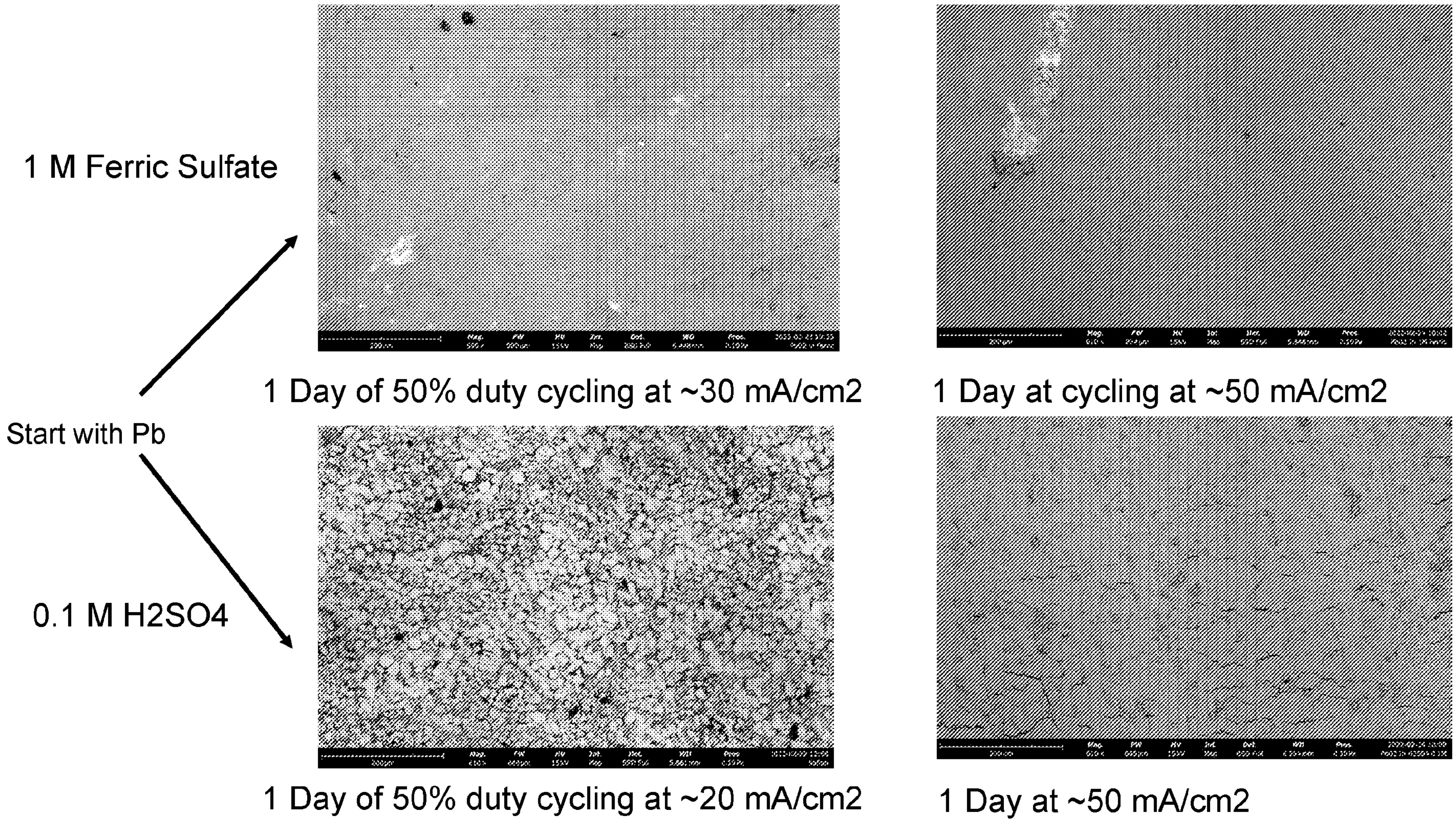

Pb in H_2SO_4
Pb in $FeSO_4$
Pb in $Fe_2(SO_4)_3$
PbO_2 in H_2SO_4
PbO_2 in $FeSO_4$
PbO_2 in $Fe_2(SO_4)_3$

FIG. 14



1 Day of 50% duty cycling at ~30 mA/cm2

1 Day at cycling at ~50 mA/cm2

1 Day of 50% duty cycling at ~20 mA/cm2

1 Day at ~50 mA/cm2

FIG. 15